SANDIA REPORT

SAND95-1318 • UC-800

Unlimited Release

Printed July 1995

Materials and Process Engineering Projects for the Sandia National Laboratories/Newly Independent States Industrial Partnering Program

Volume I

Frank J. Zanner, William C. Moffatt

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-94AL85000

Approved for public release; distribution is unlimited.

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
Office of Scientific and Technical Information
PO Box 62
Oak Ridge, TN 37831

Prices available from (615) 576-8401, FTS 626-8401

Available to the public from
National Technical Information Service
US Department of Commerce
5285 Port Royal Rd
Springfield, VA 22161

NTIS price codes
Printed copy: A21
Microfiche copy: A01

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SAND95-1318
Unlimited Release
Printed July 1995

Distribution
Category UC-800

INTERIM REPORT

MATERIALS AND PROCESS ENGINEERING PROJECTS FOR THE SANDIA NATIONAL LABORATORIES/NEWLY INDEPENDENT STATES INDUSTRIAL PARTNERING PROGRAM

Frank J. Zanner, William C. Moffatt
Sandia National Laboratories
Liquid Metal Processing Department
Albuquerque, NM 87185

Abstract

In July, 1994, a team of materials specialists from Sandia and U. S. Industry traveled to Russia and the Ukraine to select and fund projects in materials and process technology in support of the Newly Independent States/Industrial Partnering Program (NIS/IPP). All of the projects are collaborations with scientists and Engineers at NIS Institutes. Each project is scheduled to last one year, and the deliverables are formatted to supply U. S. Industry with information which will enable rational decisions to be made regarding the commercial value of these technologies. This work is an unedited interim compilation of the deliverables received to date.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *WW*

MASTER

FOREWORD

This book is a compilation of reports written by Ukrainian and Russian investigators under 30 contracts between Sandia National Laboratories (Sandia) and institutes in the Ukraine and the Urals region of Russia. Projects focus on materials and process engineering, more specifically coating technologies and process metallurgy; technologies of projects selected are those thought to have the most promise for direct US private sector investment. Projects last one year; their results should allow businesses to make sound decisions about the value of the technologies studied. Information on all of the projects is given in the following table. The table is followed by detailed statements of work and copies of reports received for each project. In some instances the statement of work stands alone because at this date deliverables have not been received.

We are grateful to many people who contribute to the success of this effort. The group which traveled to Russia and the Ukraine to evaluate technologies and place contracts at the institutes included:

- Lee Bertram (fluids and plasma technology) -- Sandia
- Nancy Davis (contracting) -- Sandia
- Harry Saxton (materials) -- Sandia
- Rod Williamson (plasma and melting processes) -- Sandia
- Frank Zanner (liquid metal processing) -- Sandia
- Dale McIntyre (coatings) -- Optex Communications, formerly Sandia
- Jack Simon -- American Society for Metals and General Motors
- Tanya Golub (logistics) -- Kaiser Research

Dennis Croessmann, Sandia's Industrial Partnering Program project manager, provided administrative support; John Hnatio, the Department of Energy project manager for the Newly Independent States/Industrial Partnering Program, provided the funds and the vision that made this effort possible. Project technical monitors include Bill Moffatt (Sandia) and the team that traveled to Russia and the Ukraine. Cincinnati Milacron, United Technologies, General Motors, Pratt & Whitney and Teledyne Allvac have provided specimens or technical guidance or services for these projects. We are grateful to Academician Gennady Mesyats from the Russian Academy of Sciences (Urals Branch) for arranging technical presentations at institutes he runs.

When the projects are completed we plan to publish a collection of final reports. Call us if you have questions about the technologies or institutes.

Editors: Frank J. Zanner, Sandia
 William C. Moffatt, Sandia

Materials Projects in the SNL NIS - Industrial Partnering Program

Number	Proposal Title	SNL PI	SNL PI Phone	NIS Country	NIS Institution	NIS PI
SNL-023	The Effect of Melt Nuclei on the Properties of Alloy 718 Castings	Brian Damkroger	845-3105	Russia	Urals Polytechnic Institute, Ekaterinburg	E Tretyakova
SNL-024	Review of Liquid Metal Processing Research in the FSU	Mike McGuire	845-3105	Russia	Moscow Steel & Alloys Institute, Moscow	L Romonav
SNL-025	Development of Face Coat Materials for Investment Casting Titanium	Mike Maguire	845-3105	Russia	Chelyabinsk Polytechnic Institute, Ekaterinburg	B Kulakov
SNL-083	Thermal Physical Properties of Liquid Metals	Frank Zanner	845-3085	Russia	Ural Mining and Geology Academy, Ekaterinburg	Vladislav E. Zinov'ev
SNL-084	Step-by-step Deformation of Metal Alloys	Frank Zanner	845-3085	Russia	Chelyabinsk State University of Technology, Chelyabinsk	G. I. Koval
SNL-085	Development of a Method of Growing Band-like single crystals of Molybdenum (Mo) and Tungsten (W)	Frank Zanner	845-3085	Russia	Institute of Physics of Metals, Ekaterinburg	Eugene Romanov
SNL-086	Directional Solidification of Ni-Based Eutectic Alloys and High Purity Ti3Al Single Crystals Using An Annular Electron Beam Gun	Rodney Williamson	845-3105	Ukraine	Institute of Metal Physics, Kiev	Oleg M. Barabash
SNL-087	Purification of Molten Metals by Application of Electric Fields	Rodney Williamson	845-3105	Russia	Institute of Metallurgy, Ekaterinburg	A. V. Kaybichev
SNL-088	Effect of Volatile Alloy components on the Vacuum Arc Remelting Process	Rodney Williamson	845-3105	Russia	The Research and Development Institute of Metallurgy, Chelyabinsk	Felix J. Shved
SNL-089	Melting, Refining and Casting of Ti-Based Alloys in an Electron-Beam Furnace with Electromagnetic Stirring	Rodney Williamson	845-3105	Ukraine	Institute of Foundry Problems, Kiev	Sergey V. Ladkhin
SNL-090	Electron Beam Spray Casting of Dense Metallic and Ceramic Coatings	Rodney Williamson	845-3105	Ukraine	E.O. Paton Electric Welding Institute, Kiev	Nikolai Trigub
SNL-091	Characterization of a Metal Vapor Arc Burning On Nickel and Nickel-Magnesium Cathodes	Rodney Williamson	845-3105	Russia	High Current Electronics Institute, Tomsk	Yuri D. Korolev
SNL-092	Novel Large Deformation Processes	Harry Saxton	845-8739	Russia	Institute of Metallurgy, Ekaterinburg	Petr Savintsev
SNL-093	Continuous Casting of Tool Steels	Frank Zanner	845-3085	Russia	Urals Polytechnical Institute, Ekaterinburg	Sergey Burkin
SNL-094	Amorphous Palladium (Pd)-based Alloys	Harry Saxton	845-8739	Russia	Institute of Metallurgy, Ekaterinburg	Vatolin
SNL-095	A Novel Accelerated and Ecologically-Friendly Method for the Production of Wear Resistant Coatings of iron Boride on Steels	Bill Moffatt	844-7062	Russia	Institute for Electrochemistry, Ekaterinburg	A. A. Ivanovich
SNL-096	Development and Production of Advanced Cutters for Super-Alloys	Frank Zanner	845-3085	Ukraine	Bakel Institute of Superhard Materials, Kiev	I. B. Chernov
SNL-097	Investigation of the Electronic Properties and Varistor Effect in Novel Diamond Compacts	Harry Saxton	845-8739	Ukraine	DonBass Civil Engineering Institute, Makeveka	Nikolai Samsonenko

Materials Projects in the SNL NIS - Industrial Partnering Program

Number	Proposal Title	SNL PI	SNL PI Phone	NIS Country	NIS Institution	NIS PI
SNL-098	The Use of a Unique Super-Heated Steam Treatment for the Enhancement of the Tribological Properties of Ferrous and Non-Ferrous Alloys	Bill Moffatt	844-7062	Russia	Chelyabinsk State University of Technology, Chelyabinsk	Herman Vyatkin
SNL-099	Multilayer Coatings for Improved Tribological Performance	Bill Moffatt	844-7062	Russia	Institute of Metal Physics, Ekaterinburg	A. Vladimirov
SNL-100	Multilayer coatings composed of alternating layers of Cu/Fe and Cu/TiC	Bill Moffatt	844-7062	Ukraine	Paton Electric Welding Institute, Kiev	Anatol V. Demchishin
SNL-101	Functionally Graded Interfaces for the Enhancement of the Performance of Hard Coatings on Austenitic Stainless Steel and Titanium Alloys	Bill Moffatt	844-7062	Russia	High Current Electronics Institute, Tomsk	Sergei Bugaev
SNL-102	Surface Treatments for the Enhancement of the Performance of Diamond Like Coatings (DLC) on Tool Steels	Bill Moffatt	844-7062	Russia	Institute of Electrophysics, Ekaterinburg	N. V. Gavrilov
SNL-103	Application of Wear Resistant Coatings to Tools Using Novel Diamond Coating and Attachment Processes and Explosive Detonation Deposition Processes	Bill Moffatt	844-7062	Ukraine	Institute for Superhard Materials, Kiev	Mariy Voronkin
SNL-104	Diffusion Barriers/Nucleation Surfaces for Chemical Vapor Deposition (CVD) of Diamond on Tool Steel Surfaces	Bill Moffatt	844-7062	Russia	Institute of Metal Physics, Ekaterinburg	Vladimir Vykhodets
SNL-105	Synthesis of Polycrystalline Diamond Films Using Super High Frequency Plasma Deposition	Harry Saxton	845-8739	Ukraine	Donbass Civil Engineering Institute, Makeveka	Nikolai Samsonenko
SNL-106	High Energy Electron Beam Treatment for the Enhancement of the Tribological Properties of Tool Steels, Cemented Carbides, and Nitride Coated Tool Steels and Cemented Carbides	Bill Moffatt	844-7062	Russia	High Current Electronics Institute, Tomsk	Vladimir P. Rotshtein
SNL-107	Genetic Bond Between the Melt Properties and the Properties of an Industrial Aluminum Alloy	Frank Zanner	845-3085	Russia	Institute of Metal Physics, Ekaterinburg	Irena Brodova
SNL-108	Growth of Nickel Base Single Crystal Alloys at High Pressure	Lee Bertram	(510)294-1545	Russia	Institute of Metal Physics, Ekaterinburg	Vladimir O. Esin
SNL-109	Damage/Healing Theory as Applied to Self-Healing Bearings and to Semi-Continuous Wire Drawings	Lee Bertram	(510)294-1545	Russia	Mechanical Engineering Research Institute (IMACH), Ekaterinburg	Eduard Gorkunov
SNL-110	Investigation of the Role of Ectons in the Vacuum Arc	Lee Bertram	(510)294-1545	Russia	Institute of Electrophysics, Ekaterinburg	Gennady Mesyats
SNL-111	Measurement of Viscosity of Liquid Metals	Frank Zanner	845-3085	Russia	Institute of Metallurgy, Ekaterinburg	Viatcheslav Lisin

Project Title: Literature Review
Principal Investigator: Lev Romonov
Moscow Steel & Alloys Institute
Moscow, Russia
AJ-0145

CLAUSE 1 - STATEMENT OF WORK

Tasks:

The Contractor Shall:

1. Provide a written plan in English for a literature review to be conducted on work in the Soviet Union about liquid metal treatment to improve solid properties of titanium alloys, mold face coats for investment casting nickel superalloys, and methods of improving casting surfaces of nickel base superalloys.
2. Upon concurrence of the plan by Sandia; conduct the review listing all patents, instruments, publications as well as authors. Provide a report of the results obtained from the work in English. List recommendations for future collaborative research.

**Liquid Metal Processing
Laboratory
Org. 1833
Sandia National Laboratories
Albuquerque, New Mexico
Fax 505-845 3430
Dr. F.J. Zanner
CONTRACT AJ - 0145**

**Literature review to be conducted on work in
the former Soviet Union according to the theme:
"Analysis of patents and publications -within the
bounds of the problem about liquid metal treatment
to improve solid properties and the casting
surfaces of nickel base superalloys."**

**Moscow Steel and Alloys Institute
Fax 095-236-2105**

1995 J.

CONTENTS

Introduction	1
1. General characteristics of nickel base superalloys	3
1.1. Composition of these alloys and methods of their strengthening	3
1.1.1. Superalloys for rocketry	4
1.1.2. Superalloys for the hundreds of thermal hover	5
1.1.3. Effect of impurities on service characteristics of superalloys. Demands for metal's purity.	6
2. Analysis of today's technologies for nickel base superalloys production	
2.1. Basic schemes of smelting these alloys	7
2.2. New trends of improving technologies for superalloys production	7
3. Treatment of liquid metal before it's casting into moulds	
3.1. Basic objects of metals treatment	8
3.1.1. Production of castings with polycrystalline structure	9
3.1.2. Production of castings with monocrystalline structure	12
3.2. High-temperature treatment of melts (HTTM)	
3.2.1. Analysis of today's methods of this treatment	13
3.2.2. Peculiarity of HTTM influence on structure formation of nickel base superalloys with carbide - intermetallic strengthening	17
3.2.3. Peculiarity of HTTM influence on structure formation of nickel base superalloys with low content of carbon	20
3.3. Inoculation of nickel base superalloys	23

3.4. Use of rare-earth metals (REM) for modification microalloying and refining of superalloys	
3.4.1. Thermodynamics of REM interaction with impurities	24
3.4.2. Analysis of conditions of formation and trans- formation of non-metallic inclusions with REM	25
3.4.3. Effect of non-metallic inclusions of REM on formation of crystalline structure of castings	28
3.5. Application of ceramic filters for refining of liquid metal	29
4. Methods of improving the casting surface of nickel base superalloys	
4.1. Technology of mould manufacture for production of nickel base superalloys castings	31
4.2. Basic surface defects of the castings	32
4.3. Mould face coats using to improve the casting quality	32
4.4. Materials for making cores	33
5. Principal conclusions and recommendations	35
Tables	37
Figures	46
References	57

Introduction

"Melt at high temperature, but found at low temperature" - this golden rule of founders had forgotten for a long period of time in Soviet Union under the production of nickel base superalloys castings because of the imitation of foreign technologies. They used multistage schemes for the production of castings for special purposes, including preliminary smelting of superalloys in electric-arc furnaces to produce ingots for further vacuum-arc-, electro-slag- and electron-beam remelting. The duration of smelting in this case must be very short to prevent contamination of liquid metal by harmful impurities: oxygen, nitrogen, hydrogen and refractories. The melts were over heated up 150-200 °C before casting into molds.

For the last 10-15 years the new trends of technology for superalloys production have been developed on the basis of new investigation of structural - sensible properties of the melts and on principles of non-metallic inclusions formation.

The constant scientists rivalry of Moscow Steel and Alloys Institute (MISiS), the Urals Polytechnic Institute (UPI Ekaterinburg) and Institute of Casting Problems (IPL Kiev) has allowed to reach appreciable development of foundry science and technology.

According to opinion of Prof. Baum B.A., Prof. Tyagunov G.B. (UPI) [1 - 9], Prof. Hasin G.A. [10,11] and Dr. Kochegura H.M. [3,56-58] (IPL) the metallic melts have polyclaster structure as a structure of solid metal. For this reason High-Temperature Treatment of Melts (HTTM) makes liquid metal more homogeneous. As for scientists of MISiS they consider that the presence of different non-metallic inclusions is cause of heterogeneity

of the melts [12 - 21].

It's interesting to note that for the last few years the views of representatives of industry and scientists of MISiS on the processes taking place into greatly overheated nickel base superalloys have been drawing nearer. According to the order of Research Institute of Aviation Technology (NIAT) in 1989-90 the department of Foundry Technology (MISiS) carried out the comprehensive investigations of overheat effect on the parameters of crystallization and structure for a number of nickel base superalloys. While researchers of VIAM, IPL, NIAT implemented the orders of aircraft industry to develop the HTTM technology [4, 22-37].

The financial difficulties in 1991 interrupted the collaboration between MISiS and NIAT. However NPO "Saturn" has received financing to begin conversion of it's armament production and to manufacture civil products of high quality corresponding to international standards. The problem to produce ultra-clean superalloys with very low detrimental impurities contents has been of utmost importance. For this reason the research experience of MISiS scientists on deep refining of high-alloyed steels and superalloys from sulphur and non-metallic inclusions has been very actual for aircraft and space-craft industry.

The results of investigation carried out at MISiS have been used to shorten HTTM duration four times, as small to modify of melts and to decrease the oxygen content in the alloys up to 0.0004-0.0010 %.

Thus a comprehensive understanding of HTTM problems, use prospect of this treatment as well as it's development demand

profound analysis of theoretical and experimental results of liquid metal-state investigations, using these results for industry and working out new points of view on the process of cast-structure control for superalloys.

1. General characteristics of nickel base superalloys
 - 1.1. Composition of these alloys and methods of their strengthening

The All-Union Institute of Aviation Materials is basic center on working out and creation of superalloys [38]. However for the last few years (up till 1991) in USSR a number of firms have appeared to all elaborate special superalloys according to their concrete aims (NPO "Energiya", NPO "Kompozit", TSNII TMASH, MI-SiS, Moscow aviation Technological Institute - MATI, IPL etc.).

A number of new superalloys with intermetallic and carbide-intermetallic strengthening have been created to produce castings with polycrystalline and oriented structure. Z-nickel base superalloys can be classified according to various indications [38], but the content of intermetallic dispersed-strengthening γ' -phase on the base of intermetallic $\text{Ni}_3(\text{Al}, \text{Ti}, \text{Tb})$ is decisive factor in these alloys.

The superalloys containing up to 30% γ' -phase have high ductility at the operating temperatures $-253 \div 850^\circ\text{C}$. There are so called deformable alloys. The structure and properties of these alloys are in a large measure the same as for steels. However the upper level of operating temperature for nickel base superalloys is above 400°C approximately.

These alloys are used for production of numerous moulded pieces and welded-moulded constructions for chemical industry, turbo-engines and rocketry.

The making of high-capacity gas-turbine plant with service life for $10^2 \dots 10^4$ hours under higher temperature has demanded creation of nickel superalloys containing up to 60% of γ' -phase. It has called for increase in contents of dispersed - strengthening elements (Al, Ti, Nb) as well as high-melting metals (W, Re, Ta, Hf). The quantitative estimations of possibility the strength increase of these alloys owing to two basic mechanisms have been given in [38]. At 20 °C and lower temperature the solution hardening makes the main contribution to strength while at 700...1000 °C intermetallic compounds and fine disperse carbides provide this service characteristic of superalloys.

1.1.1. Superalloys for rocketry

These alloys are demanded to withstand a high dynamic load and a sharp temperature difference for 0,1...5 hours as well as to be weldable, forgeable or rollable.

The most part of articles for rocketry are manufactured from alloy VZHL14 (BMJ 14) [38] and it's modifications without carbon content. The composition of this alloy is shown in Table 1. Dispersed-strengthenig of the superalloy is provided by ageing under 600-650 °C. The disadvantages of this alloy are associated with very large solidification range (100-120 °C) that makes difficulties to produce of nonporous eastings and provokes on incipency of cracks under welding.

The cast in block rotors are manufactured from the nickel base superalloys ZHS3DK (ЖС3ДК) and ZHS6U (ЖС6У). The compositions of these alloys are shown in Table 1. After thermal treatment under 1200 °C these alloys must have impact strength not less than 0.3-0.4 MJ/m². The cooling of articles produced from these superalloys has not been provided during the process of work. Sometimes they use articles manufactured by methods of powder metallurgy and utilize gas-isothermic extrusion to increase the density of metal.

1.1.2. Superalloys for the hundreds of thermal hover

There have been the hundreds of patents for compositions of these superalloys and that is why it's impossible to describe all of this review. Among the superalloys of last generations we can choose the followings: ZHS3DK (ЖС3ДК), ZHS26 (ЖС26), ZHS32 (ЖС32), ZHS6U (ЖС6У), TSNK7P (ТНК7П), TSNK21P (ТНК21П), LZH11 (ЛЖ11), TSNK8MP (ТНК8МП), ZHS36 (ЖС36) and ZHL750 (ЖЛ750). The compositions of these alloys are shown in Table 1.

Former six superalloys are strengthened by carbides as well as intermetallic compounds and latter four alloys don't contains carbon practically.

It has been possible to increase the temperature of liquidus from 1240-1270 °C to 1320-1330 °C owing to complication of composition and by sharp rise of the prices of superalloys ZHS32 and ZHS36. In one's turn the temperatures of γ' -phase desolution and homogenization of alloys as well as limiting values of gas-turbine operating temperature can be allowed to raise.

They cast rotors and blades for gas-turbine engines working at wide range of temperatures (from 600 to 1200 °C) using these alloys with polycrystalline and monocrystalline structure.

1.1.3. Effect of impurities on service characteristics of superalloys. Demands for metal's purity.

The problem of impurity effect for nickel base superalloys is very important. There are both useful and detrimental impurities [38]. The contents of these elements are not usually more than 0,1%. The concentrations of low-melting-point nonferrous metals (Sb, Bi, Cd, Pb etc.) are strictly limited for superalloys (Table 2).

The contents of B, REM, Mg as well as O, S, and N are restricted too. The number of these elements can reach 20, depending on the alloy composition. In the former Soviet Union VIAM and VNIIMETMASH were the main law-makers in this field of metallurgy. It is necessary to notice that the control of alloy's purity at the plants depends on the possibilities of equipment for metal analysis. However the rise of demands for charge's impurity is one of the basic current trends for nickel base superalloys production.

2. Analysis of today's technologies for nickel base superalloys production

2.1. Basic schemes of smelting these alloys

Today's technologies of nickel base superalloys production include several process stages. Initial charge's blank is smelted in vacuum- or open induction furnaces. Then this blank is refined from sulphur, gases and non-metallic inclusions under vacuum-arc remelting, electroslag remelting or electron-beam remelting. These schemes of superalloy production are rather expensive. The expenditures of the remelting can reach 50 % of blank cost and are not necessary for all cases.

There is so called phenomenon of metallurgical heredity. Usually the remelting of blank is carried out for a short period of time to prevent of supplementary contamination of metal. That is why the large carbide-, carbonitride- and oxide inclusions dissolving slowly can be in the castings. This is the reason to decrease the service characteristic level and to deteriorate the quality of surface of foundry products.

2.2. New trends of improving technologies for superalloys production

Imperfection of casting structure on account of in-correct preparation of melts can be eliminated by use of non-traditional schemes of smelting.

There are three main approaches to diffusion of this problem:

1) Homogenization of melts by overheating; 2) Artificial formation of interstitial phase inclusions (inoculation); 3) Change of chemical nature of impurities to nucleate of solid phases under crystallization. In all cases it is necessary to create fixed overcoolings, to change of crystallization parameters (to make them more favorable) and to increase of purity degree of melts on oxygen, sulphur and nitrogen contents.

It is important that all above mentioned that can be used within any technological scheme of casting production. Only final stage of alloy preparation for casting demands for the change of technology.

3. Treatment of liquid metal before it's casting into moulds

3.1. Basic objects of metals treatment

Preparation of liquid metal before it's casting into moulds is important production operation defining the level of article service characteristics and quality of casting surfaces. According to the results of [38] about 40% of metal properties are lost because of cast structure defects.

Method preparation of melt depends on special demands of article structure. Today a number of technologies can be chosen to satisfy these demands. The castings of polycrystalline structure are produced by modification of melts with surface active substance as well as with additions to create the centers for a nucleation of crystalline phase. It's also effective to add into melt artificial centers for crystallization, to overheat of liquid metal for subsequent deep overcooling with purpose of sharp

increasing a number of active subtracters as well as prevention of mutual heat influence of growing crystals. The infra- and ultra- sand vibration effect and application of special mould face coats (surface modification) are successfully used to produce the polycrystalline structure castings too .

Production of mono-crystalline structure castings is concerned with the decision of the following tasks [23,27,30,32,35-37]:

- elimination of superfluous centers of crystallization;
- fitting of special very cloy cooling condition;
- creation of high temperature gradients on the liquid-crystal interface;
- inoculation of special seeds to orientate the growing crystals along given axis;
- use of apparatus to cut off parasitic crystals.

3.1.1. Production of castings with polycrystalline structure

Production of castings with given polycrystalline structure is rather simple task for aluminium base alloys [39,40].

For high temperature alloys (and for nickel base superalloys too) this task is not so simple and many experts have been working for it's discussion [3,13,14,15].

According to our opinion, high molar melting heat, large interfacial energy as well as relatively not great thermal conductivity of liquid alloys are the reasons of main difficulties in the discussion of this task.

For a long period of time they have been attempting to ac-

hieve successful results by using the modifiers [41 - 43,17,19, 44].

Boron, rare and alkali-earth metals (AEM and REM) are these modifiers. Boron gives the desirable effect of crystal grain grinding when the cooling rate at least by an order of magnitude greater the ordinary cooling rate for foundry products from superalloys in practice. In this case boron content in the melt should be 10-100 times as large as its concentration in superalloys composition (0,03-0,05%).

REM exert a very strong effect on cast structure of mono-phase nickel base alloys [19]. However in high temperature superalloys this effect sharply decreases by a number of reasons. REM interact actively with interstitial phase inclusions increasing the nucleation temperature of these phases in the melt. Reactions between REM and boron are even more active. For the alloys containing niobium (Table 3, Fig.1) and a number of other elements the separation (immiscibility) takes place into melt during its solidification. Any eutectic and peritectic transformation removes overcooling, caused by additions of REM. Furthermore, excess of these elements leads to the formation of intermetallic eutectics depreciating characteristics of the superalloys charily.

AEM refines melts in great extend. First of all magnesium exerts particular favorable influence on the structure and properties of superalloys. However this effect depends upon the composition of alloy [43]. In practice magnesium content often decreases during the remelting of blank and level of properties required for the behavior of impurities and the appearance of

structure casting anomalies demand further understanding and detailed investigations.

Without the answers on these questions it is impossible to overheating effect and to work out the effective technology of HTTM to produce castings of stable and high service characteristics level.

The data for superalloy ZHS32 (ЖС32) in Table 4 [13,45] have shown an extremum on the curve of high temperature strength depending on the temperature of alloy treatment. The holding time is 20 min in this case.

Boiling of the melts take place at high temperatures . Argon is used (with the pressure 0.2 atm) to prevent this castings does not be realized. Usually REM and AEM are added to the melt as alloying compositions with AEM concentrations up to 9-12%. It allows to use these additions without appreciable slopping of metal and pyro- effects and also to increase the assimilation (to decrease melting loss) as well as the refining action of AEM to a considerable extent. Changes in metal structure taking place under this treatment involve the improvement of non-metallic inclusion morphology and the grinding of dendrites in castings.

The volume and surface modifications are used to create a fine grain structure of alloy . Surface modification is realized by special coats of first layer of ceramic mould. Cobalt oxide is actually used for these purposes [71]. Volume modification is realized by small addition of alloying compositions containing high-melting nitrides, carbo-nitrides and carbides of titanium or zirconium [46,47,48-50,51,36,52]. Besides so called contrary

modification is utilized that consist in formation of crystallization centers owing to surface activation of particles in the melt .However in nickel base alloys it is rather difficult to obtain essential changings of casting structure in this way. For this purpose it is necessary to remove from the melt the most active centers of crystal nucleation and to provide supercooling in tens of degrees Kelvin.

In superalloys with carbide-intermetallic hardening the modification of carbide is used [71]. For this purpose the same high-melting particles are utilized. The main problems in this case are the following: oxygen contamination of melt and difficulties to distribute particles homogeneously into liquid alloy and then into castings.

3.1.2. Production of castings with monocrystalline structure

Monocrystalline structure is created in castings by oriented crystallization method [34-37,53]. Ceramic mould filled up by the melt is gradually moved from isothermal zone of furnace to cooler zone when crystallization begins. The crystals grows in the direction of the greatest temperature gradient. The seeds from nickel-tungsten alloys are inoculated and fixed in ceramic mould to give specific directions of crystal growth . Structure of alloys and angle of disorientation are determined in great extent by geometry of mould, rate of it's movement, as well as contents of impurities and non-metallic inclusions in alloys.

Oxygen concentration plays the most important role under monocrystalline castings production. It is necessary to notice

that carbon forming carbides in liquid-solid zone can play a negative role in this process.

3.2. High-temperature treatment of melts (HTTM)

3.2.1. Analysis of today's methods of this treatment

Information about use of HTTM can be got from "open" publication [54,2,3,4-6,10,11,14,54,22-33,56-58,53,59-62]. However in these references not the best modifications of this treatment are described.

Technology elaborated by UPI and IPL includes the heating of melts up to some critical temperature range when structure change occurs. The homogenization temperature is close to the melting point of titanium for different alloys and according to various references is 1670 - 1680 °C (Table 5).

The method of thermocycling including heating and scoffing in the temperature interval 30 - 50 °C near the critical temperature was used. It allows to grind dendrite structure as well as carbides and carbonitrides one and half times as small.

Considerable part of these inclusions are inside grains and their sizes are about 1 μm . However a number of inclusions of white phase and primary initial γ' -phase increases by 6 - 7 % variants of technology of plasma spot were tested.

It has been shown that overheating of alloys by 20-30 % of liquidus temperature provides the best conditions for risering. In this case the average porosity decrease by 7 -39 % and the mechanical properties increase. High temperature treatment of nickel base superalloys changes morphology, sizes and shapes of

non-metallic inclusions and decreases the total amount of carbide- and carbonitride phases. HTTM increases overall and local strength 1,3 -1,5 times as much, ductility twice as much, impact strength 2-3 times as much and long-term strength at high temperature 1,5-2,3 times as much. Favorable effect of HTTM on structure and properties a number of alloys ЭП539ВД (EP539VD), ЭП538ЛМ (EP538LM), ЖС3ДК (ZHS3DK) etc. is noted in These superalloys were overheated above liquidus temperature by 340 - 350 °C. Soaking of liquid metal under this temperature was 2-3 min. After HTTM dendrite structure of alloy was more fine, the sizes of interstitial phases diminished and their morphology improved. Carbides and carbonitrides were not mainly as continuous chains at the grain boundaries but as isolated compact inclusions. Improvement of cast structure after HTTM promoted the increase of ductility and impact strength about twice as much.

The most part of researchers consider that real metallic melts are inhomogeneous or heterogeneous systems. However they have had different points of view on the reasons of this inhomogeneity.

According to the opinion of the Urals scientists the melt heterogeneity is caused by cluster structure of liquid metal. As the main proof of this conclusion they consider a presence of structural-sensible property anomalies in particular for viscosity at high temperatures. In [6,9] the viscosity anomalies were discovered for nickel base superalloys within the temperature range from 1560 to 1700 °C. After overheating above 1820 °C appreciable kinematic viscosity hysteresis was observed. Abnormal increase of viscosity was discovered also for iron-nickel melts

at 1700 - 1800 °C. This viscosity anomaly disappears during the soaking of the melts. Viscosity hysteresis does not depend on refractories of crucibles and that is why according to some authors [56,9] it is caused by the change of internal structure of the melts. It is necessary to notice that the temperature range of viscosity and electrical resistance hysteresis appearance depends essentially on method of alloy preparation. For example, after electron-beam remelting of alloys viscosity hysteresis was detected at considerably higher temperatures of overheating.

Thus abnormal changes of structural-sensitive properties of nickel base alloys are observed within the temperature range from 1650 to 1820 °C. And as a rule, viscosity increases in this case.

However all mentioned property changes of alloys can be explained by the presence of the various highmelting particles and compounds in liquid metal without use the complicated and poorly proved by experiment cluster model. For example in [12] it has been shown that chromium carbides introduced into the melt by high carbon ferrochrome can present in liquid metal over a long period of time changing its viscosity. Obviously, more stable compounds such as aluminium and zirconium oxides as well as titanium carbides and carbonitrides can exist in the melt without practical dissolution (dissociation) for longer period of time. At high temperature overheating (first of all at the melting point of element forming oxides and interstitial phases) the rate of these particles dissolution can be increased. For instance, at about 1670 °C intensive dissolution of phases with titanium begins. This value of temperature is in satisfactory

compliance with the data for optimal overheating temperatures given by N.M.Kochegura (see Table 5).

Acceleration of highmelting particles dissociation promotes increase of oxygen and nitrogen concentrations in the melt. As it has been shown in [15] in one's turn this fact causes increase the viscosity of liquid metal. Depending on kinetics of impurity behavior in the melt abnormal viscosity increase can be observed and during of alloy soaking at high temperature viscosity has to be decreasing .

For the further investigations of the processes taking place under HTTM an idea about metallic melts containing suspension of highmelting particles is probably more correct then cluster model of liquid metals.

It is necessary to note that authors of above mentioned works have concerned the problem of alloy crystallization only slightly.

However this problem is of utmost important because of formation the basic properties during crystallization of melts. Thus, density increase of ingots and castings, decrease casting shrinkage volume as well as the grinding of dendrite structure and non-metallic inclusions indicate the raise of solidification rate caused mainly by appreciable overcooling of melts. In one's turn this overcooling is bound up with the changing of chemical nature of crystal nucleation centers.

It is difficult to understand why the soaking over a long period of time reduces the positive effect of HTTM.

Today many questions concerning the structure of real liquid metals, the change of crystallization parameters of the melts

after HTTM, the behavior of impurities and the appearance structure casting anomalies demand further comprehensive understanding and detailed investigations. Without the answers on these questions it is impossible to know about the mechanism of overheating effect and to work out the effective technology of HTTM to produce castings of stable and high service characteristics level.

The data for superalloy ЖС32 (ZHS32) in Table 3 have shown an extremum on the curve of high temperature strength depending on the temperature of alloy treatment. The holding time is 20 min in this case.

Boiling of the melts take place at high temperatures . Argon is used (with the pressure 0,2 atm) to prevent this boiling. Stability of lining is the important problem under superalloy production. In the crucibles of electro-corundum has been proposed.

3.2.2. Peculiarity of HTTM influence on structure formation of nickel base superalloys with carbide - intermetallic strengthening

Influence of HTTM on a structure of superalloys is revealed in grinding of dendrits, decrease of intermetallic-eutectic inclusions and increase of compact carbide share. It points out the change of nature of non-equilibrium crystallization and, first of all, the presence of deep overcooling .

In Table 6 the HTTM influence on crystallization parameters of nickel base superalloys is shown. The compositions of these

alloys are shown in Table 1.

Crystallization of alloys begins from the formation of γ -phase and then carbides and intermetallic eutectic inclusions nucleate. The temperature at which overheating begins to determine the parameters of crystallization depends on the presence of carbides as the hardening phases. For the superalloys of carbide-intermetallic strengthening (ЖСЗДК [ZHS3DK], ЖС6У [ZHS6U], ЖС32 [ZHS32], ЦНК7 [CNK7] and ЦНК21П [CNK21P]) this temperature is above 1600 °C (Table 6).

The value of overcooling depends also on the time of melt holding at the fixed temperature. For example, there is no appreciable overcooling after soaking of alloy ЖСЗДК at the 1670-1700 °C for 1-2 min. However this alloys begins to crystallize at about solidus temperature after soaking for 5 min at 1770 °C. The increase of duration of isothermal melt holding leads to disappearance of overcooling. The most essential overcooling for alloy ЖС6У is to be observed after the soaking at 1720 - 1770 °C for 2 - 5 min. Alloy ЖС32 shows slight tendency to decreases of supercooling when isothermal holding time increases (Figure 2).

These data indicate that mechanism of HTTM influence on the structure of nickel base superalloys is rather complicated. It has not been explained only by existence of supercooling and therefore by dissociation (dissolution) of substrates for nucleation. At it has been shown in Table 7, the overcooling increase sharply again after long time soaking (for more than 15 min).

It is necessary to overheat of alloys with carbide-intermetallic strengthening above melting point of titanium (above 1650

°C). Only in this case the disactivation of carbide and carbonitride particles can be achieved by means of their transformation into liquid fluctuations enriched with titanium and other elements of interstitial phases. These fluctuations have been found around compact carbides (Nb,Ta)C in alloy ЖС32 after HTTM (Figure 3).

The melt must be homogenized and overcooled to an even greater degree after disappearance of the fluctuations. However, the overcooling ceases to decrease when interstitial phases have dissolved entirely.

The results of micro-spectral analysis by "Camebax" have allowed to reveal the inclusions of aluminium-, zirconium-, magnesium- and yttrium oxides inside carbide particles (Fig.4).

According to the arrangement of these particles they are the centers for interstitial phase formation. It has been known that nickel-aluminium spinel has the cubic lattice parameters similar to parameters of titanium carbides, nitrides and carbonitrides, as well as zirconium oxides [48,50]. These oxides are thermodynamically more stable than interstitial phases. Therefore in zones of carbides and carbonitrides dissolution oxides exist for a long period of time surrounded by melt of higher titanium concentration and hence of higher liquidus temperature. After HTTM and solidification of these shells the ready substrates can be formed in the melt and overcooling can be removed entirely.

This peculiarity of highmelting particles behavior has been used for making of clad inoculators [36,52].

Composition of oxide inclusions depend on the composition

of alloys. That is why after HTTM various behavior of these superalloys can be observed and unstable changes of structure and properties of the alloys can be obtained.

Therefor in practice careful and individual choice of the temperature and the duration of soaking has been demanded. As a rule, the duration of HTTM is much more that it is necessary for complete dissolution of interstitial phase inclusions .

3.2.3. Preculiarity of HTTM influence on stricture formation of nickel base superalloys with low content of carbon

Changes of crystallization parameters for alloy ЖС36 (ZHS36) after different regimes of HTTM are given in Table 7 an shown in Figure 5 . Initial alloy can solidify within the temperature interval from 1405 to 1340 °C. Intermetallic eutectic ($\gamma+\gamma'$) begins to form at the temperatures 1380-1350 °C.

The results of computer calculation on programme "STATGRAPHICS" of volume fraction (in %) and average size of intermetallic eutectic in dependence on various HTTM regimes are given in Table 8,9. Microstructure of alloy after HTTM are shown in Figure 6 . Maximum value of overcooling is reached after holding of melt for 15 min at 1800 °C. In this case abnormal character of changes of average sizes and volume fraction of intermetallic eutectic inclusions depending on value of overcooling as well as appreciable enlargement of these particles 1,5-2 times as much have been discovered.

The main parameters of crystallization for alloy ЖСЛ750 (ZHSL750) are presented in Table 8. Initial alloy solidifies

within the temperature range from 1360 to 1280 °C. Intermetallic eutectic ($\gamma+\gamma'$) begins to form at the temperatures from 1315 to 1290 °C. This superalloy has tendency to deep overcoolings even after heating to 1600 °C. And after overheating up to 1800 °C it begins to solidify below solidus temperature. Maximum value of overcooling is 92 °C.

The results of investigation of the alloy microstructure have shown that HTTM for a short period of time at the temperatures above 1770 °C improves the shape and nature of eutectic ($\gamma+\gamma'$) particles and the sizes of these inclusions are 2,5-3 times as small. The grinding of cast structure is concerned with faster solidification of overcooled alloys.

The soaking of melt at 1800 °C for 3 min provides the most essential decrease of size of white phase inclusions. With increasing of holding duration up to 15 min the increase of eutectic inclusion sizes (twice as much) and their volume fraction (by 2,5%) as well as sharp deterioration of the particles morphology have been observed. The difference between overcooling values for first and second regimes of treatment is about 15 °C. This beginning (below equilibrium solidus temperature of alloy) provokes formation of eutectic particles as rough conglomerate of phases (Fig.). The most part of these inclusions have disappeared after homogenization at 1150 °C. The average size of particles of non-equilibrium intermetallic eutectic has not managed to be decreased by thermal treatment.

The data of crystallization parameters and structure characteristics of alloy ИHK8MII (TCNK8MP) are given in Table 7.

As has been seen from these results the distinction of behavior of nickel base superalloys under HTTM is determined by carbon content and therefor by possibility of carbide formation in overcooled alloys.

The thermodynamic analysis has allowed to construct the diagrams with composition ranges of niobium and titanium carbides formation in overcooled nickelbase superalloys between the liquidus temperature and the solidus temperature. Within the composition range where the reaction of carbide formation takes place above solidus temperature the carbide inclusions have compact shapes and the appearance of non-equilibrium eutectic is eliminated completely. Removal of overcooling occurs because of the formation of carbide particles making easier of γ -phase nucleation. If the alloy is within the composition range, where carbide formation does not take place between the liquidus temperature, it can be overcooled with the formation of non-equilibrium intermetallic eutectics (for example, alloy ZHS32 in Figure 8).

Taking account of decrease of carbon concentrations on melts under vacuum remelting and difficulties to control of those process, it is necessary to have carbon content in alloys with carbide-intermetallic strengthening before HTTM at about upper limit. However, overcoolings as deep as possible are required to reached the maximum effect of HTTM. But these overcoolings are realized only for melts with lower carbon concentrations.

Thus, the technology of HTTM can be used successfully by fitting of optimum parameters ether in practice or by use the results of cheaper differential-thermal analysis. However, both

methods give good results only on condition that compositions of initial charge's blanks are practically the same.

3.3. Inoculation of nickel base superalloys

As has been found by the authors of this review the effect of overcooling on the alloys of carbide-intermetallic strengthening depends on the value of the overcooling which is controlled by the temperature of beginning of carbide formation.

For this reason the use of HTTM may be ineffective for the alloys with strengthening phases of niobium intermetallics and carbides. As the results of thermal analysis and thermodynamically calculations have shown, formation of NbC begins at the temperatures of alloy crystallization [17,19,44]. This leads to the presence in structure of large niobium carbide inclusions (up to 200 μm of sizes) and to low stability of casting service.

It is necessary to use the technology of forced formation of carbide inclusions by means of addition of special worked out alloying compositions and cladding of titanium carbide particles by Ni, Cr and other elements [46-50,41-43,17,19,44,26,51,36,52].

Modern inoculators are characterized by large duration of their effect (up to 30 min). Use of these inoculators under casting production of nickel base alloys allow in a number of cases to improve morphology of carbide inclusions, to increase essentially ductility properties and to stabilize high-temperature strengthen at the very high level (Table 10).

There are the following disadvantages of this method: formation of carbide- or carbonitride segregations in various parts

of castings; possibility of supplementary contamination of melts by oxygen; necessity of accurate choice of technological parameters and deficiency of inoculator production on a large scale.

3.4. Use of rare-earth metals (REM) for modification microalloying and refining of superalloys

3.4.1. Thermodynamics of REM interaction with impurities

In many works dedicated to HTTM influence on nickel base superalloys and steels the behavior of gases has not been studied. In the only work [30] the reaction between oxygen and carbon under HTTM was investigated. The authors described the phenomenon of overheated melt boiling in vacuum and discussed methods of its prevention.

The data given in Table 11 show that HTTM does not provide with necessary very low content of oxygen in the melt ($\leq 0,002\%$). Even the use of ceramic filters has not been very effective because aluminium and other deoxidizers can not add dissolved oxygen completely to form oxides in the melt at the temperature of casting (1580°C).

This problem can be settled by use yttrium as one of the most chemical active rare-earth metal.

Calculation of the equilibrium in systems Ni-O-Al and Ni-O-Y is:

$$\lg(f_{\text{Al}}^{2/3} f_{\text{O}} [\text{Al}]^{2/3} [\text{O}]) = - \frac{20204}{T} + 6,17 \quad (2)$$

and

$$\lg(f_Y^{2/3} f_O [Y]^{2/3} [O]) = - \frac{27891}{T} + 6,11 \quad (4)$$

From Eq. (2) (4) at 1580 °C we can write

$$[Al]^{2/3} [O] = 2,9 \times 10 \quad (5)$$

$$[Y]^{2/3} [O] = 1,0 \times 10 \quad (6)$$

It follows from Eq. (6) that rather small additions of Y into superalloys allow to have very low oxygen contents.

3.4.2. Analysis of conditions of formation and transformation of non-metallic inclusions with REM

Additions of REM have different effect on crystallization parameters of superalloys with intermetallic strengthening and carbide-intermetallic strengthening. The former begins to overcool by 15-20 °C under crystallization that leads to the grinding of dendrite cells and intermetallic eutectic inclusions 1,1-1,3 times as small. However, under high overheating (>1700°C) the alloy modified by Y has rather lesser overcooling than alloy without additions of this element.

In the alloys of carbide-intermetallic strengthening additions of REM increase the temperature of carbide formation by 5-10 °C and do not lead to overcooling (Table 12).

The structural changes of alloys are caused by the improvement of morphology of oxide- and carbide inclusions (Figure 9). This

can be connected with the rise of the temperature of complex carbide (M,REM)C nucleation in the melts under crystallization.

Yttrium forms oxide inclusions of high thermal stability. These inclusions can be stable even at the temperatures of HTTM. It has been shown above that oxides of REM, aluminium and complex inclusions of these elements are inactive to be the substrates for crystal nucleation of solid nickel base solutions. At the same time on the spinels of cubic lattice formed by Al_2O_3 and Y_2O_3 the nucleation of intermetallic compounds Y_2Ni_{17} and carbides has to be possible and these particles can in one's turn initiate the growth of γ -phase crystals.

Thus, the presence of REM oxides in the melt does not permit to overcool of nickel base superalloys below the temperature of carbide- and equilibrium intermetallic eutectic formation. Furthermore, according to thermodynamics complex deoxidation of melt by Al and Y provides very low residual concentration of oxygen.

According to the results of investigations of this review authors additions of REM under HTTM promote the improvement of oxide morphology and of melt refining from oxygen. REM increase thermodynamically stability of oxide inclusions and in that way prevent the formation of redundant intermetallic particles caused by overcooling.

In the superalloys with carbide-intermetallic strengthening REM form not only oxide, but carbide inclusions too. Additions of REM (0,05-0,2%) provide overcooling which is limited by the beginning of carbide formation reaction. The time of melt holding is increased twice as much to overcooling of alloys below

the temperature of carbide eutectic. In the first series of experiments REM (0,1%) were added into melt after melting - down of charge. Then after HTTM (before casting) 0,05% REM were added once again. In this case the oxygen content decreased in superalloys up to 0,0004%. However the mechanical properties of a number of castings were not at required level. The excessive REM content was the reason of intermetallic eutectic $(Y,Ni)_2C_7$ formation.

In the second series of experiments Y (0,05%) was added just after melting - down of charges blank. The duration of isothermal holding of melt under HTTM was decreased to 7-15 min. Then the melt was cooled to the temperature 1580 °C and was casted into moulds with foam ceramic filters. In this case the residual concentration of yttrium was below 0,01%. As a result of use HTTM, yttrium additions and filtration the oxygen contents in $\Pi HK7\Pi$ (TCNK7P) and $\Pi HK21\Pi$ (TCNK21P) alloys decreased up to 0,001% and even lower. It is necessary to notice that use of filters improves the stability of refining, but does not determined the minimum content in alloys.

The results of mechanical testings given in Figure show that use of HTTM and modification practically does not influence on the strength of alloy TZNK21P but it increases the strength of alloy TCNK7P considerably. These results can be explained by improvement of carbide inclusions morphology in latter because of higher carbon content.

HTTM and T-modification have an essential effect on long-term strength of superalloys. As can be seen in Figure 10, with decrease of oxygen content stabilization of long-term

strength takes place for both alloys at level 6-8 times as high as standards or specifications.

3.4.3. Effect of non-metallic inclusions of REM on formation of crystalline structure of castings.

As has been shown in works [21-25] REM are very strong deoxidizers and they can cause deep overcooling of nickel base superalloys. The use of these elements permit to decide the problem of oxygen content increasing in the melts after HTTM. An influence of REM on crystallization parameters depends on the kind and contents of these metals as well as on the concentration of oxygen.

It has been found that after REM additions non-metallic inclusions of variable compositions are formed. When temperature decreases these particles can transform into inactive oxides of REM and active centers to nucleate of solid nickel base solutions. With the increase of $[REM]/[O]$ ratio the fraction of REM oxides in the inclusions increases and the fraction of NiO decreases correspondingly. The extreme character of overcooling in nickel and iron melts containing oxygen under influence of REM additions is linked (Figure 11) with the change of oxide inclusion composition and hence with the temperature's condition of their selective disintegration.

Maximum overcoolings are ten Celsius degrees and are limited by temperatures of the beginning of eutectic nucleation containing of REM intermetallics [19].

Morphology of intermetallic eutectic inclusions can change

depending on the value of overcooling. In the case of the maximum overcoolings crystallization of alloys begins not from the sides of crucible but all over the volume of melt on REM oxide inclusions. According to this particles of intermetallic eutectic have compact shapes.

In superalloys of carbide strengthening REM are used to microalloy of carbides and nucleation of interstitial phases takes place on REM oxides.

Thus, the range of REM application and effect is rather broad and it is not restricted only by high refining ability of these elements and their influence on morphology of non-metallic inclusions. The additions of REM prevent excessive overcoolings as well as loss in service characteristics of alloys after HTTM under non-optimum parameters.

3.5. Application of ceramic filters for refining of liquid metal

Production of castings of iron and nickel base superalloys requires to use filters. The necessity of these melts filtration is caused by following reasons: formation of scabs, use of dirty charge and returned materials, formation of non-metallic inclusions as a result of dioxidation and modification of liquid metal, use of refractories and mould face coats of inferior quality.

At present the screen filters of refractory glass-carbon materials, ceramic canal filters of chamotte, filters of Al_2O_3 and other oxides have been used. For treatment of a large amount

of liquid metal the granule's filters are used in filling funnel under casting [63-68]. The foam-ceramic filters of Al_2O_3 with alumin-chromo-phosphate binders are used [68]. Filters are usually placed in filling funnels or skim bob directly. Efficiency of refining depends upon the purity of melt. The more impurities contents the higher efficiency of refining. The filters permit to detained inclusions of sizes above 60-80 μm . The inclusions of smaller sizes are removed from melt only partially. The use of the best filters allows to decrease oxygen concentration in high-alloy steel and superalloys up to 0,003-0,004% [65-68]. According to the authors of this review this concentration can be 1,5 times as low. The possibilities of filters is limited by two factors. The first one is concerned with conditions of dissociation of oxides as filter's material. Second one is determined by the fact that at the temperature of casting the concentration of dissolved oxygen in melt is rather high and therefor the most part of oxide inclusions form during cooling and solidification of alloy.

As it has been shown by the authors of this review the very low oxygen concentrations in superalloys after HTTM and additions of REM can be reached even without using of corundum foam-ceramic filters. However the use of these filters is desirable to obtain more stable results on melt refining from oxide inclusions.

4. Methods of improving the casting surface of nickel base superalloys

4.1. Technology of mould manufacture for production of nickel base superalloys castings

Nickel base superalloy castings are produced in ceramic moulds for the investment casting. Technology of the manufacture of these moulds is described in detail in the works [69-71]. There are two types of shells in dependence on methods of their making: poly-layer shells and double-layer shells.

For the casting of nickel base alloys the first type of shells is used. The surface of model block is wetted by suspension under dipping. Suspension adheres to the surface of model and reproduces its configuration precisely. Refractory introduced in suspension layer and creates the skeleton of the shell. This shell is formed step by step being applied 4-6 layers and up to 12 layer for production of large castings. This process includes the predrying of each layer for 10-60 min. The first facing layer is sprinkled (dusted) with fine-grained materials (0,1-0,16 mm) to obtain smooth surface.

After removal of model composition and final drying the shell consists of 95-97% filler and binder.

As a filler they use amorphous quartz, electrocorundum, high-alumina chamotte, disten-silimanite, zircon, mullite, magnesite and crystalline quartz. First three refractories have small linear expansion (from 0,04 to 0,4 %) that provides high thermal shock stability.

The binder of shell mould is high-melting inorganic oxide or complex oxides isolating from solution under drying and tempering (calcination) of shells.

Solutions of ethyl-silicate (quality 32 or 40) are used for these purposes usually. Furthermore aqueous solutions of ethyl-silicate (quality 32 or 40) are used. Besides aqueous solutions of silica-sols are used [70] to decrease consumption of ethyl-silicate and fare-explosion dangerous liquids.

4.2. Basic surface defects of the castings

Analysis of these defects caused by moulds and methods of their removal are in works [69-71]. The defects can be divided into 7 following groups: 1) Non-metallic inclusions; 2) Bloating of facing layer; 3) Cracks of steels; 5) Rough surface; 6) Dents and bulging; 7) Expansion scab. Origin of the defects is connected with breaches of technology of model and shell making, of regimes of drying, calcination (tempering) and storage of molds as well as with use of unqualitative materials. Besides the defects can be caused by incorrect constructions of the castings and pouring gate systems or by use of wrong regimes of casting and cooling.

4.3. Mould face coats using to improve the casting quality

The important characteristics of moulds are: accuracy of reproduction of surface micro-relief and configuration of models, strength, thermal and chemical stability, gas

permeability and heat-storage capacity.

The best wearability is reached by use of amorphous coatings in particular fused quartz. However a burnt-on sand occurs on the surface of castings because of active interaction of mould coats with components of nickel base superalloys. That is why SiO_2 content in the surface layer of mould is sought to be decreased. The use of electro-corundum with 2,5% Co_3O_4 for surface modification of superalloys is the most often. For the last few years the works [70,71] have been published about expediency of addition of disten-silimanite and high-alumina shamotte in the composition of first two layers of shell. In that case after thermal treatment of shell at 1050 - 1150 °C the formation of mullite takes place. This prevents saturation of surface layers of alloy by silicon, improves wettability and increase strengthen of mould.

High quality of casting surface is provided by use of zircon concentrates prohibited in the middle of 1980th because of uranium and thorium contents up to 0,1%.

4.4. Materials for making cores

The cores are used to produce of complex cavities and holes of diameters up to 0,4 mm. They are divided into baked cores (1 class) and cold cured cores (2 class).

The formers are made by dry solid phase sintering and liquid phase sintering [70,72-76]. For that reason polydispersed powders of electro-corundum, zirconium with silicon carbide and niobium oxide, powdered and granular quartz. Plasticizers are

mixtures of paraffin (91-95%) with polyethylene (up to 5%) and rosin. Dry sintering is realized at the temperature not lower than 0,8 melting point of pure high-melting oxide. Stabilized zirconium oxide (5%) is added in corundum mixture to decrease temperature and duration of sintering [70]. Liquid phase sintering is realized with additions of sodium silicate. However these cores can work at the temperatures lower 700 °C. Cold chipped cores are made from refractory oxide with liquid binder. After drying they are tempered (calcinated) with shell mould. The strength of these cores before tempering is about one tenth as high as the cores produced by sintering. That is why the 1 class cores have to be used for castings with thin walls (up to 0,5-1,0 mm) and for cores of small thickness (up to 0,4-1,0 mm).

The increase of thin wall cores strength is epoxy resin with curing agents. The cores are dipped in liquid resin and dried for 10-20 min. Polymerization of resin is realized at 120-140 °C for 40-60 min. Then strength of electrocorundum cores increases from 14-15 to 30 MPa. The same method easily used to increase strength of 2 class cores. Under tempering of mould a resin burns out and the strength of electro-corundum cores increases from 14-15 to 50 MPa. The disadvantage of this method is evolution of unhealthy carcinogenic substances that demands to use special safety measures.

5. Principal conclusions and recommendations

The results of carried out analysis of literature allow to conclude that the basic technological peculiarities of nickel base superalloys production are: melting of charge blank in vacuum induction furnaces and subsequent vacuum arc remelting, electroslag remelting and electron-beam remelting. However these schemes of smelting are rather expensive and do not provide desirable results on purity of metal and structure of castings for all cases. More effective scheme of casting production can be considered the following: melting of charge blank in vacuum induction furnace with subsequent hightemperature treatment of melt (HTTM) before its mould casting. Use of HTTM provides to reach high degree of homogeneity of melts to prevent a number of casting defects caused by phenomenon of heredity.

For increase purity of melts it is useful to combine HTTM with microalloying and modification of REM. In that case the residual concentration of oxygen in alloys can be lower than 0,0001 %.

However it is necessary to take in mind that efficiency of HTTM first of all depends on the correct choice of technological parameters of this treatment. The same conclusion can be made conformably to use of REM and inoculaters.

These questions demand comprehensive understanding and further detailed investigation to determine the optimum temperatures and duration of treatment as well as concentrations and methods of addition of microalloying elements and modifiers. Use of filters for deep refining of melts under casting is not so

effective method without preliminary additions of REM.

Further study to work out stable technology of superalloy castings must be directed at development of calculations methods for optimization of HTTM parameters. In these calculations not only thermodynamic principles but kinetic peculiarities have to be considered for description of the processes of dissolution and transformation of various types of non-metallic inclusions under melt treatment.

Table 1

Compositions of nickel base superalloys

Super-alloys	C, %	Cr, %	Mo, %	W, %	Nb, %	AL, %	Ti, %	Co, %	Fe, %	Ta, %
1	2	3	4	5	6	7	8	9	10	11
ZHSL750	> 0,03	15- 17	3,6- 4,6	6,2- 6,8	5,4- 6,4	0,2- 0,4	0,0	0,0	>1	0,0
LZH11	0,10 0,25	4,5- 6,5	3,5- 6,0	3,5- 6,0	6,0- 8,0	4,5- 6,5	0,0	0,0	>1	0,0
ZHS32	0,13 0,18	4,3- 5,6	0,8- 1,4	7,7- 9,3	1,4- 1,8	5,6- 6,3	0,0	8,0- 10,0	>1	3,5- 4,5
ZHS36	> 0,01	3,5- 4,5	0,8- 1,2	11- 12	0,7- 1,2	5,5- 6,2	0,0	5,0- 9,0	>1	0,0
TZNK7P	0,07 0,13	14- 16	0,2- 0,7	6,2- 7,2	0,0	3,6- 4,4	3,6- 4,4	8,0- 9,5	>1	0,0
TZNK21P	0,05 0,10	20- 22	1,0- 2,0	2,0- 2,6	0,5- 0,9	2,1- 2,7	3,0- 3,8	10,0- 12,0	>1	0,0
TZNK8MP	> 0,02	11- 13	0,3- 0,6	6,2- 7,2	0,8- 1,2	3,7- 4,5	4,0- 5,0	8,0- 9,5	>1	0,0
ZHS6U	0,12 0,24	9- 12	1,0- 1,5	9- 12	1-2	5-6	2-3	9,0- 10,0	>1	0,0
ZHS3DK	0,08 0,12	8- 11	3,7- 4,2	4,0 5,0	-	4,2 4,7	2,5 3,2	9,0- 11,0	>2	0,0
VZHSL14	0,01 0,06	18- 20	4,5- 5,5	-		1,2 1,5	2,6 2,9	-	8- 10	

Table 2

Permissible concentrations of impurities in nickel
base superalloys

Concentration (>), %								
B	O	N	Zr	Fe	S	P	Pb	Bi
0,015	0,003	0,005	0,005	1,00	0,01	0,015	0,001	0,0005

Table 4

Influence of temperature of HTTM on
high-temperature strength of nickel base alloys
(superalloys ZHS32, t-20 min)

T, °C (HTTM)	1600	1640	1700	1740	1820
280 MPa	74	90	94	133	124 ^{*)}

*) t- 10 min.

Table 5

Homogenization temperature of superalloys

Superalloy	ЖСЗДК (ZHS3DK)	ЭП539МЛ (EP539ML)	ЖС6У (ZHS6U)	ЖС6К (ZHS6K)	In-738
1	2	3	4	5	6
T, K	2073	2003	2063	1998	1988

1	2	3	4	5	6
Superalloy	ЖС26 (ZHS26)	ЖС6Ф (ZHS6F)	ВЖЛ14 (VZHL14)	4С70 (CHS70)	ЭП202 (EP202)
T, K	2033	1993	2013	1993	1983
Superalloy	ЭП741НП (EP741NP)				
T, K	1983				

Table 6

Influence of HTTM on crystallization parameters of
superalloys with carbide-intermetallic strengthening

Alloy	T HTTM, °C	Time of HTTM, min.	T beg. crys., °C	T end crys., °C	Overco- oling, °C
1	2	3	4	5	6
ЖСЗДК	1620	2	1340	1280	0
	1820	2	1260	1280	80
ЖС6У	1350	2	1340	1290	10
	1820	2	1290	1290	60
ЖС32	1600	5	1395	1320	0
	1800	5	1355	1320	40
ЖС36	1600	5	1395	1330	10
	1800	15	1310	1320	95

1	2	3	4	5	6
ЦНК7П	1600	5	1340	1280	0
	1800	5	1295	1280	45
ЦНК8МП	1600	5	1340	1285	15
	1800	5	1280	1282	75
	1800	15	1272	1278	83
ЦНК21П	1600	5	1330	1270	0
	1800	5	1280	1270	50
ЖСЛ750	1500	5	1360	1280	0
	1800	10	1276	1278	84
Х18Н9ВЛ	1600	5	1465	1390	0
	1800	2	1422	1390	43
ВНЛЗ	1600	5	1438	1366	0
	1750	2	1422	1366	35
З5ХТСЛ	1800	2	1390	1366	48

Table 8

Influence of HTTM on crystallization parameters of
superalloys with intermetallic strengthening

Super- alloy	HTTM T, °C	T, °C			
		HTTM, min			
		3	5	10	15
1	2	3	4	5	6
GS 36	1600	0	15	40	15
	1650	0	40	75	65
	1700	30	30	65	85
	1750	45	85	85	80
	1800	85	85	85	95

1	2	3	4	5	6
GSL750	1600	25	28	38	48
	1650	32	38	49	57
	1700	48	54	61	74
	1750	68	76	82	86
	1800	77	83	88	92

Table 9

Influence of HTTM on volume fraction and average size of $(\gamma+\gamma')$ -phase inclusions in alloy ZHS-36

HTTM regime,min		Volume, V %	Average size A, μm
1600	3	13,289	33,596
1600	10	7,904	22,337
1700	15	5,353	12,446
1800	3	5,818	8,163
1800	10	6,234	14,627
1800	15	7,238	18,372

Table 10

Properties of alloy LHZ-1I after inoculation

	MPa	MPa	%	%	KCU, MG/m ²	750-600	T, °C
1	2	3	4	5	6	7	8
027	990	870	8,0	16,0	0,28	-	20

1	2	3	4	5	6	7	8
027	1070	850	7,3	11,5		335	750
028	1000	820	11,0	15,0	0,27	-	20
028	980	810	6,3	19,0		452	750
029	1140	840	6,7	12,4	0,26	-	20
029	940	810	5,3	6,6		444	750
031	980	880	6,3	13,0	0,24	-	20
031	1030	840	6,7	11,5		406	750
NE	950	930	5,0	7,0	0,1-0,2		20
	900	865	3,5	5,5		45	750

Table 11
Oxygen Content in alloys TSNK 7P and TSNK 21P after HTTM

Alloy	Number of melting	Oxygen Content before HTTM, %	Oxygen Content after HTTM, %
ІІHK7П	38282	0,0009	0,0032
	38248	0,0009	0,0035
	38250	0,0010	0,0029
	38262	0,0015	0,0041
	38263	0,0018	0,0042
ІІHK21П	38274	0,0019	0,0032
	18832	0,0017	0,0054
	18833	0,0016	0,0072
	18836	0,0010	0,0038
	18870	0,0017	0,0051

Table 12
REM influence on overcooling of nickel base alloys

Addition elements, %	Dy, %	T _{b.cr.} , °C	T _L , °C	ΔT, °C	T _S , °C
1	2	3	4	5	6
Al 3,8%	0,0	1425	1436	11	1416
	0,2	1410	1423	26	1416
	0,5	1368	1398	63	
	0,9	1330	1366	106	
	1,4	1329	1362	107	
W 4,5 %	0,0	1453	1461	8	1446
	0,2	1421	1442	36	
	0,8	1374	1429	77	
	1,4	1357	1418	91	
Cr 20 %	0,0	1416	1418	2	1399
	0,3	1389	1405	22	1394
	0,9	1354	1383	53	1380
	1,4	1336	1338	69	1380
Cr 8,9 %	0,0	1440	1441	1	1421
	0,1	1429	1433	9	1416
	0,3	1409	1420	25	1411
	0,9	1349	1379	81	
Nb	1,5	1336	1368	89	
	0,0	1385	1392	7	1421
	0,2	1374	1385	12	1366

1	2	3	4	5	6
8,0 %	0,8 1,4	1356 1326	1376 1349	26 53	1370
11% Cr+ 1,5 Ti	0,0 0,4 0,9 1,3	1416 1355 1353 1354	1418 1390 1391 1384	2 63 65 64	1391 1386 1385 1385

Table 13

Combined influence of HTTM and modification by Y
on the crystallization parameters of nickel base superalloys

Alloy	[Y] add., %	T HTTM, °C	T _{b.cr.} °C	T _{reac.} °C	T _{end cr.} °C	T _{liq.} °C	T _{sol.} °C	ΔT °C
1	2	3	4	5	6	7	8	9
ЖС36 (ZHC36)	0,05	1600	1385	-	1330	1405	1330	20
		1700	1370	-	1330			35
		1800	1340	-	1330			65
	0,1	1600	1385	-	1330	1405	1330	20
		1700	1375	-	1330			30
		1800	1350	-	1330			55
	0,2	1600	1390	-	1330	1405	1330	15
		1700	1380	-	1330			25
		1800	1350	-	1330			55
	0,05	1600	1395	1355	1320	1395	1320	0
		1700	1370	1355	1320			25

1	2	3	4	5	6	7	8	9
ЖСЗ2 (ZHC32)	0,1	1600	1397	1358	1320	1397	1320	0
		1700	1375	1357	1320			22
		1800	1357	1357	1320			40
		1800	1355	1355	1320			40
	0,2	1600	1400	1360	1320	1400	1320	0
		1700	1380	1360	1320			20
		1800	1360	1360	1320			40
ПНК7П (CNK7P)	0,05	1600	1340	1295	1280	1340	1280	0
		1700	1310	1295	1280			30
		1800	1295	1295	1280			45
	0,1	1600	1342	1297	1280	1342	1280	0
		1700	1313	1297	1280			29
		1800	1297	1297	1280			45
	0,2	1600	1343	1297	1280	1343	1280	0
		1700	1313	1297	1280			30
		1800	1297	1297	1280			45

T_{b.cr.} - temperature of crystallization beginning;

T_{reac.} - temperature of carbide formation reaction; T_{end}

T_{cr.} - temperature of crystallization end.

Exfoliation in superalloy caused by additions of dysprosium

a.

b.

c.

d.

a) reflected electrons; c) Nb-distribution;

b) Dy-distribution; d) Al-distribution.

Fig.1

Influence of overcooling in average saze of inclis
ions of intermetallic eutectic

- a) influence of overcooling;
- b) influence of growth time of anormal eutectic.

Fig.3 2

Change of morphology of intermetallic eutectic
inclusions after HTTM (alloys ZHS32, ZHS36)X320

a.

b.

- a) alloy ZHS32 after overheating to 1820 °C;
b) alloy ZHS36 after overheating to 1750 °C.

Fig.3

Nucleation of carbides on oxide inclusions
(for alloy ZHS6U):

a,b) - reflected electrons;
c) - Ti - distribution;
d) - Al - distribution.

Fig.4

Changes of microstructure of alloy ZHS36 after different
regimes of HTTM

- a) - initial alloy;
b) - after overheating.

Fig.5.

Influence of overheating on sizes and morphology of carbides

a) - initial alloy; b) - overheated to 1700 °C; c) - overheated to 1700 °C.

Fig. 6

Precipitations of normal and abnormal eutectic

a.

x2000

b.

x2000

a. - overheating to 1600 °C; b. - overheating to 1600 °C.

Fig.7

Change of alloy structure caused by overheating

- a. - initial alloy;
b. - overheating to 1820 °C.

Fig.8

Fig. 9

The structural changes of alloy

Influence of oxygen content on the long-term strength
(900 °C and 850 °C)

1. - TZNK21P;

2. - TZNK7P.

Fig.10

Oxygen inclusions of Dy

- a,c) - reflected electrons;
b,d) - Dy - distribution;
a,b) - 0,1% - Dy;
c,d) - 0,5% - Dy.

Fig.11

References

1. Lapkin V.N., Tyagunov G.V. et al. Influence of thermal - time treatment of melt on characteristics of alloy 52N // Izv. VUZOV Chernaya Metallurgiya. 1981, N11, p.66.

2. Tsepelev V.S., Tyagunov G.V. et al. Characteristics of liquid steel R6M5.// Izv. VUZOV Chernaya Metallurgiya, 1987, N9, p.76-82.

3. Baum B.A. Metallic liquids - problems and hypotheses. Moscow, Nauka - 120 p.

4. Barishev E.E., Kostika T.K., Tyagynov G.V. et al. Structure and properties of nickel-chromium base alloys. Collected articles. Physical properties of metals and alloys. Sverdlovsk. 1986, N5, p. 112-115

5. Bodakin N.E., Baum B.A. et al. About anomaky on polytermic lines of viscosity of metallic melts. // Izv. VUZOV Chernaya Metallurgiya. 1977, N9, p.74-78.

6. Tyagunov G.V. et al. Viscosity and electrical resistance of nickel-chromium base alloys. // Izv. VUZOV Chernaya Metallurgiya, 1973, N5, p.149-151.

7. Baum B.A., Hasin G.A., Tyagunov G.V. et al. Liquid stell. Moscow. Metallurgia. 1984. - 208 p.

8. Baum B.A., Klimenkov E.A., Tyagunov G.V. et al. Structure of liquid alloys and technology of their production.// Stal . 1981, N10, p. 23-27.

9. Kolotuhin E.V., Baum B.A., Kuleshova E.A. et al. Influence of structure and properties of metal melt on characteristics of castings. // Stal, 1992, N7, p. 21-28.

10. Hasin G.A., Mihailov B.V. et al. Production of steels and alloys within fixed thermal-time regime. Proceedings. Kiev, 1980, p.168-173.

11. Hasin G.A., Mihailov B.V. et al. Production of steels and alloys in electro-arc furnaces under regime of programme's thermal-time treatment of melts // Stal, 1982, N7, p.18-20.

12. Kozlov L.Ya., Romanov L.M. et al. // Liteinoe proizvodstvo, 1981, N6, p.11.

13. Sardov A.A., Denisov A.Ya., Romanov L.M. et al. // Izv. VUZOV Chernaya Metallurgiya, 1993, N7, p.56-57.

14. Ostrovski O.I., Grigoyan V.A. About structural transformation in melts. // Izv. VUZOV Chernaya Metallurgiya. 1985, N5, p.98-106.

15. Arsentiev P.P., Koledov L.A. Metal melts and their properties. Moscow. Metallurgiya. 1976.

16. Utochkin Yu.I., Busif A., Mendelev V.A. Conditions of non-metallic inclusions formation under addition REM into steel. // Izv. VUZOV Chernaya Metallurgiya, 1984, N7, p.150-151.

17. Romanov L.M., Kozlov L.Ya. Effect of non-metallic inclusions on properties of metal products // Stal. 1992, N7, p.28-31.

18. Utochkin Yu.I., Mendelev V.A., Zamshin V.A. Transformation of REM oxide inclusions under cooling and repeated melting of metal // Izv. VUZOV Chernaya Metallurgiya. 1987, N7, p.166-167.

19. Kozlov L.Ya., Romanov L.M. Modification of nickel base alloys // Tsvetnie metalli. 1988, N1, p.58-64.

20. Mendelev V.A., Utochkin Yu.I., Grigoryan V.A. Analysis

of deoxidation curve.// Izv. VUZOV Chernaya Metallurgiya.1980, N7, p. 40-44.

21. Mendeleev V.A., Pavlov A.V., Utochkin Yu.I. About some regularities of formation of non-metallic phases under REM addition in iron base melts.//Izv. VUZOV Chernaya Metallurgiya. 1990, N7, p. 1-3.

22. Larionov V.N., Kulesheva E.A., Tyagynov G.V. et al. Improvement of technology of castings production of superalloys ZHS26 // Aviatsionnaya Promyshlennost. 1989, N12, p.50-52.

23. Larionov V.N., Zuev G.I., Toloriya V.N., Hlystov E.N. Use of high-temperature treatment under monocrystalline casting of turbine blades in UVNK-8P plant. // Aviationnaya Promyshlennost. 1989, N12.

24. Kalinin V.P., Avdyuhin S.P. Termal-time treatment of melts to remove "star's sky" defect in castings of superalloys // Aviationnaya Promyshlennost, 1987, N10, p.64.

25. Baryshev E.N., Larionov V.N. Dependence of micro-structure and properties of nickel base alloy on smelting conditions. // Liteinoe proizvodstvo, 1985, N7.

26. Tyagunov G.V., Avdyuhin S.p., Kolotykh E.V. et al. High-temperature treatment of melt as method of effective modification of alloy ZHS3DK by dispersed particles of high-melting compounds // Aviationnaya Promyshlennost.1989, N12, p. 26-30.

27. Sorokina L.P., Morozova S.G., Gleizer G.M. et al. Peculiarities of coagulation of hardening phase in alloy ZHS32 produced by use of high-temperature treatment of melt // Aviationnaya Promyshlennost. 1989, N12, p. 34-36.

28. Sidorov V.I., Pankratov V.A., Radionov P.D., Mironov S.O. About possibilities of casting waste use for production of superalloys with high-temperature treatment of melts // Aviationnaya Promyshlennost 1989, N12, p. 36-38.

29. Kolotuhin E.V., Kuleshova E.A., Larionov V.N. Influence of carbon content on structure and properties of nickel base superalloys in liquid and solid metal. Relation between liquid and solid states of metals. Sverdlovsk. 1987, p.15.

30. Kishkin S.T., Larionov V.N., Kuleshova E.A. et al. Influence of high-temperature treatment of melt on properties and mechanical characteristics of cast nickel base superalloys.// Aviationnaya Promyshlennost . 1989, N12, p. 6-11.

31. Petrushin N.V., Pancratov V.A., Babashkina E.V., Denisov A.Ya. Peculiarities of formation of nickel base superalloys structure after high-temperature treatment of melts.// Aviationnaya Promyshlennost. 1989, N12, p.14-16.

32. Tolariya V.N, Ignatov I.A., Samoilov A.I. et al. Study of dimensional discrepancy parameters of Lattices and phases of monocrystals in alloy ZHS32 produced with use of high-temperature treatment of melt // Aviationnaya Promyshlennost. 1989, N12, p. 17-20.

33. Kuleshova E.A., Hatsinskaya I.M., Babashkina E.V., Bogina N.M. Optimization of regimes of thermal treatment of nickel base superalloys casted by use of high-temperature treatment of melts. // Aviationnaya Promyshlennost. 1989, N12, p. 10-14.

34. Larionov B.N., Hlystov E.N., Kolotuhin I.N. et al. Method of production of mono-crystalline castings. Patent SU

1624812A1 B22 D 24/04 12.02.1989.

35. Zuev G.N., Larionov V.N., Denisov A.Ya. et al. Method of production of mono-crystalline castings. Patent SU 1526035A1 B22 D 27/00 08.04.1988.

36. Hlystov E.N., Saburov V.P., Larionov V.N. et al. Method of production of mono-crystalline castings. Patent SU 1570148 A1 B22 D 27/04 13.05.1988.

37. Fedorov S.N., Hlystov E.N., Denisov A.Ya. et al. Shell mould. Patents SU 152 26291 A1 C 30 B11/00 03.09.1987.

38. Himushin F.F. High temperature steels and alloys. Moscow. Metallurgiya, 1969. - 749 p.

39. Militzin K.N. Influence of composition and thermal treatment of melts on risering // Liteinoe proizvodstvo, 1960, N3, p.19.

40. Spasski A.G., Fomin B.A., Alenikov S.A. Thermal treatment of liquid metals and its influence on mechanical properties of castings // Liteinoe proizvodstvo, 1959, N10, p.35.

41. Maltsev M.V. Modification of metals and alloys structures. Moscow. Metallurgiya. 1964. - 214 p.

42. Shulte Yu.A., Volchok I.P., Lunev V.V. et al. Influence of REM on nature of non-metallic inclusions and properties of cast steel. In book: Rare-earth metals and alloys. Moscow. Nauka. 1971. - 117 p.

43. Lunev V.V., Shulte Yu.A. Use of complex alloying compositions of REM and AEM to improve properties of cast and wrought steels. In book: Influence of complex dioxidation on properties of steels. Moscow. Metallurgia. 1982. p.82-90.

44. Dobatkin V.I., Chursin V.M., Bondarev B.I. et al.

Discussion of problem "Modification of alloys of non-ferrous metals" // Tsvetnie metalli. 1988, N10, p.85-95.

45. Kishkin S.T., Larionov V.N., Kuleshova E.A. et al. Influence of high-temperature treatment of melt on properties and mechanical characteristics of cast nickel base superalloys.// Aviatonnaya Promyshlennost . 1989, N12, p. 6-11.

48. Romanov L.M., Kozlov L.Ya., Pinaeva O.S. Modification of carbide inclusions in high-alloy nickel-base melts. // Tsvetniye metalli, 1989, N2, p.57-60.

49. Saburov V.P. Choice of modifiers and practice of modification of cast alloys. Omsk. 1984.

50. Fatkulin O.H., Anisimova G.V., Babikova R.F. et al. Effect of zirconium carbide additions on structure of alloy EI 696. Tekhnologiya legkih splavov. Scientific-technical report of VILS. 1976, N11.

51. Chechentsev V.N., Saburov V.P., Zametaev E.V. et al. Volumetrical modification of nickel base alloys under castings production // Liteinoe proizvodstvo. 1989, N9, p.8-9.

52. Babaskin Yu.Z., Larikov L.N., Shipitsin S.Ya., Shmatko O.A. Effect of zirconium carbides additions on structure and properties of cast superalloy ZHS6K // High-temperature and heat-resistant nickel base steels and alloys. Moscow. Nauka. 1984, p.184-187.

53. Romanov L.M., Soldatov V.A., Sirotcin C.A. Peculiarities of high-melting particles dissolution in iron base melts.// Izv. VUZOV Chernaya Metallurgiya.1991, N11.

54. Fatkulin O.H., Ofitserov A.A. Modification of nickel base superalloys by dispersed particles of high-melting

compounds.// Liteinoe proizvodstvo. 1993, N4, p. 13.

55. Fedorov S.N., Hlystov E.N., Denisov A.Ya. et al. Shell mould. Patents SU 152 26291 A1 C 30 B11/00 03.09.1987.

56. Kopiliva V.A., Kostina T.K. Influence of conditions of production on structure of cast alloy N36 // Termicheskaya obrabotka and Fisika Metallov. Sverdlovsk, 1982, N5, p.94-96.

57. Kochegura N.M., Kazachkov S.P., Tkach V.N., Vishnevski A.S. Thermal-time treatment of liquid nickel base alloys // Liteinoe proizvodstvo, 1985, N10, p.13-14.

58. Popel P.S., Baum B.A. Thermodynamic analysis of one reason of metallurgical herelity. // IZV AN SSSR Metalli. 1983, N5, p. 47-51.

59. Baum B.A., Hasin G.A., Tyagunov G.V. et al. Liquid stell. Moscow. Metallurgia. 1984. - 208 p.

60. Baum B.A., Klimenkov E.A., Tyagunov G.V. et al. Structure of liquid alloys and technology of their production.// Stal . 1981, N10, p. 23-27.

61. Kochegura N.M., Kozachkov S.P., Tkach V.I., Vishnevski A.S. Time-thermal treatment of nickel base alloys in liquid state. // Liteinoe proizvodstvo. 1985, N10, p. 13-14.

62. Kochegura N.M., Kozachkov S.P., Markovski E.A. Time-thermal treatment of cast nickel-base superalloys in liquid state. New structural steels and alloys and methods of their treatment to increase reliability and operating longevity of products. Abstracts. III Vsesoyusn. nauchno-technich. konferentsiya. Zaporozhye, 1986, P. 199-200.

63. Kochegura N.M. Improvement of mechanical and phisico-technical characteristics of nickel base superalloys by

melts. New high-productive technological processes, Ohigh-qualitative alloys and foundry equipment. VII Vsesousn. konfer. Part 1. Kiev. 1986, p. 149.

64. Ten E.B. Mechanism of refining of melts by filtration. // Liteinoe proizvodstvo. 1990, N9, p. 5-6.

65. Ten E.B. Refining of metal melts by filtration. // Izv. VUZOV Chernaya Metallurgiya. 1991, N3, p. 63-65.

66. Kulikov V.A., Babilov A.M., Ten E.B. Efficiency of filtration of nickel base alloys under investment casting. Improvement of quality and efficiency of investment casting. Moscow. MDNTP - 1989, p. 115-118.

67. Ten E.B. Improvement of quality of castings by filtration under investment casting. Improvement of quality and efficiency of investment casting. Moscow. MDNTP - 1989, p.119-125.

68. Ten E.B., Grishin V.M., Bibikov A.M. et al. Efficiency of filtration under production of nickel base alloys castings.// Liteinoe proizvodstvo. 1990, N8, p.6.

69. Bibikov A.M., Kulikov V.A., Ten E.B. Improvement of quality of investment casting under ladle treatment of melts. Prospects of aircraft material science - Moscow, 1990, p. 15-16.

70. Ofitserov A.A., Zavolosnov B.S. Foam-ceramic filters for filtration of nickel base superalloys.//Liteinoe proizvodstvo. 1993, N4, p.19-22.

71. Ruskol V.I. Problems of investment casting. // Liteinoe proizvodstvo. 1992, N2, p. 3-4.

72. Chvanov V.N., Kazennov C.A., Kurchman B.S. et al. Edited by Shklenik Ya.I. and Ozerova V.A. Moscow. Mashinostroeniye.

1984. - 408 p.

73. Kulakov B.A., Aleksandrov V.M., Dubravin V.K. Improvement of quality of castings by oriented crystallization. // Liteinoe proizvodstvo. 1992, N4, p. 16-18.

74. Aksenov A.T., Tankevich B.Sh., Parshin A.N. Water-soluble compositions for cores on bases of polymers. // Liteinoe proizvodstvo. 1993, N6, p.

75. Bratuhin A.G., Kpuvov H.L., Kanonov E.B. Increase of production of precise castings by investment casting. // Liteinoe proizvodstvo. 1986, N11, p. 16-18.

76. Kozlov L.Ya., Karenin L.P., Apillinski V.V. Increase of strength of ceramic cores by epoxy resin impregnation // Liteinoe proizvodstvo. 1977, N3, p.16.

77. Landa M.M., Portnoy Ya.I. Baked ceramic cores for casting of hollow blades of gas-turbine engines. // Liteinoe proizvodstvo. 1977, N2, p. 9-11.

78. Landa M.I., Shpindler S.S., Kopytov N.M. et al. Thermal-mechanical properties of ceramic cores with ethyl-silicate binders. // Liteinoe proizvodstvo. 1978, N8, p. 26-27.

CGTU-Export Ltd.
Chelyabinsk, Russia

Sandia National Laboratories
Albuquerque, USA

P R O G R A M

Thermodynamic and chemical analysis
of investment casting molds and mold coatings

B.A.Kulakov

This program has been prepared in accordance with Task 1 of the Contract AJ-0146 between CGTU-Export Ltd. and Sandia National Laboratories "Thermodynamic and chemical analysis of investment casting molds and mold coatings".

The program specifies the details of the work required to determine thermodynamic and chemical behaviour of investment casting molds and mold protective coatings used for casting reactive metals at high temperatures (up to 1800°C) in a vacuum of 1.3 Pa . The work is confined to the process of casting of titanium alloys into investment ceramic corundum ($\alpha\text{-Al}_2\text{O}_3$) molds made on the ethyl-silica (SiO_2) binder with protective coatings based on the haloids (MeH): KCl , BaCl_2 , NaF , CaF_2 etc.

In order to carry out the work the Contractor shall perform the following steps:

Step 1: Calculate the speed of incongruent evaporation of aluminum oxide (Al_2O_3) and silicon oxide (SiO_2) in a vacuum of 0.13 and 1.3 Pa and at the temperature of 1400 to 1800°C .

Purpose:

To estimate the effect of the oxygen partial pressure and the system temperature on the process of oxide evaporation, whose products oxidize the titanium causing the formation of α -layer on its surface.

To formulate the requirements for the material of the casting mold and the external system parameters: pressure and temperature.

Step 2: Calculate the change of isobaric-isothermal potential ΔG (Gibbs' energy) in a vacuum of 1.3 Pa within the

temperature range of 20 to 1800°C for the probable chemical reactions in the systems $MeH-Ti$, $MeH-Al_2O_3$ and $MeH-SiO_2$.

Purpose:

To estimate the thermo-chemical stability of various haloids MeH with respect to titanium and the casting mold oxides.

To optimize the selection of the haloids to be used as protective coatings of casting molds.

Step 3: Using CGTU methods, investigate experimentally the processes of physical-chemical interaction in the systems $MeH-Ti$, $MeH-Al_2O_3$ and $MeH-SiO_2$.

Purpose:

To verify the calculated estimates of the thermo-chemical stability of various haloids with respect to titanium and to the casting mold material for the real systems.

Step 4: Fabricate 24 to 30 ceramic investment casting molds using 3 different technologies (8 to 10 molds for each technology):

4.1. Corundum molds made with the use of the hydrolytic solution of ethyl-silica binder having a low SiO_2 concentration without a protective coating.

4.2. Corundum molds made with the use of the hydrolytic solution of ethyl-silica binder having a low SiO_2 concentration with the chloride protective coating.

4.3. Corundum molds made with the use of the hydrolytic solution of ethyl-silica binder having a low SiO_2 concentration with the chloride-fluoride protective coating.

Purpose:

To enable Sandia National Laboratories to estimate the

effect of SiO_2 contents of the mold and the mold protective coating on the quality of titanium castings.

To enable Sandia National Laboratories to choose the optimum technology for the fabrication of investment casting molds with protective coatings for titanium casting.

In order to enable the Contractor to fulfil the above program successfully Sandia National Laboratories are requested:

- 1.To furnish the die for the fabrication of investment casting molds and to ship it to the Contractor as soon as possible. The molds shall be fabricated within 5 month after the receipt of the die.

- 2.To advise the Contractor about the maximum acceptable outer dimensions of the ceramic molds in order to enable the Contractor to determine the maximum possible number of deposited layers of refractory suspension.

- 3.To advise the Contractor as soon as possible about any suggestions on the improvement of this program.

Sandia National Laboratories
Attn: R.W.Fisher or F.Zanner, MS 0341
Post Office Box 5800
Albuquerque, NM 87185-0341
USA

Date: 28 Feb.1995

Contract AJ-0146
Task 2

Dear Bob and Frank,

I am sending you 30 ceramic molds for pouring titanium, 10 molds for each of the 3 different technologies specified in the Program "Thermodynamic and chemical analysis of investment casting molds and mold coatings".

The delay in the fabrication of the molds was caused by the fact that your consent to change the dimensions of the die for the fabrication of the molds was received here only in November 94. Therefore the duration of Task 2 specified by the Contract (6 months) has not been exceeded.

The molds fabricated according to Technology 4.1 of the Program are not marked, while those to Technologies 4.2 and 4.3 are marked by the symbols "/" and "/" correspondingly. The marks are made on the inner side working surface of the molds.

Thus:

NO MARKS - corundum molds fabricated with the binder of hydrolysed solution of ethyl silicate with low contents of silica (SiO_2).

MARK "/" - corundum molds with the chloride protective coating (BaCl_2).

MARK "/" - corundum molds with the chloride-fluoride protective coating ($\text{KCl} + \text{CaF}_2$).

The molds must be dried at the temperature of 300...350 Centigrade during 2.5...3 hours before placing them into the melting-pouring installation.

The molds fabricated according to Technology 4.1 (with no marks) may be preheated to 1000 Centigrades before pouring the metal.

The molds fabricated according to Technologies 4.2 and 4.3 (marks "/" and "/") may be preheated before pouring the metal to the temperature not exceeding 650 Centigrade.

It should be noted that in order to minimize the thickness of alpha-layer on the surface of the casting the mold must have the temperature of 25...50 Centigrade before pouring the metal.

The molds packed in a special wooden box will be sent to Sandia through Sandia's Moscow representative Mr. V.Z.Ravkin (Fax No.122-77-36, 267-03-50).

Please kindly confirm the receipt of the molds by Sandia.

I also hope that you will duly inform me about the results of the tests carried out on the castings fabricated with the use of the molds.

Sincerely yours,

B.Koulakov

Chelyabinsk State Technical University

Contract AJ-0146

Task 3

***Thermodynamic and chemical
analysis of investment casting molds
and mold coatings***

By B.A.Kulakov

1995

Sandia National Laboratories
Attn: F.Zanner, MS 0341
Post Office Box 5800
Albuquerque, NM 87185-0341
USA

Date: 18 May 1995

Contract AJ-0146
Task 3

Dear Frank,

Please find enclosed the Report according to Task 3 of Contract AJ-0146. It reflects our theoretical approaches and some results we have received concerning the process of titanium alloys casting relevant to the Contract. At the present time the quality of titanium castings depends primarily on the technology employed to fabricate the casting molds. However, further achievements in this field will to a large extent be connected with the development of special protective atmospheres for the melting-pouring installations which will replace the traditional vacuum.

Unfortunately, it is not known to me what technology of titanium casting is used in your laboratories as basic or or what equipment is utilised in US industry for this technology as well as the requirements the castings must meet and the finishing operations applied to the them. All this, no doubt, may require to introduce changes into our technology either complicating or simplifying it.

Dear Frank, if you have any questions concerning our work I would be only too glad to answer them within the limits of my competency.

Yours sincerely,

B.Koulakov

P.S. Also enclosed is the Invoice for the work of Task 3 of the Contract.

Enclosures:

1. Report on the work of Task 3 of the Contract
2. Invoice for the work of Task 3 of the Contract.

Chelyabinsk State Technical University

Contract AJ-0146

Task 3

**Thermodynamic and chemical analysis
of investment casting molds and mold coatings**

By B.A.Kulakov

1995

Ceramic molds made of electro-corundum filler ($\alpha - Al_2O_3$) with the ethyl silicate binder containing 15...20 mass per cent of silica find a wide application for the production of titanium castings. The molds are easily manufactured and have high geometric precision and strength after baking. However, such ceramic molds do not possess sufficient chemical stability with respect to titanium alloys poured into them. The physico-chemical interaction between the mold and the alloy at the temperatures of pouring and solidification results in the formation of a transformed gas-containing layer (α -layer) on the surface of titanium castings. The layer is distinguished by increased hardness, brittleness and bias towards the formation of microcracks. Due to these features the presence of α -layer on the titanium castings subject to alternating loads (working under the conditions of vibrations) is not tolerated.

Many researchers suppose that the cause of the low chemical stability of ceramic molds towards titanium lies in the physico-chemical interaction between the metal and the materials of the mold filler and binder. They represent the interaction in the form of chemical reactions of reduction between the titanium and the condensed phases (the oxides of the mold). As a consequence the stability of oxide materials of the mold towards titanium is estimated by comparing the standard values of Gibbs' energy (ΔG^0) of their formation with ΔG^0 of the formation of titanium oxide.

Such an estimate of the mold stability is only roughly approximate and does not allow to describe the relationships governing the saturation of the mold surface with gases. Under the real conditions of casting formation the total area of its contacts with the grains of the working surface of the mold is quite insignificant in comparison with the area of the casting surface.

The chemical interaction between the titanium and the gases is much more intense in comparison with its reactions with the condensed phases and

plays a major part in the formation of α -layer on the castings. Therefore the chemical stability of ceramic molds towards titanium must be estimated primarily by the stability of both the refractory filler and the binder towards the evolving gases. Under the conditions of vacuum pouring and solidification of titanium alloys the principal source of gas evolution from the mold is the products of thermal dissociation of the oxides of the filler and the binder.

Thermodynamically the most effective is the gaseous dissociation (incongruent evaporation) of the silica (SiO_2) of the binder and the aluminum oxide (Al_2O_3) of the filler of ceramic molds according to the following reactions:

where s, g mean *solid* and *gaseous* correspondingly. The reactions are accompanied by the minimal heat effect per 1 gram mole of the gaseous products.

The evolution of gases from the mold is determined by changing its temperature with time after the pouring of the metal.

The non-stationary temperature fields of the system "metal-mold" for cylindrical castings $(1...5)10^{-2}m$ in diameter were calculated by the method of elementary balances of energy. The metal temperature in the calculations was varied in the range of $50...150^\circ K$ above the liquidus.

The calculations showed that the surface of the mold with the initial temperature of $298^\circ K$, due to being in contact with the metal having the temperature of $1973...2073^\circ K$, can be heated up to the temperature of

1850...1910 °K while its inner layer can be heated above 1673 °K to the depth of (0.15...1.0)10⁻³ m and such temperatures can be maintained for 15...340 s.

The time of cooling down to the alloy's solidus temperature at the boundary "metal-mold" can be as long as 60 s while at its center 6-215 s.

As the temperature of the mold before pouring the metal is increased the time during which the high temperatures at the boundary metal-mold are maintained increases as well as the time of solidification of the surface layer and the casting on the whole.

The calculated temperature-time relationships of the mold enabled the total vapour pressure (ΣP) and the pressures P_{O_2} , P_{SiO} over the oxides in the mold to be determined and the rates of their evaporation (J) in the vacuum of 1.3 Pa to be calculated from the following equation based on the Hertz-Langmuire method using the data presented in [1] and taking into account the maximal flows of gaseous products of dissociation:

$$J_{MeO} = (2\pi\mu_{Me}TP_{O_2}R)^{-1/2}\mu_{MeO}\exp(-\frac{\Delta G}{RT}),$$

where: J_{MeO} - oxide evaporation rate;

T - absolute temperature;

P_{O_2} - oxygen partial pressure;

R - universal gas constant;

μ_{Me} , μ_{MeO} - molecular masses;

ΔG - standard change of Gibbs' energy for the reaction of oxide dissociation [2].

The results of the calculations are presented in Figs 1...4.

Their analysis shows that the heating of the mold working surface above 1860 °K at $P=0.13$ Pa and above 1970 °K at $P=1.3$ Pa results in the boiling of the silica of the binder as the pressure of its vapour becomes equal to or higher

than the working pressure in the melting-pouring installations (Fig.1). In the temperature range of $1673...1860^{\circ}K$ the silica also has a high vapour pressure and is subject to intensive evaporation in vacuum at the rates, shown in Fig.3. All this leads to the formation at the boundary "metal-mold" of the oxidizing gaseous atmosphere consisting of SiO and O_2 , leading, in its turn, to the formation of the layer with the transformed structure (α -layer) on the surface of the casting .

The corundum, as distinct from the silica, remains stable under this condition as the pressure of its vapour and the rate of its evaporation is by 3...4 orders lower (Figs. 2 and 4).

The volatility of oxides was also confirmed by experimental data. In order to do it silica gel (SiO_2) obtained from ethylsilicate (silicic ether) was heated in the air at the temperature of $1273 \pm 10^{\circ}K$ during 4...5 hours. After that it was placed in a vacuum furnace and kept at the temperature 1873, 1923 and $1973^{\circ}K$ and the remainder pressure of $1.3 Pa$ for one hour. Then the decrease of the mass was determined and found to be 4.7, 9.1, and 20.3% respectively.

The decrease of the mass of electro-corundum ($\alpha-Al_2O_3$) under similar conditions at $1973^{\circ}K$ was found to be only 1.5%. It should be noted that this corundum mass reduction is determined by the presence in it of impurities like $Fe_2O_3, Na_2O, SiO_2, CaO$ to the total quantity of 1.6% .

With the deepening of the vacuum the intensification of the processes of evaporation of refractory oxides is observed.

In practice the evolution of gases from the mold is confirmed by a sharp drop (by an order or more) of the vacuum in the melting-pouring installation during the pouring of the metal.

In order to reduce the chemical activity of a ceramic mold towards poured titanium and prevent the saturation of the surface of titanium castings

with gases it is necessary to decrease the concentration of the silica of the binder in the working layer of the mold of a certain thickness and exclude its direct contact with the poured metal.

The first requirement is satisfied by using the low-silica ethyl silicate binder (LSEB) with the conditional SiO_2 content of 6...8%, the second is ensured by depositing a protective coating consisting of the haloids (MeH) of the alkali metals and alkaline earths metals on the inner surface of the mold. The coating reduces the heating of the mold and the quantity of gaseous products of oxides dissociation evolving from it and decreases the concentration of oxygen on the boundary "metal-mold".

In order to develop LSEB ensuring the high quality fabrication and increased chemical inertion of ceramic molds a special research was carried out of ethyl silicate binders by the method of infra-red spectroscopy. It enabled to select a method and optimum parameters of the process of preparation of LSEB. The required technological and physico-mechanical properties of the mold with LSEB are achieved by introducing special strengthening addition agents into the refractory suspension.

In order to estimate the effectiveness of the action of haloids as protective coatings a combined research was undertaken.

In order to determine the probability and direction of the reactions of interaction between the protective coatings, titanium and ceramic molds material a thermodynamic analysis was carried out. The change of Gibbs' energy (ΔG^0) of the reactions was calculated for the standard state with the use of the data given in [2,3]. Then, using Van't Hoff equation

$$\Delta G_r^0 = -RT \ln K_p$$

the constant of equilibrium was calculated.

Using the constant of equilibrium the equilibrium partial pressure of the most volatile component (P_i) in the products of the reaction was found. It can be assumed that the reaction is thermodynamically possible if P_i is greater than the remainder pressure in the system $1.3 \cdot 10^{-5} \text{ atm}$ (1.3 Pa). Otherwise (i.e. if $P_i < 1.3 \cdot 10^{-5} \text{ atm}$) the reaction is thermodynamically barely probable.

The most volatile components of the systems being considered are those which have the boiling temperature below 800°K under the external pressure of 1 atm . These are the components that largely determine the composition of the system's gaseous atmosphere as a result of the reactions of interaction within the temperature range under consideration.

In the system titanium-haloid such components include titanium chlorides and fluorides, in the system SiO_2 - haloid-silicon chlorides and fluorides, in the system Al_2O_3 - haloid-aluminum chlorides and kalium oxide.

Fig.5 shows the relationship between the constant of equilibrium and the temperature of presumable reactions for the system Ti-MeH .

As the temperature increases the probability of all the reactions being considered becomes higher.

Presumable reactions of interaction for the system Ti-MeH :

1. $2\text{BaCl}_2 + \text{Ti} = \text{TiCl}_4 + 2\text{Ba}$,
2. $2\text{CaCl}_2 + \text{Ti} = \text{TiCl}_4 + 2\text{Ca}$,
3. $4\text{KF} + \text{Ti} = \text{TiF}_4 + 4\text{K}$;
4. $2\text{MgCl}_2 + \text{Ti} = \text{TiCl}_4 + 2\text{Mg}$,
5. $2\text{CaF}_2 + \text{Ti} = \text{TiF}_4 + 2\text{Ca}$,
6. $4\text{KCl} + \text{Ti} = \text{TiCl}_4 + 4\text{K}$.

The calculations show that the partial pressure of the most volatile component becomes higher than $1.3 \cdot 10^{-5} \text{ atm}$ for reaction 3 at the temperatures above 1570°K and for reaction 4-above 1820°K . Therefore, in the vacuum of

$1.3 \cdot 10^{-5} \text{ atm}$ above these temperatures the occurrence of the two reactions in the straight direction becomes thermodynamically possible. Barium chloride, calcium chloride and calcium fluoride are the most stable of all the haloids considered with respect to interaction with titanium as the equilibrium partial pressure of the most volatile components ($TiCl_4$, TiF_4) of reactions 1, 2, 5 is $9.96 \cdot 10^{-15}$, $5.90 \cdot 10^{-15}$ and $2.32 \cdot 10^{-12} \text{ atm}$ respectively even at the temperature of $2073^\circ K$. In order to have these reactions taking place in the straight direction it is necessary to decrease the external pressure in the system below these values.

Presumable reactions of interaction for the system SiO_2 -MeH:

1. $SiO_2 + 2BaCl_2 = 2BaO + SiCl_4$;
2. $SiO_2 + 2CaCl_2 = 2CaO + SiCl_4$;
3. $SiO_2 + 4KF = 2K_2O + SiF_4$;
4. $SiO_2 + 2MgCl_2 = 2MgO + SiCl_4$;
5. $SiO_2 + 2CaF_2 = 2CaO + SiF_4$;
6. $SiO_2 + 4KCl = K_2O + SiCl_4$.

It can be seen from the data of Fig.6 that the probability of interaction in the system being considered increases with temperature. The partial pressure of the volatile component exceeds $1.3 \cdot 10^{-5} \text{ atm}$ for reaction 4 at the temperatures above $1324^\circ K$ and for reaction 5-above $1820^\circ K$. Kalium chloride, kalium fluoride and barium chloride are the most stable towards interaction with SiO_2 . At the temperature of $2073^\circ K$ the partial pressures of the most volatile components of reactions 6, 3, and 1 are $1.48 \cdot 10^{-25}$, $3.39 \cdot 10^{-17}$, and $5.77 \cdot 10^{-13} \text{ atm}$ respectively.

Presumable reactions of interaction for the system Al_2O_3 -MeH:

1. $Al_2O_3 + 3BaCl_2 = 3BaO + 2AlCl_3$;
2. $Al_2O_3 + 3CaCl_2 = 3CaO + 2AlCl_3$;
3. $Al_2O_3 + 6KF = 3K_2O + 2AlF_3$;
4. $Al_2O_3 + 3MgCl_2 = 3MgO + 2AlCl_3$;
5. $Al_2O_3 + 3CaF_2 = 3CaO + 2AlF_3$;
6. $Al_2O_3 + 6KCl = 3K_2O + 2AlCl_3$.

The data of Fig.7 show that the probability of reactions of interaction in the system being considered increases with temperature.

The calculations show that the partial pressure of the most volatile component ($AlCl_3$) for reaction 4 exceeds $1.3 \cdot 10^{-5} \text{ atm}$ at the temperature as low as $920^\circ K$ and for reaction 2 it is achieved at the temperature above $1613^\circ K$. Reaction 1 becomes thermodynamically possible at the temperatures above $2038^\circ K$. The occurrence of the rest of the chemical reactions within the temperature range being considered is barely probable. At the temperature of $2073^\circ K$ the partial pressure P_{AlCl_3} for reaction 6 is $8.82 \cdot 10^{-17} \text{ atm}$ and the partial pressure P_{AlF_3} for reaction 5 is $1.78 \cdot 10^{-7} \text{ atm}$.

The most volatile component of reaction 3 is K_2O . At the temperature of $2073^\circ K$ its partial pressure is $1.74 \cdot 10^{-9} \text{ atm}$, which is considerably lower than the remainder pressure in the melting-pouring installation of $1.3 \cdot 10^{-5} \text{ atm}$.

Therefore, the thermodynamic analysis shows that the most stable of all the haloids being considered towards interaction with titanium are barium chloride, calcium chloride and calcium fluoride, towards SiO_2 -kalium chloride, kalium fluoride and barium chloride, towards Al_2O_3 -kalium chloride, barium chloride and calcium fluoride.

It should be noted that under the practical conditions with the temperature of the poured metal in the range of $1973 \dots 2073^\circ K$ the surface of

the ceramic mold contacting the metal is heated to the temperatures not higher than 1850...1910 °K. Therefore, the probability of interaction of the haloids, with the exception of $MgCl_2$, with the mold material is low. At these temperatures, the interaction with titanium is thermodynamically possible only for $MgCl_2$ and KF .

Under the practical conditions the course of the reactions is determined mostly by the kinetic relationships and depends on the concentration, aggregate state, the area of the contact surface of the reacting substances, the conditions of delivery of the reagents and removal of the reaction products, the factor of temperature and so on. Thus, a necessity arises to carry out experimental studies.

A special method has been developed to quantitatively estimate the intensity of interaction of Ti , Al_2O_3 and SiO_2 with the haloids. It is based on holding specimens of both the titanium and the ceramic casting mold in the baths of molten salts. The method permits to carry out experiments in the atmosphere of air, with the use of a protective atmosphere of inert gas, for example argon, or in a vacuum.

The salts being tested do not interact with the titanium and ceramic molds within the temperature range of 900...1900 °K both in the protective atmosphere and in vacuum.

According to the results of metallographic analyses and micro-hardness measurements the specimens of Russian titanium alloys BT5П, BT9П, BT20П do not have α -layer. Only when the salt KF is used a certain corrosion of the surface of the specimens takes place, but without the formation of α -layer.

The specimens of ceramic corundum casting molds do not change their mass as a result of holding in the baths of molten salts. This fact confirms their stability towards interaction.

However, in the case of holding the titanium specimens in the baths of molten salts in the atmosphere of air α -layer up to $25 \cdot 10^{-5}$ m in thickness is detected on their surface. It is explained by the fact that at high temperatures in the atmosphere of air there occurs salts oxidation resulting in the formation of oxides of corresponding metals which subsequently oxidize the titanium. As a matter of fact, after holding the salts in the air and subsequent dissolving in the water their water solutions show alkaline reaction. The process of salt oxidation becomes the most intensive at the temperature $T > 1200^\circ K$. Least of all inclined to oxidation is KCl (below $1850^\circ K$).

The formation of α -layer up to $35 \cdot 10^{-5}$ m in thickness on the surface of titanium specimens is also observed after holding them in the baths of molten salts of $MgCl_2$ type obtained from water solutions by evaporation. It is connected with the fact that during dissolving these salts in the water they are subjected to hydrolysis with the formation of hydro-oxides of corresponding metals intensively oxidizing the titanium.

The volatility of salts is also very important. During the process of pouring the metal under the action of high temperatures their vaporization and uncovering of the surface of the mold can take place. It should be remembered that the boiling temperature of the salts is decreased in the vacuum. The saturation of the casting surface with oxygen in this case will take place as a result of the direct interaction of the titanium with the products of dissociation of the oxides of the casting mold. The most stable of all the haloids under consideration towards volatilizing are barium chlorides and calcium fluoride.

In order to verify the results described above in the tests with molten metal under identical conditions, i.e. in one cast, a special test mold was used which was fabricated from graphite in the shape of a tumbler 0.1 m high and 0.18 m in diameter. In the tumbler 6...8 ceramic cores 0.07 m high with a cross-

section in the shape of a triangle with equal sides 0.1 *m* long and the height of 0.025 *m* were placed.

The cores were fabricated with the use of the precision casting technology by layer-by-layer depositing corundum suspension on the wax pattern. The finished cores were coated by salt compositions.

The compositions were deposited by soaking the cores in the water solutions of the salts having concentrations sufficient to ensure the formation of a continuous layer on their surfaces. The water solutions on the CaF_2 basis were made in the form of colloids as a result of the reaction of interaction, e. g., of calcium chloride with potassium fluoride. Prior to placing the cores with deposited protective layers into the mold they were subjected to drying at 300 °C for 2...3 hours.

After placing the cores into the mold it was covered with a graphite cover having an opening for pouring the metal.

The molds thus assembled were poured into with the titanium alloy BT5J1 with the use of centrifugal forces in the vacuum electric-arc furnaces. The intensity of interaction in the system "metal-mold" was estimated by the depth of the transformed layer (α -layer) which was determined by measuring the micro-hardness. The data thus obtained are presented in Fig.8.

The surfaces of the casting which were in contact with the salt coatings of $BaCl_2$ as well as of $CaF_2 + KCl$ were clean without burning on and with practically absent α -layer. The surfaces formed in contact with the coatings of $CaCl_2$ and $NaCl$ had somewhat lower quality. The worst results were obtained with the use of $MgCl_2$.

The test results described above make it possible to conclude that the haloids of the alkali and alkaline earth metals used as the protective coatings of ceramic casting molds should meet the following requirements:

- not to interact with both the poured alloy and the ceramic mold;
- not to be subject to the hydrolysis during dissolving in the water;
- not to be oxidized during heating and drying the molds;
- to have high melting and boiling temperature points;
- to possess minimal hygroscopicity.

These requirements are best (most fully) satisfied by barium chloride and calcium fluoride.

It should also be noted that the highest stability of the system "mold-coating-metal" towards interaction is displayed in the protective gas atmosphere and the stability of the system increases with the increase of its pressure.

In order to verify the experimental data under the real conditions ceramic corundum investment molds were used to produce a specimen casting. The casting had walls varying in thickness (3.5...40 mm), various fillet radii, grooves and openings in its massive parts. The working surface of the molds was covered with protective salt coatings of $BaCl_2$ and $CaF_2 + KCl$. The coatings were deposited by the method of soaking the molds in the water solutions of the relative salts having optimum concentrations. After depositing the coatings the molds were subjected to drying similar to that described above for the cores. The molds themselves were fabricated on the ethyl silicate binder with various silica contents. Pouring into the molds was carried out with the alloys BT20Л, BT5Л by the centrifugal method in the industrial vacuum melting-pouring installations of the ВДЛ-4 type.

The metallographic analyses (micro-structure, micro-hardness) showed that the castings produced in the molds with a low silica contents of the binder and with protective salt coatings practically did not have the transformed α -layer on the outer surfaces and in the fillets while on the inner surfaces of the openings its depth did not exceed $10 \cdot 10^{-5} \text{ m}$ (100 microns).

In order to estimate the mold surface quality a new electro-chemical method also developed in CGTU was used. The method of estimating the mold surface contamination is of integral nature and reflects the real picture more objectively in comparison with other existing methods based on micro-hardness measurements and alloy micro-structure analysis which are essentially very local so far as the whole casting is concerned.

The method developed is based on measuring the standard electrode potentials (SEP) and obtaining the anode polarization curves (APC) during dissolving the metal from various layers of the body (wall) of the casting. The measurements of SEP were carried out with the use of an *Ag/AgCl* electrode as the comparison electrode in the saturated solution of *KCl* with the electrode potential of 0.201 ± 0.003 V. APC were obtained in the potentiodynamic regime in which the potential was set at 1.2 V/min and the current density was measured vs the electrode potential. The current density was used as a measure of the rate of electro-chemical dissolution of the metal of the specimens. A potentiostat with the electrolytic cell having separate anode and cathode spaces was used to obtain APC.

The comparison of the electro-chemical parameters of the metal of the surface layer and the matrix metal from the casting core (or the alloy specimen) enables to estimate the degree of the change of its composition i.e. the degree of its contamination.

The closer the values of the electro-chemical parameters of the metal of the casting surface layer and of its core (or the alloy specimen) the lower the level of contamination of the surface and the less the thickness of α -layer.

It was noted that the metal of the surface layer of the castings of the alloy BT20JI fabricated in the corundum molds with protective coatings has the

values of SEP of the order of 0.45...0.48 V which are very close to those for the matrix metal-0.5V.

At the same time the castings fabricated in the ordinary corundum molds with high silica content of the binder (16...20%) and without the protective layer have the value of SEP of the metal of their surface layer equal to 0.32...0.36 V.

The anode polarization curves show that a region of active dissolution of titanium alloys exists in the range of electrode potentials of -0.5...-0.2 V with the maximum at the potential of -0.2 V related with the oxidation of titanium according to reaction $Ti - 3e \rightarrow Ti^{3+}$.

With the change of the potential from -0.2 to 0.2 V passivation of alloys takes place and in the potential range of 0.2...2.2 V the casting metal remains in a passive state.

The analysis of APC also showed that at the very beginning of dissolution of the surface layer of the castings fabricated in the molds with protective layer the rate of its dissolution is only by 23...26% lower than that of the matrix metal and in several minutes time they become practically equal.

The rate of dissolution of the metal of the surface layer of the castings fabricated in the ordinary ceramic molds at the beginning of the process is by 6...7 times lower than that of the matrix metal with the difference of 3...4 times being maintained during a prolonged time (more than 1.5 hours).

The data on the electro-chemical parameters point to an insignificant in intensity and depth (50...100 μm) contamination of the surface layer of the castings fabricated in the molds with low silica content and protective layers. As a rule, the formation of such a contaminated layer with a transformed structure (α -layer) in this case is observed on the surface of openings in the massive parts of the casting.

Therefore, the SEP and APC data received from the tests carried out with casted specimens confirm the results of microstructure and microhardness analyses of their surface and give evidence on the positive effect of low silica content of the mold binder and protective salt coatings on the improvement of the quality of the castings due to a decrease of the depth of α -layer.

Under the industrial conditions it is possible to further decrease the silica content of the binder by 1.4 to 1.5 times by varying the mold wall thickness. It gives the possibility to additionally increase the thermo-chemical stability of the molds towards the poured titanium.

In accordance with Task 2 of the Contract CGTU fabricated for Sandia 30 test corundum investment casting molds, 10 molds for each of the three different technologies specified in the Program "Thermodynamic and chemical analysis of investment casting molds and mold coatings". The molds were sent to Sandia in April 1995.

The molds fabricated according to Technology 4.1 of the Program (not marked) are corundum molds fabricated with the binder of hydrolysed solution of ethyl silicate with low content of silica (SiO_2).

The molds fabricated according to Technology 4.2 of the Program (marked "/") are corundum molds with the chloride protective coating ($BaCl_2$).

The molds fabricated according to Technology 4.3 of the Program (marked "//") are corundum molds with fluoride-chloride protective coating ($CaF_2 + KCl$).

The molds fabricated according to all the Technologies must be dried at the temperature of $300..350^{\circ}C$ during 2.5...3 hours before placing them into the melting-pouring installation.

In order to obtain the minimum thickness of α -layer on the surface of the casting it is desirable that the molds fabricated according to all the Technologies

have the temperature of 25...50 °C before pouring the metal. It is better to control the filling of the mold with metal by using centrifugal forces, i.e. by rotating the mold, than by its heating.

In principle, the molds fabricated according to Technology 4.1 (without marks) may be preheated before pouring the metal to 900-1000 °C.

It is recommended to preheat the molds fabricated according to Technologies 4.2 and 4.3 (marks "/" and "//") to the temperature 600-650 °C before pouring the metal. Under this condition their effectiveness is at the maximum.

For comparison it is recommended to analyse the depth of α -layer for both inner and outer surfaces of each specimen.

CONCLUSION

Mass-transfer in the system "metal-mold" influencing the processes of crystallization and the composition of the surface layer of the castings is based on the evaporation and sublimation of ceramic mold oxides as well as on subsequent oxidation-reduction reactions of the products of sublimation with the components of the alloy and the diffusion of the elements being formed into the metal. The principal initiating factor is the intensive incongruent sublimation of the silica of the mold binder.

The increase of the temperature of the alloys being poured and of the molds before pouring resulting in the increase of the time of crystallization and cooling of the metal as well as the deepening of the vacuum in the melting-pouring furnaces intensify the processes of interaction of the metal with the mold and, as a consequence, the processes of the formation of the contaminated layer with the transformed structure (α -layer) on the surface of the castings.

A decrease in the negative effect of the processes of interaction in the system "metal-mold" on the quality of the castings is achieved as a result of a sharp decrease of the silica content in the casting mold binder and a deposition on its working surface of special protective coatings chemically inert towards both the poured alloys and the mold itself.

However, as the practice has shown, with the increase of the mass and complexity of the castings the method of increasing thermo-chemical stability of the system "metal-mold" by adjustment and synthesis of materials for the fabrication of molds and protective coatings proves not always sufficient.

Therefore, it appears very prospective to control the processes of mass-transfer in the system "metal-mold" by creating special protective atmospheres in the melting-pouring installations with the parameters adjusted so that either to suppress the mass-transfer completely or to direct it in the required direction.

In order to carry out this method of control practically it is required to optimize the parameters of the protective atmosphere (pressure, composition, viscosity, heat-conductivity, and oxydizing potential) at various stages of the process of casting. Moreover, it becomes a necessity to change to some extent the very technology of casting, in particular, by fabricating more gas-conductive molds and decreasing the rates of metal pouring.

In spite of additional expenditures the research work in this direction appears justified as it will bring the increase in the quality of castings enabling the producers to meet rapidly increasing requirements.

References

1. Куликов И.С. Термодинамика оксидов: Справочник. М.: Металлургия, 1986.-344с.
2. *Thermodynamic Properties of 65 Elements and their Oxides, Haloids, and Nitrides.* By C.E.Wicks and F.E.Block. United States Department of the Interior.
3. Физико-химические расчеты электросталеплавильных процессов./ Григорян В.А., Стомахин А.Я., Пономаренко А.Г. и др.-М.: Металлургия, 1989.

Fig.1

Fig.2

System Al-O: 1- $\lg \Sigma P$, 2- $\lg P_{O_2}$

Fig.3

System Si-O. 1- $P = 0.13 Pa$; 2- $P = 1.3 Pa$

Fig.4

System Al-O. 1- $P = 0.13 Pa$; 2- $P = 13 Pa$

Fig.5

System *Ti-MeH*

Fig.6

Fig.7

Fig.8

(X 100)

Microhardness H_μ vs surface layer depth h of the test castings fabricated with MgCl_2 , KCl , CaCl_2 , BaCl_2 , and CaF_2 protective coatings

REPORT

of the results "INVESTIGATIONS OF THE PHYSICAL
PROPERTIES OF THE MELTED SPECIMENS OF
INCONEL 718"

CONTRACT AJ-0147

CUSTOMER: Sandia National Laboratories

CONTRACTOR: Physics department, Urals state technical
university - UPI,
19 Mira str., Ekaterinburg, RUSSIA, 620002

Authorized contractor representatives:

Tretjakova E.E. - senior reseach worker, Dr

Baum B.A. - head of department, Prof., Dr.

Tjagunov G.V. - vice-rector, Prof., Dr.

Ekaterinburg 1995

Authorized contractor representatives:

Tretjakova E.E. - senior reseach worker, Dr. *E.E.*

Baum B.A. - head of department, Prof., Dr. *Baum*

Tjagunov G.V. - vice-rector, Prof., Dr. *Murphy*

Responsible executor:

Barishev E.E. - senior reseach worker, Dr. *Bar*

Executors:

Tsepelev V.S. - senior reseach worker, Dr. *Tsepelev*

Kolotukhin Ed.V. - assistant professor, Dr. *Kolotukhin*

Vjukhin V.V. - reseach worker *V. V. Jukhin*

Selin A.M. - reseach worker *A. M. Selin*

Tjagunov A.G. - engineer *Tjagunov*

Grishenkov S.V. - engineer *Grishenkov*

Zajtseva N.A. - post graduated student *Zajtseva*

Savina L.G. - student *Savina*

Savin O.V. - student *Savin*

CONTENT

Part 1. INTERRELATION BETWEEN LIQUID AND SOLID METALLIC STATES. COMMON DATA.....	4
Part 2. PHYSICAL PROPERTIES INVESTIGATION OF INCONEL 718 MELTED SPECIMENS.....	15
2.1. Some information about alloy.....	15
2.2. Attestation of specimens and methods of investigation.....	18
2.3. Kinematic viscosity - ν	24
2.4. Density - d	29
2.5. Surface tension - σ	33
2.6. Oxygen and nitrogen content.....	35
2.7. Electrical resistivity - ρ	38
2.8. Differential thermal analysis.....	41
2.9. The influence of melt heating on the structure parameters of cast specimens.....	54
3. CONCLUSION.....	66
REFERENCES.....	68

Part 1. INTERRELATION BETWEEN LIQUID AND SOLID METALLIC STATES. COMMON DATA

Early in the our laboratory it was discovered by the experimental methods and base one's arguments on fact that mylticomponent metal compositions after melting may be in the unequilibrium state for a long time. The melts preserve some features of structure of initial solid phase. The solidification from unequilibrium state lead to unstability of the structure and properties of the formed solid metal. It was constructed the new applied direction: The studing of the melt preparing role in the formation of metal properties.

1.1 INTRODUCTION

In scientific works describing two aggregate states of the condensed matter, namely liquid and crystal states more often than not differences are enumerated. However while performing metal alloys melting it is important to prove genetic connection between solid and liquid states. One should reveal the common features of these two aggregate states that come next each other on the temperature scale. One should realize the following problems:

1. What features of structure and phase compound of initial materials can be inherited by the melt?
2. What is the degree and value of this feature stability? What are the conditions when the connection between liquid and solid states will be lost and melt structure will be defined only by composition and temperature?
3. What is the influence of melt structure (its properties respectively) on crystallization and solidified metal structure?

These main problems concern a very wide field of investigation, which requires participation of researchers in different branches of metallophysics: metallography, physics of molten state, crystallophysics. Unfortunately all these researchers, as rule, do not deal with the same scientific goal. Now it became quite evident that each of these researchers needs understanding of all the range of the problems investigated and their interdependence. To our opinion it would greatly enrich the results of their own. Finally all this would provide the development of the summarized concepts, calculations and models. Hence, our studies would enable all the above mentioned scientists to cooperate.

- NONEQUILIBRIUM, i.e. preserving some features of structure of initial solid phase for some time;

- EQUILIBRIUM, which structure and properties are determined not by pre-history but by composition and external parameters.

From the point of view of their origin both groups dependent the initial crystal state. The first group is combined by means of nonequilibrium elements of its state. The second one is combined by the interatomic interaction and by the local order.

1.2. NONEQUILIBRIUM MELTS

The interest to these systems is stimulated by following experimental facts, Fig.1:

- properties of molten samples of the same composition depend on pre-history (initial materials, heat speed and temperature);
- these melt properties are time - instable;
- non-coincidence of properties while heating and subsequent cooling.

The process of relaxation of nonequilibrium states takes a

Some examples of time $\alpha=f(\tau)$, temperature $\delta=f(t)$ and
concentrate $\rho=f(\%Cr)$ dependences

Fig. 1.1

great time and very often METASTABLE states are fixed. These states cannot be destroyed without external (thermal or mechanical) excitation. The most simple way to destroy they are heating up to some fixed temperatures, which is individual for each alloy.

Such a threshold shows rather KINETIC than diffusion mechanism of that process. More often the particle isolation from non-equilibrium formation is limited rather than particle migration and this takes high energy activation.

For example, it is known that such a regime is revealed for graphit suspension in molten Fe - cast iron; silicon drops emulsions in aluminum - silumins; mutual emulsions of tin and lead - solders; melts with remained atomic associations (non-equilibrium clusters) of carbides, silicides, oxycarbides, intermetallic compounds type and the other formation, that are inherent in the solid phase of charge components. The nature of metastability in polycomponent system is the problem to be solved. Now it is evident that solidification from metastable states leads to instability of structure and properties of solid samples. This influences the properties of the liquid received for some time while re-melting.

Thus, the fundamental properties and structure investigations of metallic melts have resulted in creating a new applied trend: THE DESIGNING OF THE RECOMMENDATIONS FOR THE EQUILIBRIUM MELT PREPARATION AIMING AT INCREASING AND STABILIZATION OF METAL QUALITY.

In a well-prepared melt, there must not be any traces of prehistory and it must be in equilibrium, i.e., homogeneous under the given conditions, it must to have the maximum possible amount of homogeneity. The microinhomogeneity, existing in such a melt is determined only by the differences in the interactive energies of

the component particles, in other words, by their nature. First of all scientifically based method of equilibrium melt preparation offers to establish temperature regime of melting. This task is done by studying in the temperature dependences of some liquid alloy properties.

The polytherms of properties of multicomponent melts extremely differ from the polytherms for simple metals. They are, as a rule, never smooth and moreover linear. For each steel composition the temperature dependences of properties have their own characteristic forms, which are caused by the chemical composition, starting materials, and the specificity of the production process.

The principal features of the properties of polytherms of the industrial melts are the HYSTERESIS (deviation between the heating and cooling branches) and DISCONTINUITIES (jumps in the property derivatives vs temperature). The presence of hysteresis indicates irreversibility occurring during the heating process and disappearance of nonequilibrium formations inherited from the solid state. The discontinuities suggest nonmonotonic behavior and sometimes jumps occur in the transition process of the system to the equilibrium state. The conversion of the melt to the equilibrium state takes place, above all, during heating to certain temperatures, called the CRITICAL temperatures t_c . Upon attaining them, the energy of the thermal motion of the particles in the melt becomes comparable to the bond-breaking energy of the strongest interatomic interaction in the nonequilibrium atomic clusters. The heat motion destroys clusters, the melt loses its heredity.

Combined analysis of data on the structure and properties of the steels and alloys in the liquid state as well as the revelation of the types of the structural rearrangements in the melt and their

influence on the structural formation process during crystallization enable us to thoroughly perfect the melting technique named MELT PREPARING technology. This technology consists in choosing optimum time-temperature regimes of melting, alloying, modifying and pouring. Some times it is appropriate to adjust the following heat treatment regimes in the solid state.

1.3. EQUILIBRIUM MELTS

One should take into account some cases of non-equilibrium melt states and therefore the properties and the structure of subjects of fundamental researches of states should be studied in detail. Without this information it is impossible to realize the peculiarities of the structure and evolution of the non-equilibrium system.

In our case some features of electron structure of the alloys of the Fe, Ni and other 3d -transition metal should be taken into account. The existence of d - level near s - level provides the indecisive behavior of d - electrons that can behave both as conductive and localized ones while forming a condensed body.

That is a matter of a variety of interatomic forces and bonds, which is displayed by Fe and Ni in different chemical compounds. The character of these forces depends on the chemical diversity of atoms of alloyed elements, specific atomic volume of substance, temperature and pressure. As can be seen from the phase diagrams, even small variations of typical admixture (O, C, N and others) concentration leads to some essential changes in areas of existence of certain phases, and new thus phases can occur.

In metallic alloys electron structure does not essentially change at raising temperature and transferring. This thesis can be

proved by experimental measurements of magnetic susceptibility, electroconductivity, density and other properties connected with peculiarities of local system order. Therefore the liquid preserves its ability in transition metal atoms for forming bonds of different compounds as well as in their changes due to the actual conditions of melt existence. After melting the role of thermal motion raises. However the strong interatomic bonds, their specific features intensity can greatly influence the atomic order and melt properties. As was proved by our experiments this order is displayed even at rather high overheating above the liquidus temperature.

The melt inherits the peculiarities of interatomic interaction and the local order of initial solid metal to the same extent as the order stability of some elements in the atomic order does (this depends on temperature and strength of bond types). So after melting, system with different types of bonds preserves the ability to change structure of local order. Although these structure modifications take place inside the same phase, they have some features that remind of polymorphic transformations. Structural changes proper are felt much weaker than in solid states and occur mainly within final temperature intervals. However, structure-sensitive melt properties can undergo considerable anomalies.

We should like to point out that structural changes in the equilibrium matrix can quickly stimulate diffusive movement of atoms and solution of non-equilibrium microheterogeneities according to solid state physics. It is quite possible that approximate quantities of the first critical temperature for some alloys with ferrous base (as well as with nickel) might be explained by the above mentioned. As a result of imposing such

structural alteration, the solidification condition of preparing melt can be radically changed.

In addition to the above mentioned we would stress that concentration dependencies of the equilibrium melt properties rather often coincide with similar dependencies for crystal samples. This confirms the identity of this impurity influence on structure and properties of the solid and liquid phases. The models for solid alloys developed suppose formation of the so-called "grouping order" (cluster) influenced by the atom of the admixture and can be used for the liquid states as well. Here the percolation theory promises good results both for the qualitative and quantitative description of concentration regularities in liquid and solid phases.

1.4. QUASICRYSTALLINITY

During studying of liquid metal state with the aim of discovery of interconnection and interinfluence of the solid and liquid states properties of the real system among the large variety of models of liquid state it is necessary to give preference to those, which are based on the conception of QUASICRYSTALLINITY description. Incidentally, the term "quasicrystallinity" sometimes equated with the specific version of superdispersed polycrystal by it's followings and especially often opponents. We understand this term as a nature of methodological approach. QUASICRYSTALLINITY - it is a physical modelling of the liquid structure on the base of real interparticular interaction, which are brightly showed itself in the crystalline state., that is to say when the thermal motion is absent. This approach is based on the unity of condensed state, the unity of interparticular attractive forces in the liquid and

solid states.

If it is necessary to briefly emphasize the qualitative differences of packing type of a various clusters in the liquid transition metals it is possible to named the more soft structure as a δ - like and the more close structure as a γ - like. Sometimes the terms as bcc and fcc - like structure used. Of course, the terminology does not means that some polymicrocrystals are means. The role of this terms are besides the indicator function they contain the instruction on the certain ordering tendency, which are in accordance to some atom groups in the condensed state.

1.5. QUASICHEMICAL MODEL OF THE MICROINHOMOGENEOUS STRUCTURE OF LIQUIDS

Worth while, the discussion of the considered question be in progress in the framework of the named model. This version is especially justly for the transition metals, because any most pure melt of such element owing to it's ambivalent nature may be examined as a particular case of the named model. It's main point are:

a) The melt is composed of extended regions - clusters, the atomic arrangement inside which is distinguished by a certain order (short-range).

b) Owing to relatively strong thermal motion of the particles, the clusters do not have any clear boundaries. For the same reason the lifetime of the clusters is limited and depends on the energy of the chemical bonds in them as well as temperature. The different clusters of two and more type of ordering can exist.

c) Inequality of interaction energies of chemically unlike atoms is the cause for generation of clusters of different

composition and structures of dissimilar stabilities with time. The most stable and long-lived clusters are formed by the most strongly interacting components (for example, ferrous and oxygen).

On principle, our version of the model of the microinhomogeneous structure of liquids is differed from the others it's versions by the accent on the INEQUALITY of interaction energies as a reason of the MICROINGOMOGENEOUS STATE. In this sense it is named quasichemical version of model.

d) This version takes into account: inequality of interaction energies of chemically unlike atoms in the melts; a substantial role of the interparticle attractive force in forming the condensed state (hear the sources of the genetic connection between liquid and solid states); equality of two types of particles motion in the liquid - vibrational and translational.

The described model idea about the structure of real (with the impurities) melts is far from the conclusion. The experimentators constantly give the new data which are difficult to explain. For example it is a oscillation dependence and some other more difficult kind of concentration, temperature and time dependences of liquid metal properties. This peculiarities need the special study with the simultaneous model development.

1.6. CONCLUSION

Give some results of melt preparing technology application in the production of more then 70 steels and alloys of different classes:

- the depth and the volume of the shrinkage hole are decreased on 6-50%, it's form is changed that give the opportunity to decrease the riser volume on the 2-3% without any deterioration of

the quality of the macrostructure;

- the zone of ingot columnar structure is decreased;
- the density of cast metal is increased. The reason of metal concentration is not only the porosity decreasing but the lattice parameters modification; weight of the experimental ingots is more than traditionally melt on 1-2%. This peculiarity is maintained on the following operations;

- the metal output is increased on 5-7%;
- the dispersity of the dendritic structure is increased on 10-15% and it's homogeneity is improved;
- the eutectic carbides quality is decreased on 15-30% for different steels and alloys;

- the dendritic segregation of alloying elements is decreased.

It lead to chaning of matrix constitution, increasing it's microhardness and changing the carbide constitution and morphology. For example, in the high speed tool steels the eutectic carbide morphology have changed from herringbone type structure to feathery and rod-liked structure.

Cast metal structure modifications due to formation of equilibrium melt are affected on it's service properties. The ductility of steels is increased on 20-40%, especially at the hot plastic deformation temperatures. It's temperature interval is expanded. The elastic steel properties is increase on 30% and temperature conductivity - on 10%. For stainless steels it was established the grouth of their creep life on 20-50% and corrosion resistence by a factor of 3-4. The cutting properties of tool steels increase by 20-40%. The service properies of the other alloys and materials (superalloys, amorphous and microcrystalline strips, powders) are improved.

Part 2. PHYSICAL PROPERTIES INVESTIGATION OF INCONEL 718 MELTED SPECIMENS

2.1. Some information about alloy

The precipitation-hardening iron-nickel based alloy INCONEL 718 is used in the manufacture of high-temperature components in combustion engines, power plants and petrochemical plants. It is a superalloy, having a compensation of high strength at moderate temperatures, corrosion and oxidation resistance, and good creep and fatigue resistance. It is one of the most highly utilized superalloys [1-3].

Usually [4,5] alloy is melted in a vacuum induction furnace and after electro-slag refining the ingot has a diameter of 65-100 mm. Then, for producing engine components the centrifugally casting is used [4].

Figure 2.1.1 shows schematically the sequence of reactions during solidification of commercial INCONEL 718. The solidification path begins with the alloy piercing the liquidus surface into the $L + \gamma$ region, with the segregation enriching the liquid in both Nb and C. Although the C concentration profile cannot be unequivocally determined with present analytical techniques, it can be expected that carbon will partition to the liquid during the solidification. Solid solution on the nickel base will continue to grow until the interfacial composition satisfies the three phase non-invariant reaction $L - \gamma + \text{NbC}$. Then, with the formation of the γ/NbC constituent, which depletes the remaining liquid of Nb and C, the local liquid composition would shift back toward the γ phase composition, re-entering the $L + \gamma$ region. Enrichment of the

Fig. 2.1.1

remaining liquid with Nb would continue during this stage of solidification until the non-invariant eutectic reaction, $L - \gamma + \text{Laves}$ was reached, terminating solidification.

Analysis of chemical composition of Laves phase (Tabl.2.1.1) shows that expected A_2B stoichiometry is not met in the alloy [1,2,3]. In INCONEL 718 the A atoms (Fe,Ni,Cr,Si) comprise 72,6 at.% of the Laves phase, and the B atoms (Nb,Mo,Ti,Al) account for 27,4 at.% of the phase. The proposal stoichiometry of Laves phase is $(\text{Ni,Cr,Fe,Si})_3(\text{Nb,Mo,Ti,Al})_{0,9}$ [1].

So, four different precipitates are identified in the cast state [1]: TiN, $(\text{Nb,Ti})(\text{C,N})$, $\epsilon - \text{Ni}_3\text{Nb}$ and a Laves phase with A_3B stoichiometry.

It has been founded [3] that the behavior of Ti in the alloy implies that it is not as important as Nb relative to the formation of the γ/Laves constituent. This suggest that Ti modification to this class of alloys might be accomplished without significantly affecting solidification behavior.

Table 2.1.1

AEM/EDS Compositional Data

Phase	Element, mas. %						
	Fe	Ni	Cr	Nb	Mo	Ti	Si
Laves [3]	11,6	45,8	13,3	22,3	4,6	1,2	1,4
Laves [1]	11,4	43,9	14,3	21,1	4,5	1,4	3,0
Interlamellar γ	12,8	58,4	14,4	9,6	2,8	1,6	0,4
Partition ratio	0,91	0,78	0,92	2,3	1,6	0,7	3,5
MC carbide	1,5	4,7	2,5	80,4	2,5	8,4	0,0

2.2. Attestation of specimens and methods of investigation

It has been investigated five different chemistries of INCONEL 718. Their form was a cylinder with 100 mm diameter and 37 mm height.

The chemical composition of ingots is given in the table 2.2.1. The basic differences are illustrated in Fig. 2.2.1.

All ingots have typical dendritic structure. The dendritic axis is a γ -solid solution on the nickel base. The carbides, nitrides, carbonitrides, eutectic are situated in the interaxis space. Analysis of the literature testifies: eutectic consists from two essential components - γ -phase and Laves-phase; the particles of the secondary hardening phases are precipitated from the supersaturated γ -solid solution after the completion of solidification. The carbides have the form of needles and octaedr-type particles in the investigated ingots.

The niobium content in the alloy influences significantly on the cast structure behaviour (Fig.2.2.2). In particular, the increasing of niobium content leads to:

- 1 - increasing of dendritic structure dispersity, in other words the distance between the secondary dendritic branches is decreased;
- 2 - the reduction of carbide amount;
- 3 - the growth of eutectic on the base of Laves-phase;
- 4 - minor increasing of γ -phase microhardness.

The exposed features of niobium influence on the cast alloy structure are exhibite for all studied titanium content.

A results of titanium content influence on the alloy structure is ambiguous (fig.2.2.3). At the low niobium concentration the titanium addition leads to the same direction as niobium. If the

Table 2.2.1

Chemical composition of the investigated alloy INCONEL 718

Number of specimen	Number of melt	Cr	Ni	Fe	Nb	Ti	Mo
1	54489	16,44	54,20	18,55	6,13	1,13	3,00
2	54493	19,12	54,32	17,89	3,95	1,19	3,00
3	54494	16,74	53,77	18,87	6,26	0,78	3,00
4	54497	19,57	52,82	18,81	4,27	0,89	3,00
5	54514	17,62	53,43	18,49	5,86	0,96	3,00

Additionally the folloing elements are in the alloys, mas. %:

Mn - 0,01-0,02

Si - 0,02

Co - 0,01-0,03

W - 0,01

V - 0,01

Al - 0,44-0,46

B - 0,0027-0,0030

P - 0,001

Cu - 0,02

Ta - 0,01

Hf - 0,01

C - 0,023-0,029

Ag - 0,0005

Pb - 0,0005

Bi - 0,00003-0,00005

Ca - 0,0050

Mg - 0,0010-0,0050

Sn - 0,0020

Cd - 0,0050

Zn - 0,0020

Sb - 0,0020

O - 0,0008-0,0010

N - 0,0011-0,0016

S - 0,0012-0,0018

Ti and Nb content in the specimens. The numeral near the point is the number of specimen in the Tabl. 2.2.1

Fig. 2.2.1.

The influence of niobium on the cast structure parameters of INCONEL 718 ingots

The numeral on the plot is the number of specimen.

1, 2 - high titanium content; 3, 4 - low titanium content.

From here on d_{II} is the distance between secondary dendritic branches;

K and E are, respectively, amount of carbides and eutectic on the base of Laves-phase;

H - is γ -phase microhardness.

Fig. 2.2.2

The influence of titanium on the cast structure
parameters of INCONEL 718 ingots.

The numeral on the plot is the number of specimen.
1, 2 - high niobium content, 3, 4 - low niobium content.

Fig. 2.2.3.

niobium concentration is high, the titanium influence is in apposition to niobium and leads to:

- 1 - decreasing dendritic structure dispersity;
- 2 - minor increasing of carbide amount and decreasing of eutectic amount;
- 3 - a reductin of γ -phase microhardness.

So, varying titanium and niobium content in the chemical composition of the INCONEL 718 does not transform the total phase content but leads to changes of phase amount and redistribution of alloying elements between them.

The following properties have been studied in the liquid state:

KINEMATIC VISCOSITY - ν . The decrement of oscillation damping of the crucible with the melt has been measured by inspection. The calculation of viscosity value were performed by standard formulas.

DENSITY - d . The penetrated through the crucible with the melt γ -ray deterioration of the intensity has been studied.

SURFACE TENSION - σ . It has been studied by the method of the "big drop" in the helium atmosphere. Calculation of σ is performed by use the mass, shape, volume and area of liquid metal drop.

OXYGEN AND NITROGEN CONTENT has been measured on the gasanalyser "O-N-mat-822" of "Shtrohlein" firm by the method of restored melting in a gas-transmitter stream (helium).

ELECTRICAL RESISTIVITY - ρ . The contactless method of rotating magnetic field has been used. The angle of cuve of the crucible with the melt that has been suspended on elastic thread has been noted.

DIFFERENTIAL THERMAL ANALYSIS - DTA. The temperature difference of studied specimen and a standard (tungsten) has been determined

during of process of heating and cooling of the unit.

All melt properties investigations have been carried out in the crucible from BERYLLIUM OXIDE in the cleansed helium atmosphere (pressure 10^2 - 10^3 Pa). The chambers with specimens have been degassing previously. Oxygen content in the helium did not exceed 0,001%.

SPECIMEN MICROSTRUCTURE. The influence of maximum melt heating temperature on the cast metal structure has been studied by the tradition method.

The cutting specimens diagram for melt properties investigations is shown in the Fig. 2.2.4.

The zone segregation influence are scarcely affected by the electrical resistivity. It shows up for the specimens cutted from the central zone of the ingot. The melt properties investigation controls specimens has been cutted on experimental grounds from the 0,5R (R - ingot radius) (Fig. 2.2.4).

2.3. KINEMATIC VISKOSITY - ν

First and foremost it should be stressed that after INCONEL 718 specimens melting the fragments of oxide film are not infrequently appeared on its surface. Sometimes such film totaly covers the melt surface. The film is destroyed during melt heating. Such process is especially actively site of temperature range from 1700 to 1800°C.

The results of the kinematic viscosity measurements are shown on the Fig. 2.3.1. Everyone polyterm (temperature dependence) is a result of averaged data of four similar dependences of the chemistries investigation. Some averaged values of ν are tabulated in Table 2.3.1, lumped together with density d (for more details see the section 2.4) and dynamic viscosity $\eta = \nu \cdot d$.

The cutting specimens diagram for investigation

1 - electrical resistivity; 2 - metal structure; 3 - DTA;
4 - viscosity; 5, 6, 7 - density, oxygen, nitrogen

Fig. 2.2.4

The influence of temperature on the kinematic viscosity ν of INCONEL 718.

The numeral on the plot is the number of specimen in the Tabl. 2.2.1.

● - heating; ○ - cooling.

Fig. 2.3.1.

Table 2.2.1

Some values of density d ($\text{kg/m}^3 \cdot 10^{-3}$), kinematic viscosity ν ($\text{m}^2/\text{s} \cdot 10^7$),
dynamic viscosity η ($\text{Pa} \cdot \text{s} \cdot 10^3$) of the melted specimens of INCONEL 718

Melt temperature $t, ^\circ\text{C}$	Number of specimen in the table 2.2.1														
	1			2			3			4			5		
	d	ν	η	d	ν	η	d	ν	η	d	ν	η	d	ν	η
1400	7.53	10.15	7.64	7.53	10.00	7.53	7.51	10.20	7.66	7.55	10.00	7.55	7.61	9.90	7.53
1500	7.34	8.90	6.53	7.45	8.60	6.41	7.45	8.90	6.63	7.36	8.70	6.40	7.53	8.50	6.40
1600	7.29	7.70	5.61	7.40	7.40	5.48	7.39	7.80	5.76	7.27	7.60	5.53	7.47	7.40	5.52
1700	7.23	6.75	4.88	7.34	6.60	4.84	7.33	7.00	5.13	7.21	6.80	4.90	7.40	6.80	5.03

The obtained results allow to make the following conclusions.

1. The polyterm $\nu(t)$ has the monotonic exponent type and has described in the temperature range from t_L to 1700-1800°C by the equation:

$$\nu = A \cdot e^{\frac{E}{RT}}$$

where $E_\nu = 37,3$ kJ/mol is a activation energy of frictional flow; $A = 6,84 \cdot 10^{-8}$ m²/s; $R = 8,31$ J/mol·K.

The dynamic viscosity $\eta = \nu \cdot d$, Pa·s

$$\eta = B \cdot e^{\frac{E}{RT}}$$

where $E_\eta = 47,3$ kJ/mol; $B = 2,51 \cdot 10^{-4}$ Pa·s.

The equations presented in this section are accurate to +4% from the calculated value. The Nb is scarcely affected on the viscosity. The more Nb content is the more viscosity. The Ti influence does not found.

2. The obtained results indicate that size of units of frictional flow and their bond energy with the surrounding atoms does not undergo the variation in the marked temperature range. Judging from the values of E_ν and E_η the major units of frictional flow are the metal atoms (or ion).

3. No transmittance of hereditary traits of initial charge, used for INCONEL 718 melting does not found. It is possible that INCONEL 718 melting process for the studied chemistries takes place at the sufficiently high temperature and intensive stirring. This operation makes possible to form the equilibrium melt before solidification.

4. The anomaly $\nu(t)$ observed above 1720°C may be centre around

with the following circumstance.

a) The change of oxide film condition, its disintegration and removal.

b) Intensive change of the structure of the liquid metal short-range order. However the viscosity is not sensitive to the irreversible part of this changes (as distinct from results of electrical resistivity, section 2.7). In another way at the 1750-1850°C the particle interaction energy is decayed and intensive structure realignment takes place thanks to increasing of atom heat movement energy. It leads to ambiguous changes of ν .

During following cooling the values of kinematic viscosity are also defined by the structural units of frictional flow (atoms, ions, their size and interaction energies) as during heating. Thus the values of viscosity are either coincide or moderately differ.

c) It is possible that the factors a) and b) are operated concurrently if the kinetic energy of heat movement of atoms is approached to the particle interaction energy and activation energy of diffusion in the film and the strongest melt atomic association (carbides and intratomic compounds of Ni_3Nb type).

2.4. DENSITY - d

The results of density investigation of the presented chemistries are shown on the Fig. 2.4.1. The procedure of experiment has been as follows. The specimen has been melted and heated to some fixed temperature 1450, 1550, 1650 or 1800°C. The density has been measured firstly during heating and then during subsequent cooling with the rates from 25 to 40°C/min in the temperature range from 1800 to 1450°C and from 2 to 5°C/min in the temperature interval from 1450 to 1370°C. The solidification of the

The influence of temperature on the density d of INCONEL 718

The numeral on the plot is the number of specimen in the Tabl. 2.2.1. The determined by DTA special temperatures are severed by vertical lines: t_l - liquidus temperature; t_k - the onset of karbide formation temperature; t_e - the onset of eutectic on the base of Laves-phase formation temperature; t_s - solidus temperature.

Fig. 2.4.1.

specimens in the temperature range from 1370 to 1050°C has been carried out with the cooling rates 10°C/min. The isothermal holding at the maximum melt heating temperature has been comprised 10 minutes. The density values during melt heating and cooling were opposed in every experiments.

Analysis of the Fig. 2.4.1 and Table 2.4.1 discloses that the increasing Nb content from 4 to 6% leads to decreasing liquidus temperature on 25-30°C or to reducing the intensity of crystal formation and evolution during cooling below liquidus temperature. As this takes place the Laves-phase formation temperature t_e is diminished too. The increasing titanium content from 0,8 to 1,2% decreases the carbide formation temperature t_k on 10-20°C.

Table 2.4.1

The values of the characteristic temperatures during solidification of INCONEL 718 specimens

Specimen number	Temperatures, °C				
	t_L	t_k	t_e	t_s	t_b
1	1295	1265	1150	1080	980
2	1320	1270	1160	1070	—
3	1290	1250	1150	1065	980
4	1320	1250	1170	1065	980
5	1320	1250	1170	1070	—

The thermal expansion coefficient of liquid metal for all chemistries are closely related. It should be particularly emphasized that this coefficient is slightly higher for specimens with the lower Ti content (N3, N4, N5).

Conclusions

1. Density values in the liquid state for all INCONEL 718 chemistries are principally temperature depended and closely related.

2. Change of the specimen density during solidification depends from the maximum melt heating temperature (t_{max}), melt cooling rates and chemistry.

The most density at the solidus temperature t_s is observed in the case of melt heating to 1550-1650°C. If the temperature is above or less than such temperature range the density at t_s appears to be lesser.

The increasing of the solidification rate leads to an earlier termination of primary phase deposition.

3. It needs to note the one of the penetrated γ -ray disadvantage. It lies in the fact that near the solidus temperature during specimen cooling it may be intensive uncontrolled shrinkage porosity formation and dramatic decreasing of ingot (solid specimen) diameter. As this takes place the path of γ -ray beam through the metal is decreased and the counter fixes the growth of the intensity of elapsed radiation. The calculation gives the sharp decrease in the density. In this case the temperature of the intensive density changes are fixed correctly but securing of it proper absolute value is needed the further special experiments. The noted phenomena takes part during investigations of the specimens N1, N2, N3, Fig. 2.4.1.

4. The different overcooling and dissimilar advancement of some solidification process (more intensive deposition of primary phase) can be achieved by the choosing of maximum melt heating temperature t_{max} and cooling rates. It is shown that the higher Nb content in the alloy the beyond the overcooling (more about that fact see in the section 2.8).

The special features of solidification process (the influence of different phase transformation on the sealing value) it is conveniently to estimated at by compared of values Δd and τ , Table.2.4.2. For example, at $t_{max} = 1800^{\circ}\text{C}$:

Specimen N1	$\Delta d_{LK} = 130 \text{ kg/m}^3$	$\tau_{LK} = 10 \text{ min}$
	$\Delta d_{KS} = 190 \text{ kg/m}^3$	$\tau_{KS} = 20 \text{ min}$
Specimen N3	$\Delta d_{LK} = 270 \text{ kg/m}^3$	$\tau_{LK} = 14 \text{ min}$
	$\Delta d_{KS} = 110 \text{ kg/m}^3$	$\tau_{KS} = 10 \text{ min}$

From this results we notice that primary γ -phase shares out more intensively in the specimen N3.

2.5. SURFACE TENSION - 6

The availability of the surface film fragments hampers the measurements of the surface tension during the liquid specimen heating. Results that has been obtained during the melt cooling are given be the unified equation for all chemistries in the temperature range from 1400 to 1800°C

$$\sigma(t) = [1580 - 0,15 \cdot (t-1400)] \text{ mJ/m}^2$$

where t is a melt temperature, $^{\circ}\text{C}$.

Dispersion of experiment point values comprises $\pm 7\%$ from the values that are shown on relationship.

Table 2.4.2

Some values of density d ($\text{kg/m}^3 \cdot 10^{-3}$) at the characteristic temperatures and its change Δd in the characteristic temperature interval during the cooling

Specimen number	Liquid			d_s	d_L	Δd_{LS}	Δd_{LK}	Δd_{KS}	$\Delta \tau_{LK}$	$\Delta \tau_{ke}$	$\Delta \tau_{KS}$
	$t_{\max}$	d_{1600}	d_{1400}								
1	1800	7.29	7.41	7.76	7.44	0.32	0.13	0.19	10	14	20
	1650	7.41	7.53	7.96	7.58	0.38	0.19	0.19	13	12	20
	1550	—	7.48	7.87	7.53	0.34	0.17	0.17	10	12	20
2	1800	7.40	7.53	7.84	7.57	0.27	0.19	0.08	12	12	22
	1450	—	7.60	8.08	7.65	0.43	0.25	0.18	22	26	40
3	1800	7.39	7.51	7.95	7.57	0.38	0.27	0.11	14	10	18
4	1800	7.27	7.55	7.86	7.50	0.36	0.28	0.08	14	8	18
	1650	7.43	7.54	7.96	7.58	0.38	0.27	0.11	12	13	20
	1550	—	7.47	7.86	7.50	0.36	0.24	0.12	12	14	20
5	1800	7.47	7.61	8.02	7.65	0.37	0.19	0.18	14	12	20

Comment: L - liquidus; K - the onset of karbide formation;
 E - the onset of eutectic on the base of Laves-phase formation
 S - solidus. $\Delta \tau$ - it is a time lapse between cooling specimen
 from one characteristic temperature to another, min.
 All the values are presented for the different maximum melt
 heating temperatures $t_{\max}$.

2.6. OXYGEN AND NITROGEN CONTENT

The first stage of oxygen content determination in specimen was the fixing of evologram, for example presented in Fig 2.6.1.

It was estimated on results of previously made investigations that the first extremum of intensive oxygen extraction (the temperature of extraction is 1360-1430°C) is consistent with nickel oxide dissociation. The seconde one (1780-1830°C) check with deposition of oxygen from chromium oxide. The third extremum is exhibited ounly for specimens N2, N4, N5 and fits to decomposition of alumina. The fourth one (2120-2160°C) is aproprate to the dissociation of niobium oxide. The fifth extreme (2215-2255°C) corresponds to oxygen deposition from titanium oxide.

The results of evologram deciphering are presented in Table 2.6.1.

Conclusions

1. The total oxygen content in the specimens depends on niobium and titanium content in the alloy. The increasing their concentration in the alloy leads to decreasing the total oxygen content.

2. All oxygen in the solid specimen is in the related form, in other words in the different oxides.

3. The greater part of oxygen in the each specimen (from 50 to 60%) is in the form of nickel oxide. It is believed that this part of oxygen was in the solution before the melt solidification. It is not improbable that the other oxides formed during ingot solidification process.

4. During the liquid metal properties investigation the oxygen content in the specimen either or both did not change and moderately increase (to 0,0015% and sometimes 0,0040%). The oxygen

The extraction time (τ) dependence of intensity of oxygen extraction from the specimen. The typical evologram

The every extremum oxygen extraction is consistent with the dissociation of different oxides. For example, the onset of oxygen extraction from nickel oxide temperature is presented.

Fig. 2.6.1.

Table 2.6.1

Oxygen content in the initial ingots of INCONEL 718

N п. п.	Ingot number	Total oxygen content, [O] mas. %	Oxygen in the oxides of the elements, mas. %				
			Ni	Cr	Al	Nb	Ti
1	54489	0.0003	$\frac{1430}{0.0002}$	$\frac{1830}{0.00004}$	—	$\frac{2150}{0.00005}$	$\frac{2250}{0.00001}$
2	5493	0.0013	$\frac{1390}{0.0007}$	$\frac{1830}{0.0001}$	$\frac{2040}{0.0001}$	$\frac{2120}{0.0002}$	—
3	54494	0.0008	$\frac{1400}{0.0004}$	$\frac{1830}{0.0001}$	—	$\frac{2140}{0.0001}$	$\frac{2300}{0.0001}$
4	54497	0.0012	$\frac{1360}{0.0006}$	$\frac{1780}{0.0002}$	$\frac{2020}{0.0001}$	—	$\frac{2215}{0.0001}$
5	54514	0.0006	$\frac{1390}{0.0003}$	$\frac{1830}{0.0001}$	$\frac{2050}{0.0001}$	$\frac{2160}{0.0001}$	$\frac{2215}{0.0001}$

Comment: The numerator - temperature of the beginning of the oxygen extraction on the evologramm, °C; the denominator - oxygen amount, extracted from oxide, mas. %.

absorbed during experiment is presented as nickel and chromium oxides in the solid specimen. Only in the one half of specimens it was found the insignificant amount of the other oxides. The amount of oxygen in this oxides does not exceed the oxygen content in the initial ingots. The oxygen soluted in the metal is found (to 0.0003%).

5. Total nitrogen concentration in the initial chemistries is tabulated in Table 2.6.2. The nitrogen content in the metal does not distinctly change during the properties investigation.

Table 2.6.2
Nitrogen content in the initial ingots of INCONEL 718

Specimen number	1	2	3	4	5
[N], mas. %	0.0013	0.0012	0.0014	0.0012	0.0013

2.7. ELECTRICAL RESISTIVITY - ρ

The main information of results of investigations of temperature dependences $\rho(t)$ is shown in Fig. 2.7.1. and 2.7.2.

As will be seen from the submitted plots the electrical resistivity of the specimen after its melting is slow rise in during heating. In the temperature range from 1700 to 1800°C ρ is elevated intensively. Following the heating to the temperature 1770-1800°C depended from chemistries the upgrading of ρ is stopped.

If the liquid metal was heated above 1770-1800°C during following cooling the electrical resistivity is slow diminished. The cooling-curve of ρ is outstripped by its heating-curve. The phenomenon of electrical resistivity hysteresis takes place.

The presented view of polyterm $\rho(t)$ is typed for great number of cast and formed superalloys. It is expected that the short range order of Ni_3Nb and $\text{Ni}_3(\text{Al}, \text{Ti})$ type would collapse in the temperature range from 1700 to 1800°C. The differences between the attractive forces of unlike atoms and like atoms cannot conserve such order. At this temperatures the atom heat movement energy may be as great as cohesive activation energy and energy of grain migration in the mentioned location of short range order.

This locations (associates of Ni_3Nb and others) does not restore during following cooling. In this connection the values of ρ are high: the melt entropy and electron scattering on the phonons

The influence of temperature on the electrical resistivity ρ of the INCONEL 718 specimens

The numeral on the plot is the number of specimen in the Tabl. 2.2.1.

● - heating; ○ - cooling.

Fig. 2.7.1.

The temperature dependence of electrical resistivity ρ of the specimen N 3 in the melting - solidification region.

The determined by DTA special temperatures are severed by vertical lines:
 t_L -liquidus temperature; t_K - the onset of karbide formation temperature; t_e - the onset of eutectic on the base of Laves-phase formation temperature; t_s - solidus temperature.
 ● - heating; ○ - cooling.

Fig. 2.7.2

are great.

During solidification electrical resistivity is changed by the complicate manner.

The initial short range order restores only after full specimen solidification and cooling below 1000°C.

Such factors as niobium and titanium content, oxygen concentration and some others in its collective form are moderately influence on the electrical resistivity value. As may be required the influence of this individual factor may be clarify by pursuance of special electrical resistivity investigation.

2.8. DIFFERENTIAL THERMAL ANALYSIS - DTA

DTA experiments were performed on a fully automated unit. Tests were performed in BeO crucibles in the tungsten cell. The cell was heated from the room temperature to 1000°C. Heating speed was 100 °C/min. Working chamber was under the pressure of 10^{-1} Pa. Then the chamber was filled up with the high-purity helium up to 10^3 Pa and the speed of heating was reduced to 20°C/min. The termogram recording was made from 1100°C up to the maximum temperature of melt heating and down to 1100°C. The tests were carried out at a constant heating and cooling rate 20°C/min, under He protection. Tungsten was the reference material. Alloy was cooling below 1000°C with the speed about 100°C/min. Reaction temperatures were determined by finding the temperature at which DTA curve deviated from local base-line.

DTA-curves during heating and cooling

The heating typical DTA-curve of the investigated specimen in the temperature range from solidus to liquidus temperatures is

Typical heating DTA curves for INCONEL 718

Fig. 2.8.1.

shown on fig. 2.8.1. It was found out the deviation from base line of DTA-curve that connected with as carbide as marix melting. For the samples with high niobium content the additional peak caused with eutectic melting was fixed. The average temperatures of phase transformations during melting of INCONEL 718 chemistries are tabulated in Table 2.8.1.

Table 2.8.1

Phase transformation of INCONEL 718 specimen, °C

Number of specimen	Liquidus	$\gamma + \text{NbC} \rightarrow \text{L}$	Eutectic γ/Laves
1	1349	1238	1157
2	1343	1243	1157
3	1353	1238	1145
4	1345	1240	1155
5	1355	1243	-
Knorovsky G.A. et al [2]	1362	1198	1252

Comment: The temperatures of the phase transection in the work [2] has been determined from the cooling curve

The DTA-curves of all samples are similar in the liquid state. After melting in metal the process connected with heat absorbtion happens. The further increasing of temperature leads to coincide of DTA-curve with base line. The derivation from base line testifies that some exothermic effects take plase in the liquid metal.

The solidification of the samples begins with formation of γ -phase. The further cooling of liquid metal leads to carbide formation on reaction $\text{L} - \gamma + \text{NbC}$. The solidification process terminates in eutectic formation on following reaction $\text{L} - \gamma + \text{Laves}$.

Though Laves- ϕ 3a is metallographic found in all investigated chemistries the thermal effect stipulated by to last reaction is not always displayed on DTA-curve.

The influence of maximum melt heating temperature
on INCONEL 718 alloy phase formation

Specimen N1

Some cooling DTA-curve in solidification zone after heating to various temperatures are shown in Fig. 2.8.2. The analysis of the curves has allowed to find the influence of maximum melt heating temperature on solidification character of sample N1.

The dependence of overcooling value from maximal melt heating temperature is conditionally possible to present as curve, passing through maximum, fig. 2.8.3 (specimen N1). If the specimen was solidified immediately after melting the minimum of overcooling value equal to 20°C is fixed. The increasing of melt heating temperature from 1360 to 1500°C leads to decreasing the beginning solidification temperature and increasing the overcooling. It reaches the maximal value at 80°C. During the further melt heating from 1500 to 1880 °C the t_1 is slightly increases and overcooling decreases.

The begin carbide formation temperature does not practically depend on t_{max} and averages 1245 °C. The small lowering of t_{mc} on 5°C is found only for specimens solidified after deep overcooling.

If the melt was not overheated above 1420°C the eutectic reaction ($L-\gamma$ +Laves) begins at 1150°C. The small increasing of melt heating temperature leads to lowering of eutectic formation temperature on 5-7°C. If the melt was heated up to 1460-1800°C the thermal effect of $L-\gamma$ +Laves reaction on the DTA-curve does not

The influence of maximum melt heating temperature on the typical view of cooling DTA curves in the solidification region for specimen N 1.

The numeral on the plot near the curve is the maximum melt heating temperature.

Fig. 2.8.2.

The influence of maximum melt heating temperature on the melt overcooling and phase transformation temperatures of INCONEL 718 specimens

The numeral on the plot is the number of specimen in the Tabl. 2.2.1.

- 1 - the onset of reaction $L \rightarrow \gamma$
- 2 - the onset of reaction $L \rightarrow \gamma + \text{NbC}$
- 3 - the onset of reaction $L \rightarrow \gamma + \text{LAVES}$.

Fig. 2.8.3.

found.

The solidus temperature does not depend from maximum melt heating temperature.

Specimen N2

The cooling DTA-curves of the specimen N2 heated during the experiment to different temperatures are shown on Fig 2.8.4. The influence of maximal melt heating temperature on overcooling value are presented on Fig. 2.8.3 (specimen N2). The process of phase formation for specimens N1 and N2 are similar. Some differences are connected only with the change of values of the investigated parameters but not with their qualitative behaviour. We indicate, for example, some following differences. Firstly maximal melt overcooling equal to 68°C is reached after its heating to 1540-1550°C. Secondly, carbide formation begins, as a rule at temperature equal to 1255 °C. At last, thermal effect of $L-\gamma$ +Laves reaction on DTA-curve does not found.

Specimens N3, N4, N5

The typical DTA-curve of specimens N3, N4, N5 in the solidification zone are shown on Fig. 2.8.5-2.8.7, respectively. The influence of maximum melt heating temperature on the overcooling of liquid metal and temperatures of phase transformation during solidification appears in Fig 2.8.3. As well as for specimens N1 and N2 the influence of melt heating temperature on phase transformation temperature of the solidified metal is similar. However the maximal melt overcooling $\Delta T_{\max}=110^{\circ}\text{C}$ is reached for the specimen N3.

The influence of maximum melt heating temperature on the typical view of cooling DTA curves in the solidification region for specimen N 2.

The numeral on the plot near the curve is the maximum melt heating temperature.

Fig. 2.8.4.

The influence of maximum melt heating temperature on the typical view of cooling DTA curves in the solidification region for specimen N 3.

The numeral on the plot near the curve is the maximum melt heating temperature.

Fig. 2.8.5.

The influence of maximum melt heating temperature on the typical view of cooling DTA curves in the solidification region for specimen N 4.

The numeral on the plot near the curve is the maximum melt heating temperature.

Fig. 2.8.6.

The influence of maximum melt heating temperature on the typical view of cooling DTA curves in the solidification region for specimen N 5.

The numeral on the plot near the curve is the maximum melt heating temperature.

Fig. 2.8.7.

Conclusions

1. Results of investigation testify that the value of liquid INCONEL 718 overcooling is defined by melt heating temperature and Nb and Ti content. The dependences of melt overcooling value from maximum melt heating temperature of maximal heating for all investigated chemistries have the identical character. It is a curve having maximum, fig.2.8.8.

The dependence of melt overcooling ΔT of INCONEL 718 specimen from the maximum melt heating temperature

Fig. 2.8.8.

2. The following influence of niobium and titanium content on the solidification process has been established.

If the titanium content was small (near 0.8 mas.%) the increasing of Nb concentration from 4 to 6% leads to the growth of maximal value of melt overcooling (ΔT_{max}) for more than two times. Whereas at most titanium content (near 1.2 %) the niobium content increasing leads to growth of ΔT_{max} only on 15 %.

The change of titanium content from 0.8 to 1.2% at minimum niobium concentration (4%) practically does not affect on the value

of $\Delta T_{\max}$. But at maximal Nb contents the Ti addition reduces the maximal value of melt overcooling.

Futhermore the increasing of Ti content in a specimen causes the change of form of dependence of melt overcooling value from the heating temperature. In particular the peak becomes more asymmetric. The high-temperature curve becomes more gently inclined for the most titanium content.

3. Deep melt overcooling achives during its heating to the temperature range where the essential structure changes does not take place. The DTA-curve is coincided with the base line, Fig. 2.8.1 and 2.8.8.

4. Analysis of the results show that the maximum overcooling that may be achived is consistent to the carbide formation temperature for the specimen that was solidified immediately after melting.

5. The beginning carbide formation temperature t_{Mc} does not practically depend on the maximum melt heating temperature. However if the liquid metal has deep overcooling the t_{Mc} may be slightly redused.

6. The solidus temperature does not depend on the maximum melt heating temperature.

7. The Laves-phase formation is most strongly appears on the DTA-curve in the such case when the alloy solidification process begins at the temperature above 1300°C and melt overcooling is more then 35-40°C.

2.9. THE INFLUENCE OF MELT HEATING ON THE STRUCTURE

PARAMETERS OF CAST 718 SPECIMENS

The specimens of the INCONEL 718 taken after studying of differential thermal analysis has been investigated with the aim of establishment the influence of maximum melt heating temperature on the cast metal structure. The specimens to be investigated has been distinguished by maximum heating temperature. The rates of heating and cooling during all experiments has been held constant.

The metallographic analysis results of the all specimens are shown in Fig. 2.9.1-2.9.5.

The obtained results testifies that character of structure chracteristics changes with the increasing of the melt heating temperature (the distance between secondary dendritic branches - d_{II} , amount of carbides K and eutectic E) is practically identical for the all investigated chemical compositions of INCONEL 718.

So the parameter d_{II} for dendritic structure firstly decreases with the increasing the melt heating temperature. At the temperature interval from 1480 to 1560°C (the value of temperature is depended on niobium and titanium content in the alloy) parameter d_{II} falls to a minimum. The further increasing of the melt heating temperature newly leads to some increasing of d_{II} .

The carbide content in the specimens either are practically unaffected or increases moderately with the growth of melting temperature.

The dependence of amount of eutectic on Laves-phase base from the maximum melt heating temperature has the form similar to changes of d_{II} .

As well as dendritic structure firstly a reduction of eutectic

The influence of maximum melt heating temperature on the cast structure parameters of INCONEL 718 specimen N 1

From here on d_{II} is the distance between secondary dendritic branches;

K and E are respective amount of carbides and eutectic on the base of Laves-phase;

H - is γ -phase microhardness.

Fig. 2.9.1.

The influence of maximum melt heating temperature on the cast structure parameters of INCONEL 718 specimen N2

Fig. 2.9.2.

The influence of maximum melt heating temperature on the cast structure parameters of INCONEL 718 specimen N3

Fig. 2.9.3.

The influence of maximum melt heating temperature on the cast structure parameters of INCONEL 718 specimen N4

Fig. 2.9.4.

amount is observed and then it essential growth occurs.

The single dependence of microhardness of γ -phase from maximum melt heating temperature for the specimens having different chemical content have not established.

Previously it has been established during solidification process of INCONEL 718 specimens by DTA method that the overcooling is dependent on the maximum melt heating temperature. It is well known that cast metal structure is dependent essentially from the overcooling value [6]. In this connection it was plotted the dependence of cast structure parameters from the overcooling (Fig.2.9.6-2.9.10).

Analysis of the obtained dependences testifies that the character of structure parameter changes for all investigated chemistries are closely related. In particular the increasing of overcooling leads to the following:

- 1 - the dendritic structure dispersity is growing;
- 2 - carbide content either increases moderately or practically are unaffected;
- 3 - the amount of the eutectic on the Laves-phase base significantly decreases.

The influence of melt overcooling ΔT during solidification on the cast structure parameters of INCONEL 718 specimen N1

From here on $\circ$ - maximum melt heating temperature of the specimen is low then temperature of maximum melt overcooling;
 $\bullet$ - the specimen during DTA investigation has been heated above the temperature of maximum melt overcooling.

Fig. 2.9.6.

The influence of melt overcooling ΔT during solidification on the cast structure parameters of INCONEL 718 specimen N2

Fig. 2.9.7.

The influence of melt overcooling ΔT during solidification on the cast structure parameters of INCONEL 718 specimen N3

Fig. 2.9.8.

The influence of melt overcooling ΔT during solidification on the cast structure parameters of INCONEL 718 specimen N4

Fig. 2.9.9.

The influence of melt overcooling ΔT during solidification on the cast structure parameters of INCONEL 718 specimen N5

Fig. 2.9.10.

3. CONCLUSION

1) Investigation of the metal melt physical properties is most often working out two problems:

a) To obtain the reference data about values of equilibrium melt properties at different temperatures. This data are needed to carry out some thepophysical, hydrodinamical, technological calculations.

b) To compare the properties of the liquid specimens that have been melted with the different technological regimes. This comparison is needed for choosing the profitable and inexpensive production regime and for elaboration of recomendation for remelting, refining, alloying, inoculation and other technological operations.

2. The performed investigation has solved for the most part the first task. The kinematic viscosity, density, surface tension and electrical resistivity has been studied for five chemistries. The differential thermal and microstructure analysis of this chemistries has been carried out. The oxygen and nitrogen content has been determined.

The obtained data is shown up as tabulated and graphical form. The conclusions are made for each property.

Furthermore, the performed investigation has discloses that the melts of the presented chemistries does not contain the unequilibrium associations of the atoms that has been heritaged from the initial charge matherials. During the melting of this specimens such temperatures are apt to be attained that obtain the reasonably full molecule stirring, in other words the production of

equilibrium melt. The pouring and solidification regimes supposedly fixed the advantages of melting technology. The zone segregation across the ingot section has not essentially detected by the used experimental methods.

REFERENCES

1. Ulrich Waldherr, Michael Pohl, Rejane Aparecida Noqueira, Angero Fernando Padilha. Microstructure and workability of Inconel 718, as cast and heat- treated/Prakt. Metallogr. 1989, v.26, N4, P.174-184.
2. G.A.Knorovsky, M.J.Cieslak, T.J.Headley, A.D.Romig, Jr and W.F.Hammetter. Inconel 718: a solidification diagram /Metallurgical Transaction, 1989, v.20A, N10, P.2149-2158.
3. M.J.Cieslak, T.J.Headley, G.A.Knorovsky, A.D.Romig, Jr, T.Kollie. Comparision of the solidification behavior of Inconel 909 and Inconel 718/ Metallurgical Transaction, 1990, v.21A, N2, P.479-488.
4. H.H.Sith, D.J.Michel. Effects of Thermal and Thermomechanical Treatments on the Mechanical Proerties of Centrifugally Cast Alloy 718/Materials Science and Engineering A, 1988, v.102, N2, P.161-168.
5. R.A.Spragye, S.J.Friesen. Superalloy Component Durability Enhancements/J. of Metals, 1986, v.38, N7, P.24-30.
6. E.V.Kolotukhin, G.V.Tjagunov. Crystallization of superaloy with various content of carbon/J. Materials Processing Technology, v.3, N1-2, P219-227.

Project Title: Melt Nuclei In Alloy 718
Principal Investigator: Elena Tretyakova
Urals Polytechnic Institute
Sverdlovsk, Russia
AJ-0147

CLAUSE 1 - STATEMENT OF WORK

Tasks:

The Contractor shall:

1. Provide a written experimental plan in English for an investigation to evaluate the effects on non-equilibrium melting and solidification which would result in a memory of the premelt microstructure. The investigation shall consider five different chemistries of Alloy 718 specimens which will be provided by Sandia. The chemistries with Nb and Ti as variants, at the expense of Cr, are (all in weight percent):

4.0% Nb - .80% Ti;
4.0% Nb - 1.2% Ti;
6.4% Nb - .80% Ti;
6.4% Nb - 1.2% Ti;
5.4% Nb - 1.00% Ti;

2. Upon concurrence of the experimental plan by Sandia; conduct experiments to characterize these chemistries by measuring viscosity, density, surface tension, and oxygen and nitrogen as a function of temperature for both liquid and solid close to the non-equilibrium solidus temperature. Other measurements may also be made at the discretion of the investigator to provide a more complete characterization. Characterize the metallography of each chemistry as a function of temperature. Provide a report of the results obtained from the work in English. List applicable conclusions. Label all specimens and return them to Sandia with the appropriate legend.

THE EXPERIMENTAL PLAN FOR INVESTIGATION
FOR CONTRACT AJ-0147

INTRODUCTION

In scientific works describing two aggregate states of the condensed matter, namely liquid and crystal states more often than not differences are enumerated. However while performing metal alloys melting it is important to prove genetic connection between solid and liquid states. One should reveal the common features of these two aggregate states that come next each other on the temperature scale.

Investigation of the structure and properties of melts is the key problem among the mentioned above. Melts, as any other thermodynamic systems, should be divided in two groups:

- NONEQUILIBRIUM, i.e. preserving some features of structure of initial solid phase for some time;

- EQUILIBRIUM, which structure and properties are determined not by pre-history but by composition and external parameters.

From the point of view of their origin both groups dependent the initial crystal state. The first group is combined by means of nonequilibrium elements of its state. The second one is combined by the interatomic interaction and by the local order.

1. NONEQUILIBRIUM MELTS

The interest to these systems is stimulated by following experimental facts:

- properties of molten samples of the same composition depend on pre-history (initial materials, heat speed and temperature);

THE EXPERIMENTAL PLAN FOR INVESTIGATION
FOR CONTRACT AJ-0147

INTRODUCTION

In scientific works describing two aggregate states of the condensed matter, namely liquid and crystal states more often than not differences are enumerated. However while performing metal alloys melting it is important to prove genetic connection between solid and liquid states. One should reveal the common features of these two aggregate states that come next each other on the temperature scale.

Investigation of the structure and properties of melts is the key problem among the mentioned above. Melts, as any other thermodynamic systems, should be divided in two groups:

- NONEQUILIBRIUM, i.e. preserving some features of structure of initial solid phase for some time;

- EQUILIBRIUM, which structure and properties are determined not by pre-history but by composition and external parameters.

From the point of view of their origin both groups dependent the initial crystal state. The first group is combined by means of nonequilibrium elements of its state. The second one is combined by the interatomic interaction and by the local order.

1. NONEQUILIBRIUM MELTS

The interest to these systems is stimulated by following experimental facts:

- properties of molten samples of the same composition depend on pre-history (initial materials, heat speed and temperature);

- these melt properties are time - instable;
- non-coincidence of properties while heating and subsequent cooling.

The process of relaxation of nonequilibrium states takes a great time and very often METASTABLE states are fixed. These metastable states cannot be destroyed without external (thermal or mechanical) excitation. The most simple way to destroy they are heating up to some fixed temperatures, which is individual for each alloy.

Such a threshold shows rather KINETIC than diffusion mechanism of that process. More often the particle isolation from non-equilibrium formation is limited rather than particle migration and this takes high energy activation.

For example, it is known that such a regime is revealed for graphit suspension in molten Fe - cast iron; silicon drops emulsions in aluminum - silumins; mutual emulsions of tin and lead - solders; melts with remained atomic associations (non-equilibrium clusters) of carbides, silicides, oxycarbides, intermetallic compounds type and the other formation, that are inherent in the solid phase of charge components. The nature of metastability in polycomponent system is the problem to be solved. Now it is evident that solidification from metastable states leads to instability of structure and properties of solid samples. This influences the properties of the liquid received for some time while re-melting.

Thus, the fundamental properties and structure investigations of metallic melts have resulted in creating a new applied trend: THE DESIGNING OF THE RECOMMENDATIONS FOR THE EQUILIBRIUM MELT PREPARATION AIMING AT INCREASING AND STABILIZATION OF METAL QUALITY.

In a well-prepared melt, there must not be any traces of

prehistory and it must be in equilibrium, i.e., homogeneous under the given conditions, it must to have the maximum possible amount of homogeneity. The microinhomogeneity, existing in such a melt is determined only by the differences in the interactive energies of the component particles, in other words, by their nature. First of all scientifically based method of equilibrium melt preparation offers to establish temperature regime of melting. This task is done by studying in the temperature dependences of some liquid alloy properties.

The polytherms of properties of multicomponent melts extremely differ from the polytherms for simple metals. They are, as a rule, never smooth and moreover linear. For each steel composition the temperature dependences of properties have their own characteristic forms, which are caused by the chemical composition, starting materials, and the specificity of the production process.

The principal features of the properties of polytherms of the industrial melts are the HYSTERESIS (deviation between the heating and cooling branches) and DISCONTINUITIES (jumps in the property derivatives vs temperature). The presence of hysteresis indicates irreversibility occurring during the heating process and disappearance of nonequilibrium formations inherited from the solid state. The discontinuities suggest nonmonotonic behavior and sometimes jumps occur in the transition process of the system to the equilibrium state. The conversion of the melt to the equilibrium state takes place, above all, during heating to certain temperatures, called the CRITICAL temperatures t_c . Upon attaining them, the energy of the thermal motion of the particles in the melt becomes comparable to the bond-breaking energy of the strongest interatomic interaction in the nonequilibrium atomic clusters. The

heat motion destroys clusters, the melt loses its heredity.

Combined analysis of data on the structure and properties of the steels and alloys in the liquid state as well as the revelation of the types of the structural rearrangements in the melt and their influence on the structural formation process during crystallization enable us to thoroughly perfect the melting technique named MELT PREPARING technology. This technology consists in choosing optimum time-temperature regimes of melting, alloying, modifying and pouring.

3. EQUILIBRIUM MELTS

One should take into account some cases of non-equilibrium melt states and therefore the properties and the structure of subjects of fundamental researches of states should be studied in detail. Without this information it is impossible to realize the peculiarities of the structure and evolution of the non-equilibrium system.

In our case some features of electron structure of the alloys of the Fe, Ni and other 3d -transition metal should be taken into account. The existence of d - level near s - level provides the indecisive behavior of d - electrons that can behave both as conductive and localized ones while forming a condensed body.

That is a matter of a variety of interatomic forces and bonds, which is displayed by Fe and Ni in different chemical compounds. The character of these forces depends on the chemical diversity of atoms of alloyed elements, specific atomic volume of substance, temperature and pressure. As can be seen from the phase diagrams, even small variations of typical admixture (O, C, N and others) concentration leads to some essential changes in areas of existence

of certain phases, and new thus phases can occur.

In metallic alloys electron structure does not essentially change at raising temperature and transferring. This thesis can be proved by experimental measurements of magnetic susceptibility, electroconductivity, density and other properties connected with peculiarities of local system order. Therefore the liquid preserves its ability in transition metal atoms for forming bonds of different compounds as well as in their changes due to the actual conditions of melt existence. After melting the role of thermal motion raises. However the strong interatomic bonds, their specific features intensity can greatly influence the atomic order and melt properties. As was proved by our experiments this order is displayed even at rather high overheating above the liquidus temperature.

The melt inherits the peculiarities of interatomic interaction and the local order of initial solid metal to the same extent as the order stability of some elements in the atomic order does (this depends on temperature and strength of bond types). So after melting, system with different types of bonds preserves the ability to change structure of local order. Although these structure modifications take place inside the same phase, they have some features that remind of polymorphic transformations. Structural changes proper are felt much weaker than in solid states and occur mainly within final temperature intervals. However, structure - sensitive melt properties can undergo considerable anomalies.

We should like to point out that structural changes in the equilibrium matrix can quickly stimulate diffusive movement of atoms and solution of non-equilibrium microheterogeneities according to solid state physics. It is quite possible that approximate quantities of the first critical temperature for some alloys with

ferrous base (as well as with nickel) might be explained by the above mentioned. As a result of imposing such structural alteration, the solidification condition of preparing melt can be radically changed.

In addition to the above mentioned we would stress that concentration dependencies of the equilibrium melt properties rather often coincide with similar dependencies for crystal samples. This confirms the identity of this impurity influence on structure and properties of the solid and liquid phases. The models for solid alloys developed suppose formation of the so-called "grouping order" (cluster) influenced by the atom of the admixture and can be used for the liquid states as well. Here the percolation theory promises good results both for the qualitative and quantitative description of concentration regularities in liquid and solid phases.

PLAN OF INVESTIGATION

1. The investigation of temperature dependencies of kinematic viscosity, density, surface tension, electrical resistivity of the some specimens of Alloy In 718 in liquid state. The analysis of polyterm. The establishment of critical temperatures, that are respective to the transferring of the melt to the equilibrium state.

2. The investigation of the influence of melt condition (i.e. the maximum temperature of the melt heating) on the solidification process of the specimens of Alloy IN 718 by the method of differential thermal analysis. The reveal of the special temperatures of process.

3. The establishment of the oxygen and nitrogen content in the specimens by the method of melting in the reducing atmosphere on the apparatus "O-N mat 822". Analysis of the evologramm. The stydling of the melt condition on the form of evologramms and temperatures of the dissociation of oxides and nitrides.

4. The investigation of the melt condition on the structure of the cast Alloy: the dendritic cell size, morphology and quantity of carbides of eutectic origin and eutectic γ - γ' -type, microhardness by the methods of quantitative metallography, for example by computer analazer of "SIAMS" type.

5. The establishment of the alloying influence (as a variant the maintenance of niobium and titan) on the physico-chemical properties of the spesiments of Alloy In 718 in the liquid state, process of it solidification and structure of the cast metal.

METHOD OF INVESTIGATION OF THE PROPERTIES OF THE LIQUID METAL

Kinematic viscosity (ν) will be measured by the method of trash of the crucible with the melt and electrical resistivity (ρ) by the contactless method of rotating magnetic field.

The surface tension of liquid specimens (6) will be studied by the method of the "big drop" in the helium atmosphere. Calculation of is performed by use the mass, shape, volume and area of liquid metal drop.

The temperature was measured by the tungsten-tungsten-rhenium thermocouple.

The investigation will be held in the temperature range from melting temperature to the 1800-1850°C.

BACKGROUND INFORMATION
PROVIDED BY CONTRACTOR
AJ 0147

MELTS

A translation of *Rasplavy*

July, 1989

Volume 2, Number 2

March-April, 1988

CONTENTS

Engl./Russ.

Quasicrystalline Long-Range Order of Molten Metals and Amorphous Alloys - Yu. V. Efimov and V. N. Dmitriev.....	101	3
Measurement of Thermal Diffusivity of Refractory Metals near the Melting Point - S. G. Taluts.....	105	8
A Comparative Method of Estimating the Viscosity of Molten Multicomponent Silicates - L. B. Bruk.....	110	14
Interratation between Liquid and Solid Metallic States - B. A. Baum.....	113	18
Thermo-Emf of High-Pressure Zinc and Cadmium Chalcogenide Phases - V. V. Shchennikov.....	127	33
Structure and Features of Mutual Solubility of Components in Stratifying Gallium-Based Melts - Ya. I. Dutchak, N. M. Klym, V. P. Gal'chak, and S. I. Mudryi.....	134	41
Systems with Upper Critical Dissolution Temperature at Pressures up to 200 MPa - M. Z. Faizullin and V. P. Skripov.....	138	46
Platinum/Molten-Alkali-Silicate (Borate)-Glass Interface. 2. Nature and Kinetics of Reactions at Potentials More Positive Than That of Reversible Oxygen Electrode - Yu. M. Tyurin, G. L. Gol'denberg, V. I. Naumov, and A. A. Borisenko.....	143	52
Impedance of Electrode-Molten-Carbonate Interface Under Reducing Gas-Mixture Atmosphere - A. B. Vandyshv and A. P. Chernov.....	150	59
Stability of Liquid-Electrode-Electrolyte Interface at Limited Depths of the Electrolyte and Metal - Yu. G. Mikhalev, L. A. Isaeva, V. V. Skripachev, and P. V. Polyakov.....	156	66
Electrochemical Complex UP1-PU-85K - A. V. Vasil'ev, E. A. Novikov, A. V. Ishutin, and Y. N. Shirshov.....	161	72
Synthesis of an Asymptotic-Program Model for the Control of Potentio- dynamics in Ionic Melts - N. F. Balakhonov, S. L. Gol'dshtein, and V. Yu. Turchik.....	166	77
Extremal Current Control during Electrolysis of Molten Titanium-Containing Chlorides - S. L. Gol'dshtein, S. V. Gudkov, V. E. Kuzema, G. B. Smirnov, and E. B. Solonin.....	170	82

The Russian press date (podpisano k pečati) of this issue was 3/16/1988.
Publication therefore did not occur prior to this date, but must be assumed
to have taken place reasonably soon thereafter.

INTERRELATION BETWEEN LIQUID AND SOLID METALLIC STATES

B. A. Baum

UDC 532.7:541.66:669.15

Experimental data on the properties of real, liquid, iron-based alloys are analyzed near the crystallization temperature. A strong effect of the features of the interparticle-interaction force in these systems on the structures in the liquid and solid states is noted. The properties on both sides of the melting range are ascertained to be close. It is thought that this is caused by the unique nature of the condensed state and is the basis for using the quasicrystalline model of the liquid structure while studying the problems of interaction between the properties of the solid and liquid.*

1. Nonequilibrium States of Molten Metals. The experimental investigations of properties and the structure of liquid metals and alloys are divided into two directions closely interwoven with each other. One of them is caused by the traditional problems of natural sciences, i.e., by the attempt to produce new, deeper knowledge of the properties and structure of objects in a given aggregate state [1-6], and the other by the immediate practical requirements [7-10].

It is well known to the metallurgists (those engaged in production as well as researchers) that the properties of a steel of the same specification differ from melt to melt. For example, ingots or castings of one heat have a good surface and a small volume of shrinkage defects, more homogeneous structure and composition on the cross-section of the ingot, better mechanical properties, etc., whereas a metal of another heat has other, worse properties. Thus, a natural random scatter is observed in the properties from heat to heat with out-of-range data not only on the high side but also on the low side of magnitudes.

Usually two causes are considered to be responsible for such scatter. The nature of the first is related to fluctuations of the chemical composition including gases and non-metallic impurities. However, if we select heats with very close compositions, the second cause clearly becomes manifest, viz., the effect of the prehistory (charge materials and their melting conditions) of a solid metal on its properties. This cause also includes the so-called fact of "metallurgical memory effect." The structure of the starting cast irons affects the quality of steels melted in a Marten furnace, especially if the remelting temperatures are low. Remelting without boiling in a Marten salt furnace of a fine-grained scrap metal leads to the production of a similar fine-grained structure of the steel melted. Phosphorus introduced into the charge in the form of ferrophosphorus improves the liquid-state viscosity of the melt less than the phosphorus of the cast iron.

The data on "radiation memory effect" are interesting [11]. If irradiated and unirrad-

*E. A. Klimenkov participated in the preparation and discussion of the review given here.

S. M. Kirov Ural Polytechnic Institute. Translated from *Rasplavy*, Vol. 2, No. 2, pp. 18-32, March-April, 1988. Original article submitted February 27, 1987; revision submitted September 14, 1987.

Fig. 1. Temperature dependence of the surface tension σ of a commercial Fe, Cr, and Ni alloy. The dark points represent results of measurements while heating the sample and the light points while cooling it. The melt makes a transition to the equilibrium state only upon heating up to 1700°C (the data are from E. E. Tret'yakov).

irradiated samples of metals and alloys are melted and then slowly cooled, then the micro- and substructures of the metal that is first irradiated sharply differ from those of the unirradiated ones. The memory of the radiation is retained even after completely melting the sample.

Much data is also present in the literature about the role of a different kind of effect on melts. In particular, low-frequency (and also high-frequency) vibration of molten silumin leads to changes in its surface tension and strong grain refinement in the structure of the casts, i.e., to modification [12].

In the above examples, the starting charge materials and conditions of their melting influence, foremost of all, the structure and properties of the melt and, through these, the properties of the newly produced solid metal. This conclusion has been repeatedly verified by comparing properties of a liquid steel before crystallization and the properties of the solid metal formed. It is noteworthy that the higher the viscosity of a steel of a given specification, the better are the plastic properties of the sample that is solidified [6].

Let us consider some data on metallic melts that reveal the possible aspects of interaction and mutual influence of the liquid and solid states.

The above observations as well as facts of the time instability of the values of properties of the metallic melts indicate their ability to be in nonequilibrium states for long times [7]. The free energy of such a nonequilibrium system $F = U - TS$ exceeds its equilibrium value $F_{\min}$, whereas the entropy happens to be less than the equilibrium value $S_{\max}$. For example, suspensions of graphite in liquid iron, i.e., cast irons [13], emulsion of silicon drops in aluminum, i.e., silumins [8], and mutual emulsions of tin and lead, i.e., solder [14], melts with clustered atoms (nonequilibrium clusters) of carbides, silicides, oxycarbides, and intermetallic compounds of the intrinsic solid phases of the charge components that are retained in them have high stability [7].

Isothermal holding for 2-6 h does not always lead to an appreciable change in the properties of such systems. Transition to the equilibrium state takes place due to heating, even when it is short, above all at temperatures up to the peak temperature determined (see Fig. 1), or due to a certain mechanical effect of the type of ultrasonic vibrations, electromagnetic stirring, etc. This signifies that the relaxation time of the nonequilibrium states of multicomponent melts is very long. Metastable states are also found to exist, from which the system cannot spontaneously escape without thermal or mechanical action. Such states are generated, for example, in eutectic melts in the form of colloidal systems of a dispersion on the order of 100 Å [14]. The stability of such a microemulsion is related to the presence of a local minimum in the dependence of the free energy of the system on the thickness of the transition layer of the drop as well as on other factors. In this case, the decrease in the dimensions of the nonequilibrium drop is no longer limited by the bulk diffusion of the contacting phases but by the transport of the particles through the energy barrier on their boundary. In contrast to the usual diffusive dissolution, such a condition may be termed kinetic.

Thus, the structure of nonequilibrium melts, to which the majority of the commercial compositions apparently belong, depends not only upon the chemical compositions but also upon

their prehistory. Accordingly, all of its other properties, including the diffusive and re-active abilities of the elements, and the main things, mechanism and kinetics of crystallization, depend on the prehistory of the melt [7].

It is precisely the nonequilibrium of the melt that is the most important source of the correlations observed, which connect the properties of liquid and solid samples. Since for a complete occurrence of the processes of establishment of equilibrium in the melt, above all, sufficiently long time is required and additional effects are not rare, the degree of completion of the relaxation processes of the structure at the moment of crystallization can be different. The course of the structural change with temperature is reflected in its properties, whereas for crystallization from different states, it is reflected also in the properties of the solid metal.

Judging by the data of the experiments, the process of transition to equilibrium, which is accompanied by either the destruction of the nonequilibrium atomic clusters with strong internal bonds or by the overcoming of potential barrier by the particles, goes on nonmonotonically with temperature, and frequently occurs with jumps. Polytherms of properties are complicated in shape [7]. They reflect features that exist both as equilibrium component of the melt, e.g., of the equilibrium matrix, and the features of the processes of disappearance of nonequilibrium atomic formations. Systematic laws are revealed which relate the conditions of production of the equilibrium melt and its composition or the prehistory. In particular, it is found that some elements facilitate producing the equilibrium state when introduced into the melt, and yet others complicate this process [15, 16].

Thus, real multicomponent metallic melts are, as a rule, nonequilibrium systems, the structure of which is genetically related to the structure of the phase states of the solid materials. Revealing the systematic features of the changes in properties of the nonequilibrium melts has not only scientific but also applied significance. On the one hand, such investigations provide new information regarding the stability of the different states of the melts related to their prehistory and, on the other hand, they enable one to formulate the preparation conditions of the melts to crystallization with the object of stabilizing the required structure of the ingots and castings. For this purpose, the most important of all is to determine whether or not the alloy of a given composition and prehistory has the special temperature ranges within which the structural-relaxation processes are markedly accelerated.

It is natural that for the study and description of the systematic features of nonequilibrium systems, one has to have sufficient data on properties and structure of the equilibrium melts for solving the problems posed above.

2. Equilibrium States of the Melts. The structure of such systems is determined only by the composition, i.e., the nature of their atoms formed, and the state parameters, viz. T, P, and V. Due to the nonequilibrium between the interaction energies of different elements, the system can have a microinhomogeneous state. The most strongly interacting atoms form relatively long-lived but, of course, dynamic associates, which are termed groupings, clusters, or complexes. Their formation decreases the internal energy of the system. The equilibrium volume distribution of all types of clusters increases entropy. As a result, the free energy of such a system acquires a minimum value.

Fig. 2. Effect of vanadium on the viscosity η of liquid iron (1) and the microhardness H_{μ} (2) of solid iron (the data are from I. N. Igushin).

Fig. 3. Effect of carbon on the magnetic susceptibility χ of liquid (1600°C, curve 1) and solid (1200°C, curve 2) iron (the data are from V. E. Sidorov).

Let us turn to dilute solutions. The interest in them is related to the fact that at present there are metals available on a commercial scale that are well refined from impurities, such pure metals include the ones that are most widely used, viz., iron and aluminum. It is also important to know how the residual impurities influence the properties relative to those of pure metals. Thus, the problem of finding the optimum concentrations of microalloyed and modified additions comes in.

In describing the properties of such solutions in the literature, for a long time experimental data have more and more frequently appeared indicating the extremal or even oscillating nature of the isotherms of their properties [7, 10, 17-22]. One, two, or three oscillations are usually observed (Figs. 2-5). It is remarkable, for example, that, in general, an extremum appears at an impurity concentration corresponding to its solubility limit in the solid state. But oscillations in the properties are also observed in the solid-solution region.

The nature of the first oscillation (maximum or minimum) depends not only on the nature of the solvent and the solute but also on the property being studied and, what is very important, on the degree of purity of the solvent. For example, upon adding a soluble element to very pure iron, its viscosity decreases at first, which leads to a minimum in the isotherm [6]. If the sample contains impurities, particularly oxygen, then the introduction of this element increases the viscosity [22]. In such a case, the isotherm begins as though from the position of the first minimum, i.e., the first descending branch of the isotherm cannot manifest itself in such an experiment.

It should be especially emphasized that isotherms of magnetic susceptibility, optical constants, and other properties of alloys are identical on both sides of the melting range [20-24]. Once again, this confirms the notion of Ioffe and Regel' [2] regarding the absence of any principal difference in the electrical properties of solids and liquids and regarding their controlling role in the transport processes of charges of the short-range-order atoms of the metallic system. On the other hand, such experimental results demonstrate that interatomic correlations are retained at the level of short-range order even after the melting. In particular, this refers to alloys of iron with oxygen, carbon, chromium, nickel, and other elements.

We note that such an oscillatory nature of the isotherms was discovered a very long time ago in the solid state [25]. The reason given by the model for the solid alloys, which assumes the formation of the so-called "ordered domain" (essentially, the same "cluster") under the action of impurity atom, is fully applicable also for the liquid state. The corresponding calculation method of this model enables us to estimate the sizes of such clusters [20, 24]. Percolation theory gives values that are in good agreement with these estimates [24].

What concerns the properties of the concentrated, equilibrium melts is that the correspondence of the isotherms of their phase diagrams was discovered long ago and has been confirmed by all the later investigations [1, 24].

Fig. 4

Fig. 5

Fig. 4. Effect of oxygen on the electrical resistivity ρ of liquid (1600°C, curve 1) and solid (1200°C, curve 2) iron [20].

Fig. 5. Effect of chromium on the thermal coefficient of electrical resistivity $\partial\rho/\partial t$ of solid (1) and liquid (2) iron [24].

Fig. 6. Magnetic-susceptibility (χ) polytherms of iron containing 0.002 (1); 0.016 (2); and 0.035 wt. % oxygen (3) [21]. The dark points indicate heating and the white ones cooling.

Let us examine the features of polytherms of equilibrium metallic melts. Recent discussions on structural transitions in metallic melts [26, 27] have shown the main experimental fact: different kinds of features (jumps, bends, and scatter of the experimental points) are detected on the polytherms of their properties in a narrow temperature range. It is not possible to ignore them. The instability of the effect from experiment to experiment up to its disappearance in some cases indicates the presence of a potential barrier during a discontinuous restructuring of the melt structure, small driving forces of this process, and, accordingly, the kinetic difficulties. From above, the strongest effects are found to be due to the experimental conditions and the sample composition [26].

For example, it is well established that an anomaly on the magnetic-susceptibility polytherm of liquid iron detected 30 years ago [13] is seen only in samples with very low oxygen contents. Increasing the oxygen concentration in iron from 0.001 to 0.02 wt. % shifts the anomaly to a region of higher temperatures and decreases the jump in the magnetic susceptibility to its complete disappearance (Fig. 6). The same was confirmed by investigations of viscosity as well (Fig. 7). Polytherms of aluminum also have a complicated nature (Figs. 8 and 9). Other impurities, both in pure iron and aluminum and in that alloys based on them, influence the position and magnitude of the discontinuous changes in the properties, each according to its nature. (Here, it is appropriate to emphasize that there are simply no absolutely perfect and perfectly homogeneous samples of metals. Therefore, any sample must be regarded as a strongly dilute solution of impurity elements in the solvent.)

X-ray-structural analysis demonstrated that, at the temperature of the anomalies iron (see Figs. 6 and 7, polytherms 1) and its alloys, particularly the nickel alloys, undergo a structural transition, which is accompanied by a spontaneous, discontinuous jump in the most

Fig. 7. Polytherms of the kinematic viscosity ν of iron containing 0.002 (1); 0.004 (2); 0.006 (3); 0.01 (4); and 0.02 wt. % oxygen (5) [22]. The experimental points were obtained while heating the samples.

probable interatomic distance by 1.5-2.0% [6]. Without dwelling on the details of its nature, viz. whether it is isomorphous or is related to some kind of specific change in the short-range-order structure, let us look at the following important circumstance.

Upon heating an equilibrium, metallic melt, its structure (we will call it low-temperature structure) can discontinuously transform into a high-temperature structure. The latter is capable of supercooling to the crystallization temperature. Thus, a melt can crystallize either from its low-temperature state or high-temperature state. In the latter case, the chemical and physical homogeneity of the solid metal substantially increases [7]. As an example, we will cite here the data on the commercial alloy 52N [28]. An anomaly is detected in the properties of the melt at 1620°C in the form of a jump in their values. Upon attaining the above temperature during the course of heating, a hysteresis arises in the properties. Upon melting in a vacuum-induction furnace, the increase in the temperature is accompanied by a decrease in the oxygen content in the alloy although beginning with the temperature of the anomaly, its increase is observed (Fig. 10). Also other properties of the melt and process deteriorate during this process. It was determined that the optimal melting temperature of the alloys 52N is a little bit above the temperature of the anomalies. The high-temperature structure of the melt supercools very well. As a result, under the conditions employed only on account of introducing the new melting-temperature conditions, it was possible to decrease the oxygen and nitrogen concentrations in the melt, as well as to decrease the amount of the deoxidizer introduced and the content of nonmetallic inclusions. The shrinkage cavity and shrinkage porosity decreased, the zone of the columnar crystals shrank, the technological ductility increased, and the macro-, micro-, as well as substructures improved. The magnetic properties approached some of the world's best values in practice for such alloys.

Thus, the nature of the concentration changes of the properties of the equilibrium metallic melts agrees with similar dependences for crystalline alloys. This indicates the similarity between the mechanisms of impurity effects studied on the structure and properties of the solid and liquid phases. An analysis of the polytherms of the properties demonstrates that melting of the metallic alloys is not accompanied by a significant amount of reconstruction of the electronic structure and the nature of the interatomic interaction [20, 21, 24]. Moreover, discontinuous structural changes can take place upon heating the melt.

Fig. 8

Fig. 9

Fig. 8. Polytherms of the kinematic viscosity ν (1) and density d (2) of liquid aluminum [27]. The dark points indicate cooling and light ones the successive heating.

Fig. 9. Polytherms of the emf of the galvanic cell for liquid aluminum characterizing the solubility of oxygen in it [27]. The dark points indicate heating and the light ones cooling.

Having completed a brief review of the experimental information, let us turn once again to the nonequilibrium melts. Sometimes, the polytherms of their properties have a very complicated shape mainly generated by the breakdown processes of the nonequilibrium clusters. Judging by the experimental data, these processes principally have a nonmonotonic, discontinuous character. Apparently, they can be stimulated by structural transitions in the equilibrium matrix, which (as it has been demonstrated in solid-state physics) sharply increase the diffusive mobility of the atoms.

When nonequilibrium states are generated, the optimal melting temperature seems to be the so-called critical temperature, heating up to which ensures a complete transition to the equilibrium state. Attainment of this temperature during melting leads to stabilization and because of the decrease in the scatter to improvement in the properties of the solid metal [7].

3. A Molecular-Dynamics Model of the Structure of Real Metallic Melts. Let us distinguish three [3, 4, 29] of the recently published studies.

In the first two of these studies, ways of describing the structure of liquids have been given and the fruitfulness of its modeling has been established. In the third study [29], some results of the computer-simulation "experiments" are analyzed in detail and this approach is offered as an "unpreconceived" one for studying the liquid always and under any condition that, in principle, contrasts the liquid and solid states.

Recognizing the directions of investigations of the studies cited here by the selected authors as generally promising, we assume that further interest in studying the liquid state, particularly modeling, is related to the following circumstances:

- 1) the liquid phase is a form of existence of the condensed state;
- 2) specific features of interparticle interactions in the real liquids play a certain role in forming the structure and properties.

The authors of the programmed studies [3, 29] as well as many other investigators [30] have mainly paid attention to the so-called simple liquids, i.e., systems of identical particles with dipole-free, spherically symmetric interaction. This is very convenient for analyzing the model. However, the conclusions arrived at while investigating similar systems are practically inapplicable to real liquids in the preliquidus region of their existence and do not have sufficiently predictive capability even for liquid inert gases, which correspond most to the characteristics of the model used.

Experiments of the type performed by J. Bernal on the compression of plasticene spheres actually reveal the structural features of only a dense compressed gas above the critical temperature, where the repulsive forces predominate over the attractive forces. Since this model does not take the interatomic attractive forces into account and cannot explain the transition from the liquid to the solid state, its applicability to a description of the structure of liquids is very controversial. At temperatures near crystallization or after

Fig. 10. Effect of the heating temperature of the commercial liquid alloy 52N in the vacuum-induction furnace on the oxygen and nitrogen contents in it [28].

the melting of the substance, the application of this model is incorrect in its systematic nature because here an insurmountable barrier artificially comes in between the two manifestations of the condensed state.

Apparently, even in other similar cases (some computer models, hard spheres, etc.), underestimating the restrictions of the starting models is capable of attributing inappropriate properties to a liquid.

At the same time, the facts indicate that along with those properties that are opposite between the liquid and solid states from one another, this state is inherent too and with surprisingly similar properties [31]. It is very noteworthy that the closeness observed between some properties increases several times when both varieties of the condensed state are compared under close conditions of existence, e.g., in narrow temperature ranges on both sides of the melting point, but not when the liquid is considered near the critical temperature, whereas the solid is considered near the absolute zero of temperature.

The experimental features of isotherms and polytherms of properties of real melts based on iron described in sections 1 and 2 demonstrate that these systems are not, in principle, simple liquids after layer separation. Changes in the spherical interparticle interactions in them that are caused, for example, by the introduction of impurities or heating up to quite specific temperatures exert a strong influence on the macroscopic properties and, of course, on the structure of the melt.

The question arises then as to what model concepts can adequately describe the structure of a melt, which has the aforementioned features, and is it correct to consider the interrelationship found in the experiments between liquid and solid states of the same real substance? In our opinion, the most complete answer to the problem is the quasichemical model of the microinhomogeneous structure of liquids, which is a result of development of the views of Stuart, Frenkel', and Eyring [6, 7].

The model essentially consists of the following. The melt is composed of extended regions (cybotaxes or clusters), the atomic arrangement inside which is distinguished by a certain order (short-range). Owing to relatively strong thermal motion of the particles, the clusters do not have any clear boundaries. The predominant atomic coordination is continuously replaced by other arrangements as the distance from the core of the cluster increases. For the same reason, the lifetime of the clusters is limited and depends on the energy of the chemical bonds in them as well as temperature.

Above all, the structural order of the liquid is characterized by the quantitative parameters of the first coordination spheres, viz., by the most probable shortest distance r_1 and the number of the next-nearest neighbors Z_1 (sometimes the latter is also considered from the next-nearest-neighbor coordination spheres), as well as the average sizes of the clusters, i.e., the correlation radii. At the same temperature, clusters of two or more types or order can coexist simultaneously.

The types of ordering can sometimes be conveniently characterized from the point of view of their qualitative changes during interchange of the composition or conditions of existence.

of the liquid in analogy with packing in hard states, i.e., basing on the numerical values of the parameters r_i and Z_i : bcc-like, etc. In this terminology, the model of a microinhomogeneous structure externally acquires the traditional traits of clusters. The presence of the corresponding microclusters in the liquid does not follow from this at all. In view of the ordering tendency, there is an ensuing symmetry of the force field of atoms, which compose a given liquid.

The quasichemical model of the microinhomogeneous structure of a liquid takes into account the following essential points:

- a) equality of two types of particle motion in the liquid, viz., vibrational and translational;
- b) a substantial role of the interparticle attractive force in forming the condensed state;
- c) the symmetry of the atomic force field, which does not undergo radical changes during melting in the majority of the metals [5];
- d) inequality of interaction energies of chemically unlike atoms in the case of binary or higher-component systems.

The last point is the basic concept behind the cause for the generation of clusters of different compositions and structures of dissimilar stabilities with time. With these considerations, one can define the structure of each liquid alloy more precisely and, in principle, distinguish a given variant of the microinhomogeneous structural model from its other variants, viz., the models of various structures [32], interacting spheres [19], the quasicrystalline model [33], etc.

The aforementioned experimental facts indicate that the most stable clusters are formed by the most strongly interacting components. This variant of the microinhomogeneous structural model is also termed quasicrystalline precisely in this sense.

These days, attempts are being made to quantitatively take into account the notions of the inhomogeneous, structural model in calculating the properties of real systems. The different variants of the cluster-component method [34], incorporation of the concrete features of the short-range order of the melt [35], and some others can be included among them. However, in the majority of the cases, it is most convenient to use these notions tentatively for a qualitative understanding of the phenomena that take place in the complex melts. In this regard, the development of a structural model of a specific complex melt requires studying all its structure-sensitive properties as well as the information on the effect of the conditions of preparation of the melt on the structure and properties of the solidified metal [7, 36, 37].

Let us briefly examine the course of arguments in the case of X12 steel as an example [7]. Investigations of its properties in liquid and solid states demonstrated that heating to 1640-1670°C leads to hysteresis of the kinematic-viscosity polytherms. The magnitude of viscosity of the melt turned out to be higher during cooling than during heating. The density of the melt before crystallization increased as a result of the above heating and the electrical resistivity decreased, but the coordination number increased according to the x-ray-diffraction analysis. All this indicates the occurrence of an increase in the homogeneity of the melt.

Studies on the effect of the melt temperature on the structure of the cast X12 steel revealed the following. The dendritic and eutectic structures, which form during crystallization of a melt that was superheated before to the critical temperature of the melt, are very fine. The eutectic in such a steel enriched in chromium is distinguished by the predominantly rod shape of the eutectic carbides and has a high thermal stability. The primary dendrites are enriched in carbon and depleted in chromium. The mechanical and technological properties of the steel improved due to this reason.

A combined analysis of the structural data and the properties of the steel in liquid and solid states using the information on the diffusion coefficients of the components in the melt and features of the crystallization of Fe, Cr, C-alloys that were close in composition to the X12 alloy enabled us to refine the transitions occurring during heating and cooling of this liquid steel. Near the starting temperature of the crystallization, it consisted of microscopic regions, the atomic coordination in which was close to the corre-

sponding atomic coordination in alloyed austenite (metallic matrix) and carbide-like M_xC microclusters where the M's are iron or chromium atoms interacting with the carbon atoms surrounding them and x is the number of atoms in a cluster. Increasing temperature led, above all, to the usual reversible refinement of the cluster structure of the melt, in which the fraction of the carbide-like microclusters decreased. Heating above 1640-1670°C gives rise to a strong decomposition of these clusters with the breakdown of, foremost of all, the weak Fe-C bonds themselves. The latter transition happens to be irreversible under the given conditions. On the one hand, it leads to increased coordination number, density, viscosity, and thermal diffusivity (apparently, it is related to the decrease in the degree of localization of electrons in the melt) and, on the other hand, the diffusive mobility of chromium atoms increases, which enter now into the small clusters. The consequence of such a transition is that carbon concentration increases in the metallic matrix of the melt and, subsequently, also in the primary dendrites of the solidified steel. This is also the reason for the decrease in the volume fraction of the eutectic carbides. Higher thermal conductivity of the melt promotes refinement of the primary dendrites, whereas increasing chromium concentration in the eutectic promotes refinement of the eutectic carbides.

Combined analysis of data on the structure and properties of the steel in liquid and solid states as well as the revelation of the types of the structural rearrangements in the melt and their influence on the structural formation process during crystallization enable us to thoroughly perfect the melting technique of steels, particularly in developing the optimum temperature-time conditions. For example, for the X12 steel, we succeeded in developing a condition, melting under which produced 7% increase in the output of the usable metal at a higher level of service properties of the deformed steel.

The quasichemical model of the microinhomogeneous structure of the melts corresponds to the aforementioned principles (condensed state, consideration of the specific properties of the interparticle-interaction forces) and happens to be most acceptable in solving problems of bonding and mutual influences of the properties of the liquid and solid states. In this case, the main thing is precisely the commonality between the structures of the liquid and the solid and not their differences. It is unacceptable to go about solving such problems based on models in which a fundamental contrast between a liquid and a solid is built in from the very beginning.

The question is on what is the commonality between the solid and liquid phases of the same substance based. An equivalent question is: what does a unit of the condensed state consist of? Any state of a microscopic body is a sum of the competition between the interparticle forces and thermal motion of the structural units composing this body. The specific features of the condensed state, which are in contrast to those of a gas, consist of the fact that the interparticle interaction dominates here over the thermal motion since the reverse picture holds in the gaseous state. In the absence of any external restrictions, both liquid and solid bodies easily retain their integrity and constant volume. Moreover, interparticle forces qualitatively and almost quantitatively remain identical on both sides of T_m . This is indicated by small qualitative changes at T_m of the electronic [20-23] and phonon spectra (see [30, pp. 195-240]) of molten transition metals. Moreover, in a metallic liquid and in a solid metal, the structural units are essentially the same, viz. the same atomic shells and free-electron quasigas, but in the gas phase (metallic pairs), the structural units are altogether different, viz. free atoms.

Thus, a unit of the condensed state involves a substantial role of the very same interparticle attractive forces in all temperature ranges of existence of this state. What concerns the melting point is that here only the ratio of the average energy of thermal motion to the activation energies of some relatively displaced particles changes. Retention of the effect of the interparticle forces and their concrete specifics (e.g., the type of chemical bonds) on the mutual position in space of the neighboring atoms remains an important factor for the formation of the structure and properties of the melt at a relatively small superheating over T_m .

It is very complicated to take into account the specifics of the interparticle forces mathematically while describing the structure of a real liquid, and it is practically impossible to do so at the present stage of the investigations. One reason for this is that it is difficult to select a "zeroth-order approximation." As a half-measure, we can also resort to the notions of "quasicrystallinity." Here, we start out from the facts that, first of all, in a crystal, the specific properties and role of the attractive forces are maximum

and, second, during transition through T_m , these forces do not change qualitatively. It is very important to note a third circumstance, which is, unfortunately, absolutely ignored by the opponents of quasicrystallinity. The properties of crystalline real substances near T_m are formed not so much by their regularity as by the sets of different kinds of deviations from regularity that accumulate at this temperature (defects of different kinds, high diffusive mobility of the shells, etc.) [2, 7, 31]. Meanwhile, a large part of the physical properties (except mechanical) change very little during melting compared to those changes that take place in the crystalline phase while heating it from 0 K to T_m . In other words, by giving up the concept of "crystals" as only an attribute of the spatial regularity, we render it practically useless for a description of the properties of even a real solid state under the usual conditions and, at any rate, near the melting point. Conversely, assuming that the degree of regularity of a crystal is only a result of competition between the interparticle-interaction forces and thermal motion under specific temperature conditions, we acquire a deeper knowledge of the true nature of the solid and, in a broader sense of the word, of the condensed state and, of course, also of the nature of the liquid.

Of course, in a typical solid at low temperatures, only which are essentially considered in traditional solid-state physics, the regularity is very high, which thus as well as for the original reason and completely ignoring the specific nature of the interparticle interaction enables one, in many cases, to satisfactorily describe the physical properties of the object.

Thus, for an understanding of "quasicrystallinity" as an idea of the principles of model description of the liquid state, regularity, which is so widespread, is not essential. It cannot be observed at all or can be observed as some "vestiges of regularity" depending on the degree of superheating above the liquidus. The main point is that "quasicrystallinity" is an indication of the nature of the interparticle-interaction forces of liquid and solid phases. The latter consist of two different kinds of a single condensed state of a specific substance.

From above, it follows that models of the liquid state can be divided into two large groups: quasicrystalline, in which the characteristics of the interparticle-interaction are the starting point for the considerations, and quasigas. The attractive forces are either completely ignored in them and then the existence of the liquid itself has to be secured by constructing some "external neighbor" (e.g., by assigning a packing-density coefficient) or the attraction is taken into account but only within the framework of a spherically symmetric pair potential of the Lennard-Jones type, which is certainly inadequate for a real liquid metal.

Without denying the usefulness of quasigas models to any extent, especially in describing properties of liquids obtained by means of compression of gases as well as high temperatures, it is necessary to admit that an "unbiased position" [29] does not solve or eliminate the problems in the state, which take the quasicrystalline approach.

What concerns such matters as the "atomic ordering of the fcc-type" and a "bcc-like atomic ordering" is that their application in describing the dynamic structure of liquids is no less sensible and competent (although, unfortunately, it is no more so either than the terms "icosahedron," "tetrahedron," "octahedron," etc.).

The usefulness of application of the quasicrystallinity concept in describing the structure of real liquids, especially of complex transition-metal based metallic melts, is beyond doubt at present. An evidence of this is the fact that within the framework of, e.g., the quasicrystalline model of microinhomogeneous structure of liquids, explanations are found for all the experimentally observed features of iron-based melts (see above). A similar interpretation of results obtained for samples of a number of steels enabled us to assert and realize the suggestions on optimization of their melting technique [7].

In conclusion, we touch upon the question regarding the possibility of a complete description of properties of a liquid of a specific chemical nature in all regions of its existence (see also [30, p. 135]).

A characteristic feature of the liquid state is the fact that, by occupying an intermediate position between the ordered crystalline and disordered gaseous states, it retains a number of features, which tie it to both states. It is very important that the specific state of these different kinds of features is very mobile and strongly depends upon the conditions of existence of the liquid.

The physical basis for the contradictory nature of the liquid is the equally justified coexistence of the vibrational and translational motions of atoms in this state of the substance. In the quasigas models, ultimately, the translational displacements of atoms are fully taken into account, and in the quasicrystalline models, the vibrational ones are fully taken into account. Therefore, as the melt is heated and the contribution by the translational displacements increases more and more, the adequacy of the quasigas models improves. Conversely, upon relatively small superheats above the melting point, the quasicrystalline models become more adequate because the role of the vibrational motion of the atoms plays a strong role. A complete description of all the properties of a melt in all regions of its existence requires a combined consideration of the results of both the approaches, which are contradictory in their essence, in the spirit of Niels Bohr's complementarity principle (in analogy with the description of electromagnetic radiation in the wave-mechanical and corpuscular models, the role of which decreases with increasing wavelength).*

Indeed, both quasicrystalline and quasigas models are mechanical forms (e.g., a system of hard spheres) of a phenomenon, the real subject matter of which belongs to the microscopic world, viz., the atomic-molecular systems. The hamiltonian of the quasigas model is, in principle, the kinetic energy whereas the hamiltonian of the quasicrystalline model is essentially related to the potential energy of the system. Since in quantum mechanics, which provides an adequate theory for the atomic-molecular systems (clusters are exactly such objects), the potential- and kinetic-energy operators do not commute, the quasigas and quasicrystalline forms of these objects are complementary to each other.

CONCLUSIONS

1. Real (i.e., with certain impure compositions obtained by melting a specific charge held in the liquid state for a finite time), multicomponent, metallic melts are primarily nonequilibrium systems. Their structure is genetically related to the structure of the phase components of the starting solid materials.
2. The forms of isotherms of equilibrium metallic melts are identical on both sides of the melting range. This indicates the identical nature of the impurity-effect mechanisms on the structure and properties of solid and liquid phases and about the retention of the interatomic correlations at the short-range-order level after melting.
3. An analysis of polytherms of properties in the crystal-liquid phase-transition region shows that melting in metallic melts is not accompanied by a substantial restructuring of their electronic structure or interatomic interaction. While heating the melt, discontinuous structural changes can take place in them.
4. The present new approach to the problem of the liquid state structure of a real substance cannot be abstract. It must be based on experimental data and take into account the specific conditions for the existence of a real liquid, its prehistory, as well as the main objectives of the investigation.
5. While investigating aspects of interaction between solid and liquid phases of the same substance, especially of a complex nature, a basis for the study (including modeling) of the melt structure near the crystallization temperature can be the concept of the condensed-state units. It involves the concept of retention of the specific properties of the interparticle-interaction forces and their substantial role along with that of thermal motion in forming the structure of the system in every region of existence of the condensed state.
6. The embodiment of the concept of the condensed-state units in its application to a description of the liquid-state structure is the concept of "quasicrystallinity." Modern ideas regarding it consist of the recognition of retention of the nature of interparticle-interaction of forces (potentials) after melting, i.e., of the chemical characteristics of the different bonds, elements of directionality of the bonds, manybody-interaction effects, etc.
7. While studying questions of the interrelationships between the properties and structure of real iron-based melts, which differ in terms of their complex ratios of the localized- and collectivized-valence electrons, with properties and structures of the correspond-

*The idea of applicability of the complementarity principle in describing properties of liquids is due to E. A. Klimenkov.

ing solid substances, the quasichemical model seems to be the most satisfactory among the models of the inhomogeneous structural state of the melt. The usefulness of the latter is caused by its retention of information regarding the real bond between liquid and solid states and consists of the possibility of predicting the results of physicochemical effects affecting the melts and the properties of the final solid product.

8. Disagreement and even the incompatibility that exists at present between the liquid-state models is covered in the end in contradictions in the nature of the liquid, the atoms of which equally undergo the two different forms of motions, viz., vibrational (as in typical crystals) and translational (as in typical gases). The degree to which these various types of motion are taken into account can be used as a basis to classify all these models of liquids into two groups, viz., the quasicrystalline and quasigas. In view of the intermediate nature of the liquid state, other ("intermediate", typical liquids) models cannot, in principle, be ruled out.

9. Under specific conditions, description of a specific group of properties of liquids of the same chemical nature requires the application of either quasigas or quasicrystalline models depending upon exactly what is being studied. A complete description of the liquid-state properties is possible, owing to a fundamental contradiction in its nature, only by way of a joint application of the results of opposing approaches (quasigas and quasicrystalline) in the spirit of a general principle of complementarity.

LITERATURE CITED

1. N. A. Vatolin and É. A. Pastukhov, Diffraction Investigations of the Structure of High-Temperature Melts [in Russian], Nauka, Moscow (1980).
2. A. R. Regel' and V. M. Glazov, Systematics of Formation of the Electronic Structure of Melts [in Russian], Nauka, Moscow (1982).
3. Yu. I. Naberukhin, "What kind of structure do liquids have?", Zh. Strukt. Khim., 22, No. 6, 62-80 (1981).
4. V. A. Polukhin and N. A. Vatolin, "Modeling the structure and cooperative atomic movement in liquid and amorphous metals," Abstracts of Scientific Reports to the VIth All-Union Conference on the Structure and Properties of Metallic and Slag Melts [in Russian], Ural Scientific Center, Acad. Sci. USSR, Sverdlovsk (1986), Part 1, pp. 3-7.
5. A. V. Romanova, "Structure and Properties of Metallic Melts," in: Metals, Electrons, and Lattices [in Russian], Naukova Dumka, Kiev (1975), pp. 168-202.
6. B. A. Baum, Metallic Liquids [in Russian], Nauka, Moscow (1979).
7. B. A. Baum, G. A. Khasin, G. V. Tyagunov, et al., Liquid Steel [in Russian], Metallurgiya, Moscow (1984).
8. Yu. N. Taran, "Problems of the morphological analysis of eutectic alloys," in: Systematics of the Formation of Structure of Eutectic Alloys [in Russian], DMETI, Dnepropetrovsk (1986), Part 1, pp. 3-7.
9. V. Ya. Prokhorenko, Structure and Electrical Properties of Liquid Metals. Reviews of Thermophysical Properties of Substances [in Russian], IVTAN (TFTs), Moscow (1980), No. 6 (26).
10. G. N. Elanskii and V. A. Kudrin, Structure and Properties of Liquid Metals [in Russian], Metallurgiya, Moscow (1984).
11. Sh. Sh. Ibragimov, "Problems of radiation physics of low and medium energies," Izv. Akad. Nauk SSSR, Ser. Fiz., 43, No. 1, 16-31 (1979).
12. P. K. Mitra and I. N. Bhattacharya, "Studies on the effect of vibration on modification and surface tension of Al-Si liquid melts," Trans. Indian Inst. Met., 39, No. 2, 150-152 (1986).
13. A. A. Vertman and A. M. Samarin, Properties of Molten Iron [in Russian], Nauka, Moscow (1969).
14. P. S. Popel', "Phase transition or decomposition of metastable clusters?," Izv. Vyssh. Uchebn. Zaved., Chern. Metall., No. 5, 34-41 (1985).
15. G. V. Tyagunov, "Properties of metallic melts - basis of a new direction in technology," in: Experimental Investigations of Amorphous and Liquid Metals [in Russian], Ural Scientific Center, Acad. Sci. USSR, Sverdlovsk (1983), Part 2, pp. 124-126.
16. S. P. Burmasov, G. V. Burlaka, S. G. Bratchikov, et al., "Effect of elements on the nature of viscosity polytherms of molten iron," in: Experimental Investigations of Amorphous and Liquid Metals [in Russian], Ural Scientific Center, Acad. Sci. USSR, Sverdlovsk (1983), Part 2, pp. 81-83.

17. V. V. Pavlov, Solidification and Its Molecular Model [in Russian], Nauka, Moscow (1985).
18. P. P. Arsent'ev and A. A. Koledov, Metallic Melts and Their Properties [in Russian], Metallurgiya, Moscow (1976).
19. E. S. Filippov, "Theoretical principles of the structure of liquid metals," *Izv. Vys. Uchebn. Zaved., Chern. Metall.*, No. 11, 115-122 (1976).
20. V. N. Epin, B. A. Baum, G. V. Tyagunov, and E. A. Klimenkov, "Electrical resistance iron-oxygen alloys," *Izv. Vyssh. Uchebn. Zaved., Fiz.*, No. 12, 100-102 (1980).
21. V. S. Gushchin, V. E. Sidorov, and B. P. Gol'tyakov, "Effect of oxygen on the magnet properties of iron at high temperatures," *Izv. Akad. Nauk SSSR, Met.*, No. 3, 51-57 (1983).
22. Yu. A. Bazin, I. N. Igoshin, B. A. Baum, and E. E. Tret'yakova, "Kinematic viscosity of liquid iron-oxygen alloys," *Izv. Vyssh. Uchebn. Zaved., Chern. Metall.*, No. 9, 16- (1985).
23. K. M. Shvarev, B. A. Baum, and V. A. Kudryavtsev, "Effect of magnetic and phase transitions on the optical properties of iron," *Teplofiz. Vys. Temp.*, 23, No. 3, 429-499 (1985).
24. L. V. Govorukhin, E. A. Klimenkov, B. A. Baum, et al., "Electrical resistance of iron-chromium melts," *Ukr. Fiz. Zh.*, 30, No. 4, 534-536 (1985).
25. I. B. Borovskii and K. P. Gurov, "Theory of transition-metal-based solid solutions," *Fiz. Met. Metalloved.*, 4, No. 1, 187-195 (1957).
26. O. I. Ostrovskii and V. A. Grigoryan, "Structural transitions in metallic melts," *Izv. Vyssh. Uchebn. Zaved., Chern. Metall.*, No. 5, 1-12 (1985); No. 9, 132-141 (1986).
27. Yu. A. Bazin, V. M. Zamyatin, Ya. A. Nasyrov, and A. V. Emel'yanov, "Structural transitions in liquid aluminum," *Izv. Vyssh. Uchebn. Zaved., Chern. Metall.*, No. 5, 33 (1985).
28. V. N. Lapkin, G. N. Tyagunov, N. E. Bodakin, and B. A. Baum, "Effect of temperature-time treatment of the melt on the properties of the permalloy 52N," *Izv. Vyssh. Uchebn. Zaved., Chern. Metall.*, No. 1, 44-47 (1981).
29. V. P. Skripov and A. E. Galashev, "Structure of simple liquids," *Usp. Khim.*, 52, No. 176-185 (1983).
30. H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (eds.), *Physics of Simple Liquids*, North-Holland, Amsterdam (1986).
31. Ya. I. Frenkel', *Kinetic Theory of Liquids*, Clarendon, Oxford (1946).
32. T. S. Ree, T. Ree, and H. Eyring, "Fortschritte in der Theorie der Flussigkeiten," *Angew. Chem.*, 77, No. 22, 993-1000 (1965).
33. I. A. Novokhatskii and V. I. Arkharov, "Quantitative evaluation of the structural microinhomogeneity of liquid metals," *Dokl. Akad. Nauk SSSR*, 201, No. 4, 905-909 (1971).
34. A. N. Men', M. P. Bogdanovich, et al., *The Method of Cluster Components* [in Russian], Nauka, Moscow (1977).
35. M. S. Petrushevskii and P. V. Gel'd, "Consideration of the short-range order in calculating the activities of components of binary solutions," *Izv. Akad. Nauk SSSR, Met.*, No. 4, 67-72 (1973).
36. S. I. Popel', M. A. Spiridonov, and Yu. I. Maslennikov, "Structure of liquid metals," *Stal'*, No. 9, 17-21 (1981).
37. G. S. Ershov and A. A. Poznyak, *Microinhomogeneity in Metals and Alloys* [in Russian], Metallurgiya, Moscow (1985).

Project Title: Thermal Physical Properties of Liquid Metals
Principal Investigator: V. Zinoviev
Ural Mining and Geology Academy
Ekaterinburg, Russia
AM-7658

CLAUSE 1 - STATEMENT OF WORK

Tasks:

The Contractor shall:

1. Provide a report describing the testing apparatus and test procedure that will be used to measure the thermal diffusivity and enthalpy at ambient pressure of five (5) Sandia selected and provided Fe or Ni base alloys as a function of temperature from 100(C below the solidus temperature to 300(C above the liquidus point.
2. Measure the thermal diffusivity and enthalpy at ambient pressure of five (5) Sandia selected and provided Fe or Ni base alloys as a function of temperature from 100(C below the solidus to 300(C above the liquidus point. Measurements shall be made at 10(C intervals in the region between the liquidus and solidus temperature, and expanded intervals outside this range. Provide the test data and results.
3. Provide a final report analyzing the results of the test.

CONTRACTOR:

Ural Mining and Geology Academy

ATTN: Vladislav E. Zinov'ev

Kuibishev st.,30

Ekaterinburg, Russia 620219

Phone: 07 - 3432 - 226303

Fax: 07 - 3432 - 226679

Project Title : Thermal Physical Properties of Liqued Metals.
Test Apparatus and Test Procedure.

TASK 1

REPORT

Document No AM-7658

Document Date - October 10, 1994

Invoice in to:

Sandia National Laboratories

Supplier Services

For Contract No. AM-7658

P.O. Box 5130

Albuquerque, NM 87185

USA

FAX (505)-844-6504 for N.S.Davis

1. Introduction.

The thermal diffusivity and heat capacity of metals and their alloys were measured in a vacuum using a modified variant of the dynamical method of plane temperature waves in conjunction with fast heating of the sample [1-3]. The main idea of this method is the following. Combine heat flux consisting of linear-increasing up to $q+Vt$ and harmonical $q_m \cos \omega t$ components heats the plane parallel sample with thickness δ . The sample placed in vacuum is strong overheated regarding surrounding medium and the heat evolution from sample surface is achieved only by radiation. In such conditions the average temperature of the sample will constantly increase but temperature waves appear on its opposite surface:

$$\theta = \theta_0 \exp(i\omega t) \quad , \quad (1)$$

A temperature waves appeared and initial heat flux are phase shifted by angle φ . On the assumption that the amplitude of temperature oscillation created is small, the temperature dependence of investigation material thermophysical properties is weak and the radiation heat exchange effects weakly on the temperature wave propagation (for thin metals $B_1 = \varepsilon \delta T^3 / \lambda < 0.01$) the relation for φ and θ_0 determinating at average temperature during one period of modulation can be expressed as :

$$\varphi(T) = \arctg \frac{\operatorname{sh} x \cdot \cos x + \operatorname{ch} x \cdot \sin x}{\operatorname{sh} x \cdot \cos x - \operatorname{ch} x \cdot \sin x} \quad , \quad (2)$$

$$\theta_0(T) = \frac{q_m}{C_p \rho \omega \delta} \times \frac{\sqrt{2} \alpha}{\sqrt{\operatorname{sh}^2 \alpha + \sin^2 \alpha}}, \quad (3)$$

$$\alpha = \frac{2\pi\nu \times \delta}{\sqrt{a}}, \quad (4)$$

where a , C_p , λ - the thermal diffusivity, heat capacity at constant pressure, heat conductivity respectively; ρ - the density, ν - the frequency of temperature oscillations.

The numerical computer simulation of experiment conditions by means of finite-difference method shows that these equations operate well even near the phase transitions where strong dependence of thermal diffusivity is observed. Thus, at heat temperature ~ 1000 K/c, $\nu = 160$ Гц, $\frac{1}{a} \frac{\partial a}{\partial T} \leq 0.07$ $1/K$, $\frac{1}{C_p} \frac{\partial C_p}{\partial T} \leq 0.01$ $1/K$

the deviation of calculated values for φ and θ_0 from (2) and (3) doesn't exceed 3 %.

Except that, with the proviso that $\alpha \gg \pi/4$ the relation (2) can be written with high accuracy as

$$\alpha = \varphi - \pi/4. \quad (5)$$

Thus, measuring simalteniously φ , θ_0 and T and determining α with the help of φ it shall be possible to define a temperature dependence of C_p and a by means of relations (3) and (4). The temperature dependence of enthalpy is calculated as

$$H(T) = H(T_0) + \int_{T_0}^T C_p(T) dT, \quad (6)$$

where $H(T_0)$ - the enthalpy of research material at initial temperature T_0 .

2. Experimental apparatus.

The modify plane temperature waves method in conjunction with fast heating working out by us during 10 years was used in this experiment. Figure 1 shows the block diagramme of our setup for this purpose. A plane-parallel sample (1) placed into a vacuum chamber (2) is the anode of specific diode system. The cathode which was made of tungsten and built of plane Arkhimed's helix is heated by a power source (4). High temperature sample heating and creation of temperature waves in the sample are achieved by a high-voltage power source and modulator (5) controlled by a sound generator (6) and computer (7). Infrared receiver (8) transforms the varying heat radiation of the sample into electrical signal which passes through an amplifier (9) to digital amplitude-phase measurer controlled by computer (7). The average sample temperature was measured by thermocouple, the dynamical temperature - by micropyrometer (8) combined with photoreceiver (8). Processes of melting and sample shape changing are controlled by videocamera and monitor (11) for which current values of amplitude, phase and thermal diffusivity are fed. A heating is stopped automatically at visible changing of sample shape. The test of sample thickness and shape was conducted

after each experiment. Experiments in which the thickness was changed 2% more in comparing with initial one were neglected.

3. Investigations results of thermophysical properties of Fe-Ni alloys.

3.1. Alloys preparation.

Initial materials were standard high-purity iron B-3 (99.98 wt.%) and nickel H-0 (99.98 wt.%). Alloys were obtained by direct melting in vacuum furnace in pure-Ar atmosphere. After melting and cooling alloys were forged and then tempered for homogenization at 1450 K for 1.5 hours with follow cooling together with tempering furnace. Impurities contents was controlled by spectrometer "Hitachi". Contents of oxygen (O_2) didn't exceed 0.01 %, total impurities contents (O_2 , N_2 and C) didn't exceed 0.05 %. X-raying showed good coincidence of our alloys lattice parameters with known literatural data.

This article includes information about Fe-rich Fe-Ni alloys with Ni contents (wt. %) : 0, 1.0, 1.9, 3.0 (such alloys are marked a_0^{Fe} , a_1^{Fe} , a_2^{Fe} , a_3^{Fe} in Fig.2) and information about Ni-rich Fe-Ni alloys with Ni contents (wt.%) : 100, 89.9, 79.9, 50.8 (such alloys marked a_0^{Ni} , a_1^{Ni} , a_2^{Ni} , a_3^{Ni} in Fig.3 consiquently).

3. 2. The thermal diffusivity investigations results.

Parts of iron-nickel diagramme appropriated to investigated alloys are shown in Fig.2 ,3 . Perculiary points of Fe-Ni diagramme, binary areas and concentrations of studied alloys are also marked here.

The thermal diffusivity investigations results of Fe-Ni alloys near the melting point in solid and liquid states together with data

for pure Ni and Fe are presented in Fig.4 and 5 . Data for pure iron and nickel published earlier and our new data obtained for carrying out of measurements at temperatures 300 K higher than melting point are presented in this article. It seems new data confirm sufficiently well the preliminary one and coincide within 5 %. Our new results got the opportunity to conduct measurements at temperatures 300 K higher than melting point.

These results show that the thermal diffusivity is practically constant above melting point. Measurements getting at higher temperatures in liquid phase are made difficult because of processes dealing with change of sample thickness and effects of metal evaporation to vacuum. Minimums with navel in the middle of γ -phase are observed in Fe-rich Fe-Ni alloys. The thermal diffusivity depends only slightly on the temperature in γ -phase and in liquid state. It is of interest that minimum depth raises together with increasing of δ -phase concentration. Data offered were obtained at high frequency of modulation (approximately 30 Hz) and this fact deals with necessity of measurements in wide area of liquid state . Therefore effects connected with phase transition heat influence on thermal diffusivity weren't practically observed and anomalies $a(t)$ are blurred.

The thermal diffusivity minimum as indicated by Fe-Ni diagramme is also observed in two-phase area in Ni-rich Fe-Ni alloys. Its width and its position have a good correlation with the width and position of two-phase area. For example, the Fe +3% Ni alloy anomaly is narrower than Fe+ 1% Ni one . The thermal diffusivity for these alloys has only a weak dependence on the temperature.

Reference.

1. Zinov'ev V.E. Metals at high temperatures. Hemisphere publ. corp., N.-Y, -W -Phil- , 1989,247p.
2. Zinov'ev V.E., Taluts S.G. Phys. met. metalloved. 1985, v.59, N 1 , p.79 - 84.
3. Gorbатов V.I., Zinov'ev V.E., Taluts S.G. Teplofizika vis. temper., 1990, N 6, p.1105-1111.

Fig.2. Fe-Ni phase diagramme near the pure iron.

Fig.3. Fe-Ni phase diagramme near the pure nickel.

Fig.5. The thermal diffusivity of Ni-rich investigated alloys versus the temperature.

pure Ni - a_0^{Ni} ; Fe + 89.9% Ni - a_1^{Ni} ;
 Fe + 79.9 % Ni - a_2^{Ni} ; Fe + 50.8 % Ni - a_3^{Ni} .

Project Title: Step-by-step Deformation of Metal Alloys
Principal Investigator: Gregory Koval
Chelyabinsk State University of Technology
Chelyabinsk, Russia
AM-7659

CLAUSE 1 - STATEMENT OF WORK

Tasks:

The Contractor shall:

1. Provide a report describing the step-by-step deformation machine and the process that will be used for deformation.
2. Deform a 150mm diameter x 1500mm long bar of alloy, to be specified by Sandia, to an elongation of six (6). Heat treat the material to a Sandia specified heat treatment (solution, stabilization, and age), and characterize the microstructural and tensile properties of the deformed heat treated bar. Ship all of the deformed heat treated material to Sandia. Provide a video of the deformation process while the bar is being deformed.
3. Provide in report form, a metallurgical analysis characterizing the quality of this material and the raw ingot material, and list the properties of the deformed gamma1 alloy. This analysis shall include representative microstructures before and after deformation and tensile properties of material before and after deformation.

RUSSIAN FEDERATION
STATE COMMITTEE FOR HIGHER EDUCATION
CHELYABINSK STATE TECHNICAL UNIVERSITY

STEP-BY-STEP ROLLING PROCESS
AND STEP-ROLLING MILL

Contract AM-7659

Task 1

Principal Investigator :

A handwritten signature in black ink, appearing to be 'G. KOVAL', written in a cursive style.

G.KOVAL

Chelyabinsk

1994

CONTENTS

	Page
1. Basic features of step-by-step deformation process and step-rolling mill	3
2. Step-rolling mill RF 600	5
3. Rolling on the mill RF 600	13

Step-by-step deformation process and the step-rolling mill with rocking rolls developed at the Chelyabinsk State Technical University (CGTU)/1/ are used for metal deformation under Contract AM-7659. A commercial mill RF 600 built on the basis of these developments is installed at the Chelyabinsk Integrated Iron-and-Steel Works /2/.

1. Basic Features of Step-by-Step Deformation Process and Step-Rolling Mill

Characteristic feature of the step-by-step deformation process is formation of a transitional zone called deformation cone on a portion of length L of the billet 1 to be deformed (Fig.1) , where the cross-section is changing from the cross-section of the initial billet S_0 to the cross-section of the finished section S_1 . It offers a high elongation $\lambda = S_0/S_1$ per pass of the billet through the mill stand.

The step-rolling mill with rocking rolls has a mill stand 2 with a drive 3, a feeding device 4 and a receiving device 5.

Four rolls 6 mounted in the mill stand 2 on shafts 9 are linked to a fixed support 8 by means of connecting-rods 7.

During the rolling process the rolls 6 reciprocate along the billet 1 and rock simultaneously about the shafts 9. At each step of deformation, the shafts 9 travelling from the position O_1 to the position O (working travel), the rolls reduce the billet along the deformation cone. When the shafts 9 travel from the position O to the position O_1 the rolls revolve around the deformation cone without metal reduction (idle travel) and at the end of the travel they lose their contact with the billet. At the moment the billet is moved a feed step m in the

A - A

Fig.1. Diagram of the mill with rocking rolls

direction of the working travel of roll shafts and at the same time the billet is tilted by 45° about its longitudinal axis by means of the feeding or receiving device.

At the beginning of the rolling, the feeding device holds the billet by the tail end, feeds it and tilts it. To finish rolling the tail end of the billet, its holding and tilting is carried out by means of the receiving device, and its feeding is carried out by means of the feeding device.

2. Step-Rolling Mill RF 600

Kinematic diagram of the commercial mill RF 600 used for billet deformation under Contract AM-7659 is shown in Fig.2. The mill includes feeding device 1, receiving device 3, mill stand 2 and main drive 4. The feeding device is designed to speed up the feed of the billet to the rolls, to direct the billet along the axis of rolling when holding it by the tail end, to feed the billet in step-by-step mode of operation and to tilt it simultaneously by 45° when rolling the head end. The device comprises a carriage 5 mounted on guides 7 by means of rollers 6, the carriage to be driven by a direct-current motor 15, two worm reduction units and power screws 16 with nuts 17. The carriage 5 is connected to the nuts 17 by means of damping air cylinders. The carriage has devices mounted on it to clamp and tilt the billet and a pusher. These devices consist of a hollow cylindrical body 8 mounted on the carriage. Support 13 with tongs 9 is fixed at one end of the body 8 on the mill-stand side, and at the other end there is an air cylinder for tongs grip with a hollow rod 1 connected to the tongs 9. Air cylinder 11 with a pusher-ram 12 passing through the hollow rod 1 is attached to the air cylinder of the grip. Lever of the body 8 is hinged to the rod of the tilting air cylinder 14 mounted in the carriage.

Fig.2.Kinematic diagram of the mill RF 600

The mill stand has a roll housing 19, four roll assemblies, wedge-type roll-separating mechanisms 23 and roll-balancing mechanisms 24. Each roll assembly has a roll chock 25, a roll body 20 and an interchangeable working insert. Roll bodies are hinged to the brackets of frame 27 of the receiving device by means of bars 26. The receiving device of the mill holds the billet by the rolled head end, directs it along the axis of rolling and tilts it. The receiving device consists of a frame 27 with a hollow tumbling device 28 supported inside in bearings, the tumbling device having through holes for two pairs of gripping rollers 29 and 30 to be mounted there. Two rollers are spring-loaded, and the others are connected to the rods of air cylinders 31 and 32. For tilting the billet the tumbling device 28 is hinged to the rod of air cylinder 33 by means of a lever and the air cylinder 33 is rotatable mounted in the frame 27. The main mill drive designed to reciprocate the mill stand 2 has a motor 34, a tooth-type coupling 35, a twin gear transmission 36 with cranks 37 and connecting rods 38 connected to the roll housing.

The mill RF 600 is a part of the production line for working of high-alloy steels and high alloys. The line (Fig.3) consists of a pusher 1, transfer device 2 for billet transportation from furnace to the mill, step-rolling mill RF 600 3, lifting 4 and receiving 5 roll tables, cut-off machine 6, sliding stop 9, pusher 10 and pocket 8.

Photographs of the mill RF 600 are shown in Fig.4, 5 and 6.

Working tool (roll) /3/ of the mill RF 600 used for billet deformation under Contract AM-7659 is shown in Fig.7.

Fig.3. Equipment layout of the production line
for working of difficult-to-form steels

Fig.4.Step-rolling mill RF 600. Plan view

Fig.5.Step-rolling mill RF 600.Side view of the mill stand

Fig.6.Step-rolling mill RF 600. View of the mill stand on the feeding side

Fig. 7. Roll of the step-rolling mill RF 600 for rolling of rounds

Main specifications of the mill RF 600:

Distance between rotation axis of rolls	
and axis of rolling, mm	600
Size of initial billet, mm:	
diameter	150-200
square side	150-180
length	1500-2000
Finished section, mm:	
rounds	50-180
squares	50-125
Number of rolls	2-4
Stand travel, mm	580
Number of stand travels per minute	40-60
Advance per stand travel, mm	5-30
Mill stand drive power , kW	1700
Overall dimensions, mm	8420x12910x2700

3. Rolling on the Mill RF 600

The process of billet production on the mill RF 600 goes as follows. The heated initial billet is drawn by pusher 1 (Fig.3) from a continuous heating furnace on the platform of transfer device 2 and conveyed to the tongs 9 of the feeding device (Fig.2), then it is adjusted along the axis of rolling and clamped by tongs. After that the billet is fed to the mill stand 2. When the billet is approaching the rolls 20, the drive 15 of the feeding device is changed over to

feeding mode of operation, the drive 34 for reciprocating motion of the mill stand is started and the step-by-step rolling of the billet begins.

After every step of deformation, when the roll gap exceeds the height of the billet, the billet is moved for a feed distance and tilted by 45° by means of the air cylinder 14.

When approaching the rolls, the tongs 9 open. After that the billet is fed to the rolls by a pusher-ram 12, and it is held along the axis of rolling and tilted by rollers 29,30 and by air cylinder 33 of the receiving device respectively. The finished section is conveyed by roll tables 4 and 5 (Fig.3) to the cut-off machine 6, where it is cut to length, marked and packed.

REFERENCES

1. U.S.Patent 4,157,025. Method and Mill for Rolling Metal Billets. V.N.Vydrin, E.N.Berezin, V.G.Dryomin, O.I.Tishchenko, G.Z.Serebrennikov. Published Jun.5,1979.
2. I.A.Koppel, G.I.Koval, V.G.Dryomin a.o. (1992). Experimental-Commercial Step-Rolling Mill RF 600. Stal, No3, 46-48.
3. U.S.S.R. Inventor's Certificate No 1,537,336. (1990). Method for Step-Rolling. B.I., No3.

Sandia National Laboratories

P.O. Box 5800
Albuquerque, New Mexico 87185-1134

December 8, 1994

Prof. G.I. Koval
Chelyabinsk State University of Technology
16 Lenin Ave.
Chelyabinsk 454080
RUSSIA
FAX 01173512656481

Dear Prof. Koval

Re: Contract AM-7659

Thank you for your recent FAX. My response is as follows: I would appreciate it if you could use the Nickel Base Alloy labeled 1 in your FAX. We propose the following procedure for forging and evaluation:

Before forging, heat treat the material for 2 hours at 1090 ° C. Stop the forging operation before all of the bar is deformed so that the transition between the un-forged and forged bar can be examined. Section the as-forged bar longitudinally and send me one of the halves which includes the transition, a 250 mm long region of un-forged material, and a 500 mm long region of forged material. Use the other half of the bar for your metallurgical evaluation. Remember we will use this data to try to sell your process to US Industry.

Also, please provide the following information: forging temperature, transfer times from the furnace to the forging machine, and optical pyrometer readings during forging (both on die and off die).

My very best wishes to you and your team for a good holiday season!

Thank you very much.

Sincerely,

Frank J. Zanner

Distinguished Member of the Technical Staff

Copy to Nancy Davis

Вниманию господина
Равкина В.З.

Факс 122-77-36

Для господина ф. Заннера

Dear Mr. Frank Zanner,

We would ask you to confirm your consent to use our metal for step-by-step deformation under Contract AM-7659, namely one of then following alloys:

1) XH73МБТЮ(14%Cr; 70-73%Ni; 2%Ti; 0.7%Al; 2%Mo;
1.8%Nb; $\leq 4\%$ Fe; $\leq 0.08\%$ C).

2) XH30BMT($\leq 0.1\%$ C; $\leq 0.6\%$ Si; 14-16%Cr; $\leq 0.6\%$ Mn;
27- 30%Ni; 3-4%Mo; 4.5-6.0%W; 1.9-2.4%Ti; $\leq 0.015\%$ S;
 $\leq 0.02\%$ P; $\leq 0.5\%$ Al; $\leq 0.02\%$ Zr).

and to inform us of specified heat treatment conditions for the deformed material.

Please define more precisely the amount of the material to be shipped to Sandia, taking into consideration that the cost of one bar without its step-by-step deformation and heat treatment and expenses on its transportation to the USA including to the payment due upon completion of Task 2.

Yours very sincerely,

G. Koval

Project Title: Development of a Method of Growing Band-like Crystals of Molybdenum (Mo) and Tungsten (W).
Principal Investigator: Eugene Romanov
Institute of Metal Physics
Ekaterinburg, Russia
AM-7660

CLAUSE 1 - STATEMENT OF WORK

Tasks:

The Contractor shall:

1. Provide a report describing a technique which includes the use of gradient crystallization in a vacuum chamber with an electron beam to produce monocrystal foils of W and Mo. The report shall also include a description of a process involving plastic deformation and annealing temperature.
2. Produce 20 single crystal foils - 10 each of Mo (25mm wide x 0.5mm thick x 100mm long) and W (100mm wide x 0.5 mm thick x 100 mm long). Characterize the quality and microstructural properties of the foil and provide a report.

Tungsten and molybdenum tape crystals growing
Romanov E.P. (Institute of Metal Physics, Ekaterinburg, Russia)
Report on the first step of the project AM-7660.

Tungsten and molybdenum single crystals are of considerable importance in modern engineering due to a number of unique properties which are lacking in polycrystals. Along with high melting temperatures they are characterized by plasticity, high thermo-emission properties with pronounced anisotropy, stability in cesium and other alkaline metals plasma.

Production difficulties conditioned by the high chemical activity and refractoriness of tungsten and molybdenum single crystals retard their technical application. The most considerable advance in the production of refractory metal crystals has been made due to the use of the crucible-free zone melt with electron-beam heating. However, the crystals manufactured in this manner for the practical use in technical devices and especially in the electro-vacuum meters should be intensively treated to obtain the special form of thin plates, wires and so forth. That is why the interest to the development of the procedures enabling to obtain tungsten and molybdenum single crystals in the form closely approximating those of the practically used products of these materials doesn't decrease.

This approach can be realized during the crystal growing in the solid state. As applied to tungsten and molybdenum which are free from the polymorphous transformations recrystallization processes during the metal annealing after preliminary plastic deformation can be used.

The general principles of single crystal production by recrystallization are sufficiently well studied but it is often difficult to use them for the concrete materials. It is necessary to take into account the cleanness and the state of the initial material, the way of its manufacturing which significantly affect the single crystal formation and growth. The heating method and the atmosphere of the process are also of great importance.

Tungsten was the first metal to manufacture single crystals by recrystallization of a filamentary billet. As early as 1913 Julius Pinch's firm had successfully realized the process of tungsten wire single crystal growth [1]. Pinch's process is based on the intensive growth of crystal grains in the appropriate temperature conditions. The initial material in this process is a fine tungsten powder containing 2% thorium oxide. A wire billet is extruded from this powder mixed with an organic binder and after its heating by electric current in hydrogen atmosphere it transforms into a

solid and brittle filament with a fine grain polycrystal structure. After that this filament is slowly drawn through the zone heated to a high temperature with the help of a tungsten coil. The internal diameter of this coil is slightly larger than that of the treated wire. The coil temperature provides a local heating of the wire to 2000-2200°C. The temperature gradient obtained by this means provides the conditions for the recrystallization grain growth. The grown grains occupy all the cross section of the wire, and their length extends for the width of the temperature zone of grain growth.

The wire is drawn slowly and a new fine grain material consistently delivers to the hot zone. If the wire movement rate doesn't exceed the crystal growth rate this results in the production of wire consisting from one single crystal.

The advance of Pinch's method is determined by the successfully chosen scheme as well as by very fine initial grain size and by doping to the metal a material inhibiting the grain growth till the certain temperature.

A similar method of tungsten single crystal wire production has been devised by Gucher [2] in 1920 and independently by Yakobi [3]. They used the stretched wire. When the drawn wire is heated by translation through the hot zone after preliminary recrystallization annealing as well as without it the coarse grainstructure is obtained instead of single crystal.

For single crystal production in Gucher's process the short preliminary recrystallization annealing is used to create the structure with very fine equiaxed grains and this annealing is followed by drawing of this wire with 5-7% reduction.

In the wire treated by this means a single crystal is obtained after drawing through the hot zone at the temperature of 2000-2200°C with the appropriate rate.

Later on the similar schemes of recrystallization annealing in gradient furnaces as applied to different refractory metals including Mo, W, Ta, Nb, Fe were used by Andrade [4], Tsien [5], Goodman [6], Savitsky with collaborators [7].

The majority of the mentioned methods have been used for single crystal growth in the form of wire or small diameter rods.

The tape crystal production is the most well known for Fe-Si alloys in which the tape form and the certain crystal orientation are necessary to lower electromagnet losses connected with the cyclic

magnetization of transformer core. The main mechanisms of recrystallization processes in deformed metals have also been widely studied for this material.

A limited number of investigations [8,9] are devoted to Mo and W tape crystal growth.

By the character of driving forces of the crystal growth process recrystallization methods can be separated into two groups. These are the methods of recrystallization annealing after critical plastic deformation and the methods based on the great acceleration of grain growth during the secondary and collective recrystallization of fine grain matrix.

By the mode of heating the methods are separated into the annealing in the uniform temperature field and the annealing in the conditions of temperature gradient.

The annealing after critical deformation for the production of Mo and W crystals was found not to be promising for several reasons.

It is difficult to maintain an exact degree of plastic deformation because it is sensitive to the cleanness of the initial material and its temperature. During the annealing in the uniform temperature field large thermal stresses do not arise in crystals and the distribution of impurities is sufficiently uniform and this results in the sufficiently high structural perfection. However it is impossible to obtain large and extended crystals by this procedure and it is complicated to give the necessary orientation.

To overcome these difficulties the process is performed in the temperature gradient. A specimen is drawn through the furnace with certain rate. The availability of temperature gradient during the specimen movement through the hot zone is needed to avoid the spontaneous formation of nucleating centres in different parts of the specimen. The most favourable growth conditions take place when one nucleus is injected into the hot zone and grows so rapidly that it manages to absorb the fine grain mass before a competitive grain forms in it.

The optimum specimen movement rate and temperature gradient are conditioned by the temperature dependence of the formation and growth rates. This scheme of recrystallization growth enables to obtain crystals of necessary form and sizes.

The use of the secondary recrystallization or the regime of the excessive growth of some grains provides more extended opportunities. An abrupt acceleration of some grains development in the still retained mass of relatively fine grains when a certain temperature is exceeded and a high rate of grain boundary movement provide more reliable conditions for the production of tape crystals.

The driving force of the primary recrystallization is the system tendency to decrease its energy connected with dislocations and point defects contributed by deformation. As a result of primary recrystallization the formed nuclei grow by boundary migration towards the deformed matrix.

During the secondary recrystallization the grains capable for excessive growth absorb fine grains retained after the primary recrystallization. It is thus seen that for the crystal growth at secondary recrystallization temperatures preliminary deformation is required sufficient for the creation of fine recrystallized grains. It is more easily to achieve such conditions than to provide a critical deformation. Deformation with a reduction from 40 to 70 % provides a sufficiently fine grain structure in Mo and W.

Not only the initial fine grain structure is favourable for the high mobility of growing grain boundaries. The texture of a specimen is also of great importance. If in such matrix a new grain appears in which some crystallographical directions are turned relatively to matrix around some common axes to about 38° then it begins to grow intensively. Such a relationship between the initial texture and the texture of recrystallization is found quite often and it has a special name - Kronberg-Wilson rotation[10]. Consequently, in more textured matrix the development of grains with such orientation will be more rapid.

Of great importance for the tape specimens is also an anisotropy of surface energy. Experimental data for different metals show that the difference in the values of surface energy for (100) and (111) planes can reach 30 %. And if the sheet is sufficiently thin this anisotropy may be large enough to initiate the growth of preferably oriented grains and the absorption of the others by them.

On the base of all the preceding and in accordance with the results obtained previously [8,9] the most preferable for the growing of Mo and W tape crystals is the method of high temperature zone movement

along the tape billet subjected to a preliminary plastic deformation to a degree of 40-80 %. The electron-beam heating is preferable for heating and creation of an abrupt gradient because it enables to obtain temperature drop along the tape specimen of several hundred degrees for a millimeter. The stable performance of such a heater in vacuum for Mo and W is preferable. It maintains a sufficiently clean atmosphere in which crystals grow.

To perform the investigations under the programme of the project AM-7680 the devices for crucible-free zone melting with electron-beam and induction heating have been modified. For the goals of this project the special electron-beam cathode device and induction concentrator have been created enabling to heat tape specimens with sufficiently uniform distribution of temperature through the width of tape specimens and temperature gradient along the specimen reaching the value of 100-150°C/mm.

The devices are equipped with specimen holders preventing the advent of mechanical stresses in a specimen during its heating and movement through the hot zone.

Mo and W rolled tapes of technical cleanliness and after electron-beam melting served as the initial materials for single crystal growing. Preliminary results confirm the validity of the chosen technology and the earlier received data

10.01.95 E. P. Romanov

References

1. Patent of Germany No 291994, 1913,
Patent of Great Britain No 16620. 1914.
2. Patent of Great Britain No 174714, 1920.
3. Patent of USA No 1546899, 1920.
4. Andrade E.N. Proc.Roy.Soc.(A), 1937, v.163, p.16.
5. Tsien L.C., Chow Y.S. Proc.Roy.Soc.(A), 1937, v.163, p.19.
6. Gifford F.E., Cowes E.A. J.Appl.Phys., 1960, 31, 235;
Goodman C.H.L, private communication.
7. Савицкий Е.М., Бурханов Г.С., Оттенберг Е.В., Анисимов А.М.
"Монокристаллы тугоплавких и редких металлов, сплавов и соединений", Наука, 1977, 52-55.
8. Кралина А.А., Пермяков А.И., Пузанова Л.В., Романов Е.П. и др.
"Выращивание монокристаллов тугоплавких и редких металлов",
Наука, 1973, 52-62.
9. Кралина А.А., Пузанова Л.В., Смирнов Л.В., Пермяков А.И., Романов
Е.П. ФММ, 1975, 39, 1, 135.
10. Kronberg M.L., Wilson H.F. Trans.AIME, 1949, 185, 501.

Project Title: Directional Solidification of Ni-based Eutectic Alloys and High Purity Ti_3Al Single Crystals using an Annular Electron Beam Gun.

Principle Investigator: Oleg Barabash

Institute of Metal Physics

Kiev, Ukraine

AM-7661

CLAUSE 1 - STATEMENT OF WORK

Tasks:

The Contractor shall:

1. Provide a report detailing previously developed information that characterizes the performance, microstructure, physics of alloying influence on the physical and mechanical properties of eutectic alloys and Ti_3Al single crystals, including representative data and analysis.
2. Determine:
the concentration and temperature parameters of the eutectic transformation and L(g-Ni in the Ni-Mo-C-Al system at four (4) different Al compositions (2-6 W/0 Al); the influence of Al concentration on the regularities of the oriented structure formation under directional crystallization; temperature intervals of solid/solid and solid/liquid phase transformations in Ti_3Al alloys at four (4) to five (5) different Al concentrations in the range from 5-35%.
3. Work out optimum conditions of directional crystallization:
estimate influence of Al concentration on the volume content of strengthening phases of g_1 and Mo_2C in eutectic composite, determine direction of dominating growth of Ti_3Al single crystals and $g/g_1 Mo_2C$ research morphological stability of the directional solidification front for both Ti_3Al and Ni base and provide the following material samples: high pure Ti_3Al single crystals of various composition, $g/g_1 Mo_2C$ eutectic composites, containing up to 6% Al, with improved mechanical properties produced by complex alloying
4. Using the physical model of directional solidification, obtain superperfect structure and high strength properties in Ni-based eutectic composites and Ti_3Al single crystals under optimum conditions. Also provide material samples.

CONTENT

	Page
Introduction	1
Physical and mechanical properties of eutectic alloys, containing nickel and cobalt with carbides.	2
Physical-mechanical properties of Ti_3Al based alloys.	4
Analysis of regularities of eutectic transformation in ternary systems with interstitial phases.....	6
Computer modelling of main regularities of fusibility diagrams for ternary systems with interstitial element.....	9
Phase morphology and their interaction in nickel based alloys with molybdenum and carbon.....	13
— Thermodynamic calculation of phase equilibrium in Ni-Mo-C system.....	15
— Concentration- temperature parameters of eutectic transformation $\gamma + Mo_2C$	18
— Structure of Ni-Mo-C directionally crystallized alloys.....	24
Influence of alloying metals on the structure of eutectic nickel with carbide alloys.....	28
— Phase equilibrium and structure of cast alloys.....	28
— Morphology of directionally solidified alloys.....	29
Analysis of methods and installations for directional crystallization of eutectic alloys and single crystals.....	37
Conclusion.....	41
References.....	43

STRUCTURE AND PROPERTIES OF NICKEL BASED EUTECTIC COMPOSITES AND TITANIUM ALUMINIDE (Ti₃Al) ALLOYS

Barabash O. M.

Introduction

Directional solidification of metal materials is one of the most effective methods to obtain new materials with high unique physical-mechanical properties. For example, directional solidification of eutectic alloys allows us to obtain so called "natural composites", in which two phased structure is formed directly during crystallization of the melt. Phase components of such material are close to thermodynamically equilibrium ones. They possess low interphase surface energy and high thermal stability. This allows us to achieve high level of mechanical properties in this materials at high temperatures. In this case, eutectics, which belong to faceted-nonfaceted type, are the most interesting. They have one phase, which is crystallized facetedly, and the second one, which is crystallized without retaining of facets. Faceted phase (usually, it is carbide, nitride or refractory metal) is crystallized in the shape of fibres, plates or more complicated structures. It is regularly oriented in metal matrix, formed by nonfaceted phase.

For example, eutectic alloys, based on nickel or cobalt carbides, which belong to faceted-nonfaceted type, possess very high refractory properties at high temperatures (up to $0.9 T_{\text{melt}}$). On the basis of these alloys, there have been worked out γ/γ' -NbC type composite materials with complex alloying or COTAC, used for units of gas turbines of airplanes engines, high power energetic installations, etc.

Modern eutectic composites, which are worked out by now, have very complex composition. This is caused by the necessity of increasing the number and concentration of alloying elements and is accompanied by essential change in concentration and temperature parameters of eutectic transformation, enlarging of its temperature interval and decreasing of directional crystallization rates. That is why, it is very urgent to determine optimal content of alloying element for eutectic composites. First of all, it is necessary to obtain accurate knowledge on the structure of base ternary equilibrium diagrams.

Working out optimal content of eutectic composites and parameters of their directional solidification is connected with a large volume of experimental investigations. Region of cooperative crystallization (RCC) is a very important system characteristic. It is known, that RCC determines intervals of element content in the alloys and intervals of directional

crystallization rates, at which formation of composite structure is possible. Thus, determination of the cooperative crystallization regions (RCC) and regularities of their position on the base equilibrium diagram is an important and necessary part of such investigations. This allows us not only to work out purposeful technology of performing eutectic composites, but also to develop modern ideas about general regularities of the oriented structure formation during eutectic transformation.

Intermetallics are another class of materials, for which directional crystallization essentially increases the level of their physical-mechanical properties. In particular, they are nickel aluminides (NiAl , Ni_3Al) and titanium aluminides (Ti_3Al , TiAl). Absence of large angle boundaries in such materials results not only in increasing of strength limit at high temperatures, but also in improving their technological properties (plasticity) at room temperatures. From the standpoint of growth problems, distinctive feature of these materials is the fact, that, in the majority of cases, they are formed as a result of peritectic transformation $L + \alpha_1 = \alpha_2$. That requires such conditions of directional crystallization, under which this peritectic transformation would take place completely [1].

Physical -Mechanical Properties of Eutectic Alloys, Containing Nickel and Cobalt with Carbides.

At present time most completely there are studied nickel based eutectic composites with monocarbides TaC (NITAC) and NbC (COTAC) and cobalt based alloys with chromium carbides- Cr_7C_3 (alloy of 73C type). All these alloys are directionally crystallized composites, in which three strengthening mechanisms are realized: solid solution, dispersion hardening with γ' -phase particles and composite hardening with carbide fibres. For example, NITAC 13 has high properties during prolonged tests, much exceeding characteristics of cast directionally crystallized alloys. Shortcoming of this material is low resistance to oxidation. Different modifications of this material were worked out (for example NITAC 116A) and others [2-4]. Lessening of vanadium content and increase of Al content to 6,5 % in these alloys allow us to increase resistance to high temperature corrosion.

COTAC 74 alloys and its modifications [5-8] consist of γ/γ' matrix and carbide fibres. They are distinguished by high thermal stability and can work at multiple heats. Advantages of these materials are the most distinct during prolonged tests at temperatures exceeding 1000°C.

During directional crystallization of these alloys two-phase composite structure is formed. This kind of structure provides high exploitation characteristics of alloys. It consists of single crystal carbon fibres, which are orientedly situated in dispersively strengthened

matrix. Maximum rate of directional solidification (v_{CR}), at which composite structure is usually formed, can be evaluated from equation $G/V_{CR} = \Delta T/D$, where G - is temperature gradient at crystallization front; D - diffusion coefficient for element, which controls formation of carbon phase; ΔT - temperature interval of eutectic crystallization. It essentially depends on composition. It follows from above-stated results, that ΔT can be decreased to zero value by appropriate select of alloy's composition (at the same time, monovariant eutectic will have the highest melting temperature). As a rule, eutectic composites, intended for practical utilization, contain not only base elements, but also the whole complex of alloying elements. Each of them is responsible for certain properties of materials.

Aluminium. As it was mentioned above, considered eutectic composites obligatory contain up to 6 mas % Al. It causes formation of γ' - phase. Its amount increases, when Al content is increasing. Presence of γ' -particles determines mechanical properties of alloy at intermediate (up to 900°C) temperatures [9].

Chromium. It is well known , that chromium increases resistance to oxidation and to gas and salt corrosion in nickel and cobalt alloys at high temperatures. Chromium content in composites with carbide strengthening is usually not more than 10 mass%. Exceeding of this value leads to carbide transformation $23[Cr] + 6MeC = Cr_{23}C_6 + 6[Me]$ at boundary between matrix and carbide fibres, causing destruction of carbide fibres and decreasing material's strength [6,10,11]. Besides, both aluminium and chromium decrease volume content of carbide fibres in complex alloyed eutectic materials.

Cobalt. Eutectic composite materials are doped with cobalt to strengthen the matrix and to raise temperature of γ' -phase solution. Such materials have intensified dependence of carbide solubility in matrix on temperature.

Tungsten. Introduction of this element is caused by necessity of both additional strengthening of matrix and increasing of volume content of γ' -phase. Tungsten content in alloys with TaC is not exceeding 2-4 mass% and in alloys with NbC - 8-10 mass%. Eutectics, based on cobalt, contain 6-8 mass% W. Exceeding of these values of tungsten concentration deteriorates plasticity of alloys and their specific strength characteristics.

Tantalum, niobium and vanadium. In a number of alloys tantalum or niobium are elements, which form carbide fibres. At the same time, tantalum content cannot be less than 3 mass% for nickel based alloys and 7 mass% for cobalt based alloys. In combination with Al, W and V tantalum content cannot exceed 15 mass % (for nickel based alloys). Niobium and vanadium are introduced as tantalum substitutes in order to cheapen the alloy. Optimum Nb content is 1.6 mass%, exceeding of this value essentially spoils properties of alloys. Vanadium

content in alloys is about 4-7 mass%. Heat resistance of alloys decreases, if it is more, than 7 mass %. Meanwhile, composite strength decreases, when it is less than 4 mass %.

Rhenium in eutectic materials essentially increases their heat resistance.

Titanium takes part in formation of γ' -phase. In complex alloyed eutectic materials its content is about 1 mass %.

Boron promotes increasing of prolong strength of refractory alloys. Microalloying of eutectic materials with boron in amounts 0.01-0.015 mass% improves their plasticity in transverse direction [4].

Analysis of all data about content and properties of eutectic composites allows us to formulate the following directions in working out eutectic composites:

- 1) working out of alloys with intermetallic, carbide, boron, silicon strengthening;
- 2) introduction into eutectic alloys of elements, which provide all possible strengthening mechanisms: solid solution (W, Mo, Cr, V, Re) strengthening; dispersion (Al, Ti, Nb, Ta) strengthening; composite (Ta, Nb, Cr, Mo, W, Al) strengthening and also elements, which increase heat resistance of alloys, (Cr, Co, Si, Pt);
- 3) working out eutectic contents, which will provide high value of melting temperature (more than 1300°C) and small temperature interval of solidification (less than 15°C). It is necessary to provide high stability of plane front of directional solidification and formation of highly perfect composite structure.

Physical-Mechanical properties of Ti_3Al based alloys.

At present time, materials, based on high temperature intermetallics, in particular titanium aluminide, are intensively studied and worked out. According to their properties, these materials occupy intermediate position between nickel based superalloys and ceramics.

Intermetallic Ti_3Al is formed according to peritectic reaction $L = \beta - Ti_3Al$ and exists in two modifications: high temperature (β -phase), which possesses disordered BCC structure and low temperature (ordered α_2 -phase) with lattice of DO_{19} type. Usually alloys, based on Ti_3Al , are two phased [12]. Depending on both aluminium content and nature and concentration of alloying elements in these alloys, structures $\alpha_2 + \gamma - (TiAl)$ or $(\alpha_2 + \beta)$ are formed. At room temperatures α_2 -phase is badly deformed: its plasticity is usually equal 1-2%. In two phased $(\alpha_2 + \beta)$ state, intermetallics plasticity slightly increases, reaching 3-5% [13-14]. Alloying and thermal-mechanical treatment increases strength and plasticity of this compound. Both metals and non-metals are used as alloying elements. Among metal elements niobium is used more

often in the amount from 10 to 20 at%, which occupies position of Al atoms in α_2 phase. When Nb content is higher than 30at%, orthorhombic phase with parameters close to that of α_2 -phase appears in the alloy. Microstructure of alloys, based on Ti_3Al with Nb dopes, essentially depends on thermal and thermal-mechanical treatment. For example, in the alloy Ti-25Al-11Nb, being thermally treated at 1423K during 2700s, β -phase was formed. Such treatment increased cooling rate, decreased size of α_2 -phase lamellae and changed their distribution from colony to cellular [15]. In the structure of alloy Ti-25.3Al- 10.8Nb, annealed in atmosphere of H_2 for formation of solid solution, size of α_2 - phase particles decreases, and content of residual β and transformed β_2 phases essentially increases. At the same time transverse and tensile strength and plasticity of the alloy are increased [16].

From the standpoint of increasing plasticity of Ti_3Al based alloys, the best results gives two stage rolling. It results in the formation of α_2 -structure with texture in [001] direction. During the rolling high stable α_2 -phase is not recrystallized and its lamellae are stretched along the rolling direction [17]. This structure possesses much more plasticity, than alloys based on Ti_3Al or Ti_3Al -Nb without texture. In the temperature interval 20-600°C elongation is linearly increasing with temperature increase, and in the temperature interval 600-800°C it increases much more intensively. For example, in the alloy Ti-25Al-10Nb after rolling in temperature interval 900-1000°C, elongation is equal: 10%-at 20°C; 60%-at 800°C; 400-500%-at 1000°C. That means, that plasticity level permits to use hot pressing for this alloy [18,19].

Besides niobium, as an alloying element there can also be used Ni, Mo, V, Cr. For example, doping Ti_3Al with more, than 3mass%Ni, results in segregation of coarse eutectic TiNi net in the matrix, causing essential increase of its plasticity. Doping with molybdenum increases plasticity of alloys [20]. For example, alloys Ti-(13-17)Al-(1-10)Mo at the temperature 700°C possess plasticity about 5-6% [21]. Besides, Mo has modifying influence on the structure of alloys: increase of its content from 3.4 to 4.5 mass% results in grinding of ($\alpha_2 + \beta$) structure [22].

During joint doping with nickel and molybdenum, the last one is grinding TiNi segregation net and improves its distribution in the matrix. Thus it is suppressing negative influence of Ni [20]. For Ti_3Al based alloys, doped with Ni and Mo, the following relations of properties and composition were established [20]:

$$\sigma_b = 603 + 86.7 \text{ Ni} + 81.8 \text{ Mo} - 4.7 \text{ NiMo};$$

$$\sigma_{0.2} = 481 + 36 \text{ Ni} + 76.8 \text{ Mo} - 1.6 \text{ NiMo};$$

$$\delta = 30.5 - 7.5 \text{ Ni} + 3.7 \text{ Mo} + 1.7 \text{ NiMo}.$$

Mo is increasing the specific strength of the alloys, based on Ti_3Al , due to the solid solution hardening. Ni increases it due to dispersion hardening.

In Ti_3Al based alloys vanadium is doped mainly, as molybdenum substitute, in order to decrease specific gravity of the alloy [23]. For dispersion hardening Ti_3Al based alloys are also doped with < 1% of one or several elements: Sc, Ce, Er or Y [23].

Among the nonmetals, influence of hydrogen and silicon is studied most completely. Doping of Ti_3Al based alloys with silicon (usually together with Nb) results in the appearance of ξ -phase - $(TiNb)_5(AlSi)_3$. For example, in the structure of the alloy Ti-23.5Al-6.5Si in cast state, there are present α_2 -grains and eutectic $\alpha_2 + \xi$ [24,25]. Oxygen deteriorates plasticity of alloys, based on Ti_3Al and TiAl [26].

It was established, that a lot of intermetallics are plastic in single crystal state: NiAl, Ni_3Al , Cu_5Zn_8 and so on [27,28]. Information about the structure and properties of Ti_3Al in single crystal state is very scanty. It is only known, that during the compression tests the elastic limit ($\sigma_{0.1}$) of Ti_3Al single crystals monotonously increases from 1.2 GPa at 300 K to 1.9 GPa at 1130 K, and then it sharply falls to 400 MPa at the temperature 1273 K [29]. Temperature dependence of the yield point in pyramidal plane of Ti_3Al single crystals also has maximum at 1123 K [30].

Thus the formation of oriented structure in the alloys, based on Ti_3Al , and their production in high purity state (from oxygen) improves essentially their plasticity properties. That is why, it is of great interest to obtain Ti_3Al based alloys in single crystal or directionally crystallized state, and to study their properties. Such single crystals can be obtained by means of zone melting without crucible.

Analysis of regularities of eutectic transformation in ternary systems with interstitial phases.

Peculiarities of equilibrium diagrams structure of eutectic type mainly determine conditions and mechanism of formation of eutectic type composite structure. Now the most actual systems are systems of alloys, formed by transition metals or with interstitial phases or with metals of VA and VIA groups of the periodic system of elements. Among them ternary systems of the alloys, formed by transition metals, are of a special interest. Transition metals (Ni, Co, Fe, V, Nb, Cr, Mo, W) are base metal of the alloy (Me) with interstitial element (C) and alloying metal (Me'), which is more active than base metal (Al, Ti, Zr, Hf, Nb, Ta, Cr, Mo). These alloying metals are able to form high strength and refractory compounds with interstitial element (carbon or nitrogen).

In [31] it was suggested to classify these ternary equilibrium diagrams into four groups (Fig.1). It was shown that alloys, corresponding to diagrams of II or III groups retain their structure and properties during the prolonged time. In alloys, having the III type of equilibrium diagrams, interaction between phases is slight, meanwhile in alloys, having the II type equilibrium diagrams the extent of interaction between phases depends on the position of tie-line (conoda) triangle $Me-MeC-Me'C$ on the diagram. Position of the corresponding tie-lines determines the extent of the interaction between the strengthening phase and matrix of the alloy.

Described fusibility diagrams are characterized by lengthy regions of monovariant eutectic transformation $L=Me+Me'C_\gamma$ or $L=Me+Me'$, resulting in the formation of composite structure, which provides the unique physical-mechanical properties of the alloys at the highest temperatures [32-34]. Presence of the thermodynamically stable and refractory phase, which takes part in eutectic transformation, causes appearance of minimum at temperature dependence of monovariant eutectic transformations on alloy's content. This maximum is a saddle point of fusibility diagram of such system. At the maximum point isotherms of liquidus surface between the melt and base metal (L/Me) and of liquidus surface between the melt and interstitial phase (L/MeC) are touching each other. Region of three phase equilibrium $L=Me+Me'C_\gamma$ is degenerating into straight line - tie-line (conoda) of three phase equilibrium [35]. On this straight line monovariant eutectic equilibrium takes place at constant temperature and its behaviour is similar to that of the monovariant eutectic equilibrium in binary system, having zero temperature interval of transformation (Fig.2). Alloys, corresponding to the point of touching **R**, which is called Van-Rein point, will solidify at the largest rate. Formely, it was considered, that point **R** belongs to stoichiometric section $Me-Me'C_\gamma$ of ternary equilibrium diagram $Me-Me'-C$ and section itself is quasibinary. Later, more accurate investigation of phase equilibrium in systems of such type showed, that point **R** and tie-line of three phase equilibrium usually do not coincide with stoichiometric section $Me-Me'C_\gamma$, being situated aside from it [36,37].

If tie-line direction is known, fusibility diagram of considered systems allows us to determine not only the temperatures of monovariant eutectic transformation, but also its temperature interval in each certain alloy. It is also possible to determine region, in which only two phase structure is formed during directional crystallization. In this way, concentration intervals of alloy's content, optimal for directional crystallization, will be determined unambiguously.

On other hand, optimization of conditions for strengthening thermal treatment requires detailed knowledge, of how alloying metals influence stability of interstitial element in solid

Fig. 1. Main groups of ternary equilibrium diagrams
a) I group; b) II group; c) III group; d) IV group.

Fig. 2. Scheme of fusibility diagram of ternary system Me-Me'-C; — conoda of three phases equilibrium $L \rightleftharpoons \text{Me-Me}'C_\gamma$, - - - stoichiometric section Me-Me'C_γ.

solution of matrix metal. All this raises requirements to determination of base equilibrium diagrams of ternary and more complex systems; stipulates application of different mutual complementary methods of investigation, including computer modelling and thermodynamic analysis.

Computer Modelling of Main Regularities of Fusibility Diagrams for Ternary Systems with Interstitial Element [38,39].

For solid solution, we used quasichemical model of substitution solid solutions, which contains interstitial atoms in its octahedron intersites [40-42]. It allowed us to determine interstitial atom's concentration and temperature of alloy's desintegration, depending on alloying element content. For the melt, we used usual model of regular solutions. For interstitial phase, which has composition BC_γ and is formed by metal B and interstitial element C , at the supposition, that in this phase solubility of other i atoms is small, we can write for free energy the following formula:

$$\psi = N_B^{(2)} \mu_0 + N_i^{(2)} kT \ln \{ N_i^{(2)} / e N_B^{(2)} \} + N_i^{(2)} \varphi_i, \quad (1)$$

Using the same supposition, we shall obtain analogous expression for intermetallic $A_\gamma \cdot B$:

$$\psi' = N_B^{(2)} \mu_0' + N_i^{(2)} kT \ln \{ N_i^{(2)} / e N_B^{(2)} \} + N_i^{(2)} \varphi_i', \quad (2)$$

where a sum is taken over reiterating indices; μ_0 and μ_0' - thermodynamic potentials of binary compounds BC_γ and BA_γ correspondingly; φ_i and φ_i' - thermodynamic parameters, depending on composition; $N_i^{(2)}$ - a number of metal atoms, which are dissolved in interstitial phase or intermetallic.

As was shown above, performance of composite materials by means of directional solidification is based on eutectic reaction, resulting in formation of two solid phases from the melt : metallic matrix and fibres or lamellae of interstitial phases. In usual binary or quasibinary systems this reaction is nonvariant and takes place at constant temperature and concentration. Variantness of this transformation increases, when number of components increases. In multicomponent systems, which include real alloys, this type of transformation occupies the whole region of concentrations and occurs in certain temperature interval. The search for eutectic alloys with maximal melting temperature and correspondingly minimal interval in such systems is a very complicated and hard task. Knowledge of regularities of fusibility diagrams of such systems allows us to predict composition of eutectic alloys and to take into account influence of different factors, helping to solve such task.

Establishment of such regularities we fulfilled by modelling fusibility diagram of ternary system with interstitial element. Equilibrium diagrams with nickel and cobalt have a great practical meaning. For analysis of such systems let us consider that melt is in equilibrium with interstitial phase BC , intermetallic $AB\gamma'$ and with interstitial element C . Then for this case, we have system of three equations, which determines equilibrium between the melt and solid solution; three equations for describing equilibrium between the melt and interstitial phase; carbon and intermetallic compound.

Solution of the equilibrium equations was carried out numerically by means of Newton-Rafson iterated technique. The most complicated were the programs for solving equation, which describes equilibrium between the melt and solid solution in three or four component system. That is why, we shall give a short description of the computing program, which we worked out for such case in three component system. The detailed description of algorithm for determination of phase equilibrium is given in [46]. Solution of the equations is carried out by using recursion relations: $X_2^{k+1} = X_2^k + \Delta X_2^k$; $Y_1^{k+1} = Y_1^k + \Delta Y_1^k$; $Y_2^{k+1} = Y_2^k + \Delta Y_2^k$, here k defines step of iteration from initially chosen values $X_2^{(0)}, Y_1^{(0)}, Y_2^{(0)}$, where X_2, Y_2, X_1, Y_1 are correspondingly concentrations of B and C elements in solid and liquid phase. Corrections $\Delta X_2, \Delta Y_1, \Delta Y_2$ to the former iterated values X_2, Y_1, Y_2 are found as determinants.

Iterated process is finished, when relative error between two consecutive iterations will be less, than some given limit: $|\Delta X_2^k| \leq \varepsilon |X_1^k|$; $|\Delta Y_1^k| \leq \varepsilon |Y_1^k|$; $|\Delta Y_2^k| \leq \varepsilon |Y_2^k|$. Here X_1 is chosen as an independent variable. Let us note that this choice of the independent variable is arbitrary. Then we set temperature T and choose initial value X of the independent variable. Process of iteration is continued until it will give satisfactory values X_2, Y_1 and Y_2 . Then X_1 is changed by small value ΔX_1 , and the process is repeated, using previous values of X_2, Y_1 and Y_2 . It has been found out, that described program does not work well, because at arbitrary value X_1 of the independent variable, it is possible to occur that corresponding solutions X_2, Y_1 , and Y_2 do not exist. In this case, iteration process does not converge. In order to improve convergence of the iteration process, we used ratio X_1/Y_1 as an independent variable. This ratio was varied from very small value to the unit, then ratio X_1/Y_1 was taken as a new variable. It was also varied from the unit to very little value. Then variables X_2, Y_1, Y_2 were found for any certain value X_1/Y_1 or Y_1/X_1 , value X_1 was also found, using this ratio. Making use of such choice of independent variables, there were no cases of divergence of iteration process. Two sets of curves were determined by means of this procedure. They are liquidus (X_1, Y_1) and solidus (X_2, Y_2), which delineate phase regions for considered pair melt- solid solution at each temperature. Solving these equations, we obtain five sets of curves (Fig.3): liquidus isotherms

Fig. 3. Calculation of the fusibility diagram isotherms (a) and position of the line of monovariant eutectic transformation $L \rightleftharpoons A+BC$ (b) in ternary system A-B-C; — experiment, - - - calculation.

- melt-interstitial element (1), melt-solid solution (2), melt-intermetallic(3), melt-interstitial phase (4); and solidus isotherms - melt-solid solution (5). Intersection of any pair from the set of liquidus isotherms defines coordinates of monovariant equilibrium, meanwhile intersection of three liquidus isotherms defines position of points for nonvariant tetraphase transformations. For example, in Ni-Nb-C system intersection of isotherms, which belong to sets (4) and (2), defines coordinates of monovariant eutectic *melt = solid solution + interstitial phase* (curve $e'e''$ at Fig.3). Simultaneous intersection of three isotherms, which belong to (1), (2) and (4) sets, defines temperature and position of tetraphase equilibrium between the melt, interstitial element, solid solution and interstitial phase. This program allows us to determine intersection point of any pair of liquidus lines.

Let us analyse in details monovariant eutectic transformation (ET) $L=A+BC$ ($\gamma=1$), which is interesting by its practical application. In ternary system $A-B-C$ this transformation depends on thermodynamic potential of formation of interstitial phase ΔG_{bc}^0 and on four thermodynamic parameters, describing interaction between atoms' pairs in the melt and in solid state and also on three parameters $V_{ii}^s - V_{ii}^l$. These parameters can be defined by analysing corresponding binary equilibrium diagrams. Our calculations show that projection (ET) on the concentration triangle is represented by smooth curve $e'e^0e''$, which is turned by its convexity to the side of component A . This curve is restricted by the points e' and e'' , which are the points of tetraphase nonvariant equilibrium. Temperature (ET) depends on alloys' composition and reaches its maximal value (T^0) in the point e^0 - saddle point at fusibility diagram of the considered system. In this point tie-line (conoda) triangle, which describes three phase equilibrium between the melt, solid solution and interstitial phase, is degenerating into straight line -tie-line (conoda), on which three phase equilibrium $L=A+BC$ takes place at constant temperature. That means that temperature interval of the (ET) existence in the point e^0 is equal to zero. Coincidence of such tie-line with polythermal cross section is one of indications of the fact, that this section is quasibinary in ternary system $A-B-C$.

Let us consider parameters, which define coordinates of point e^0 and position of tie-line of three phase equilibrium. Its position at the equilibrium diagram is conditioned by touching of two liquidus isotherms (melt-solid solution and melt-interstitial phase) and mostly depends on value ΔG_{BC}^0 .

Fig.4 illustrates influence of value ΔG_{BC}^0 on coordinates of point e^0 . It can be seen, that, the less is $|\Delta G_{BC}^0|$, the farther from section $A-BC$ is the position of eutectic and the less is temperature ET. Influence of interaction parameters $W_{AB}^L, W_{AB}^S, W_{AC}^L$ and W_{BC}^L on characteristics of ET is not univalent. Computer modelling has shown, that at constant values

of other parameters, increase of one of the parameters W_{AB}^L , W_{AC}^L or W_{BC}^L results in mutual change of position of liquidus surfaces. ET monovariant line $L=A+BC$ removes in direction of interstitial phase with simultaneous decrease of the transformation temperature. More essential is influence of parameter W_{AB}^S (Fig. 5). Increase of parameter W_{AB}^S causes increase in ET temperature and displacement of ET curve into the side of BC interstitial phase. At the same time, point e^0 moves away from the section $A-BC$. Variation in wide interval of values ΔG_{BC}^0 , W_{AB}^L , W_{AB}^S , W_{BC}^L does not result in getting point e^0 on the section $A-BC$. Such behaviour is caused by the following fact: liquidus isotherms of melt-interstitial phase are similar to parabolas (Fig.3). The less is value of $|\Delta G_{AB}^0|$, the more is their distortion and displacement in the direction of interstitial phase in ternary system. On the other hand, liquidus isotherms of melt-solid solution in ternary systems $A-B-C$ are usually assymetric and displaced in direction of boundary metal system $A-B$. All these factors results jointly in the fact, that point e^0 removes to the region of compositions, for which condition $C_B^L/v > 1$ is fulfilled. The less is value $|\Delta G_{BCI}^0|$ (that is, the less thermodynamic stability does interstitial phase possess), the more essential is this displacement. Therefore, fulfilled analysis of phase equilibrium in ternary systems with interstitial element shows, that there are no thermodynamic reasons for obligatory coincidence of quasibinary sections with equiatomic sections $A-BC$. In such systems tie-lines of three phase equilibrium $L=A+BC$ usually exist. In this case, it is quasinonvariant eutectic equilibrium, which does not coincide with equiatomic section of ternary equilibrium diagram. These results can be directly generalized for the case, when interstitial phase $BC\gamma$ ($\gamma \neq 1$) is in equilibrium with metal A . At present time, this fact was experimentally confirmed by investigations of a large number of ternary systems with interstitial element, see, for example [47]. Thus, computer modelling of phase equilibrium with the presence of liquid phase has shown, that saddle point on fusibility diagram of ternary system, which corresponds to quasinonvariant eutectic transformation $L=A+BC\gamma$, does not coincide with stoichiometric section $A-BC\gamma$. It is situated in the composition region of alloys, for which condition $CC/CB < \gamma$ is held. Obtained result allows us to determine composition region of alloys, which are optimal for directional crystallization. Such alloys have maximal possible temperature and minimal temperature interval of eutectic transformation.

Morphology of Phases and Their Interaction in Nickel Based Alloys with Molybdenum and Carbon[48-50].

One of shortcomings of eutectic alloys of COTAC series is relatively low content of strengthening phase (about 6 v%), which causes rather low composite strength at room and intermediate (below 900 °C) temperatures and appearance of composite strengthening only at

Fig. 4. Influence of thermodynamic potential of formation ΔG_{BC}° on the coordinates (T° , composition) of saddle point at the fusibility diagram of ternary system A-B-C.

Fig. 5. Displacement of eutectic transformation $L \rightleftharpoons A+BC$ curve in ternary system A-B-C at varying thermodynamic parameters W_{AB}^L . $W_3 > W_2 > W_1$.

high temperatures [51]. From thermodynamic relations follows, that the main parameter, which defines content of refractory and thermodynamically stable phase in eutectic, is its thermodynamic potential of formation: the less is its absolute value, the higher is content of this phase in eutectic. Absolute value of thermodynamic potential of formation for carbon phases of metals from VIA group is less than that of monocarbides of metals from IV-VA groups. This results in larger content of carbon phase in eutectic with metals from VIA group than in other eutectics. Besides, thanks to large chromium solubility in nickel and carbide of molybdenum one can expect, that nickel based eutectic alloys with molybdenum carbide can be alloyed with large chromium percent. Their phase content will be stable at high temperatures during long time. That is why, Ni-Mo-C system is actual for working out new materials on its basis.

Thermodynamic Calculation of Phase Equilibrium in Ni-Mo-C System.

Thermodynamic parameters used in this calculation were determined by means of above-stated method. They are listed in Table 1. As for determination of thermodynamic parameters, it is necessary to know position of liquidus and solidus curves in Ni-Mo binary system with high precision. This system was studied by means of absolute thermal analysis. Fusibility diagram was built, using results of this analysis. At Fig. 6 for comparison there are shown curves of phase equilibrium, obtained by means of thermodynamic calculation.

Calculation of phase equilibrium in ternary system was carried out in the temperature interval 1510-1710 K with a step 5K. There were determined liquidus and solidus isotherms, tie-lines of two phase regions and line coordinates $e'e^0e''$ of monovariant eutectic transformation $L=\gamma+\text{Mo}_2\text{C}$ (Fig. 7). According to the results of calculation, this transformation is represented by smooth curve, which is assymetrically situated relatively to stoichiometric section Ni-Mo₂C in nickel part of equilibrium diagram and turned by its convex part to nickel side. Position of this curve is conditioned by peculiarities of liquidus curves arrangement for melt-carbide and melt- γ -solid solution relatively to stoichiometric section. First of all, it is determined by values of thermodynamic potentials of carbide formation $\Delta G^0_{\text{Mo}_2\text{C}}$ and by parameter W^L_{NiMo} , which characterizes interaction of metal atoms with each other in the melt. The less is $|\Delta G^0_{\text{Mo}_2\text{C}}|$ and W^L_{NiMo} , the more assymetrical are corresponding liquidus lines and the more essential is displacement of point e^0 relatively to stoichiometric section Ni-Mo₂C. Space curve of eutectic transformation from carbon side is restricted by ternary eutectic $L=\gamma+\text{C}+\text{Mo}_2\text{C}$ (point e') and contains saddle point of equilibrium diagram - point e^0 . Temperature intervals of proceeding of eutectic

Fig. 6. Fusibility diagram for system Ni-Mo;
1 - experiment, 2 - calculation.

Fig. 7. Calculation of fusibility diagram isotherms (a) and line of monovariant eutectic transformation $L \rightleftharpoons \gamma + Mo_2C$ (b) in ternary system Ni-Mo-C; — experiment, - - - calculation.

transformation $L=\gamma+\text{Mo}_2\text{C}$, depending on alloy's content are shown at Fig.6. This dependence has maximum at the point C_1 and two minimums, equal to zero, at points e' and e^0 . Point C_1 restricts region of alloys, in which two phases are formed during crystallization: γ and Mo_2C (at the point C_1 ternary eutectic $\gamma+C+\text{Mo}_2\text{C}$ appears for the first time). This point also distinguishes region of alloys, which are the most actual for directional solidification.

Concentration - Temperature Parameters of Eutectic Transformation $L=\gamma+\text{Mo}_2\text{C}$

Experimental investigation of Ni-Mo-C fusibility diagrams was fulfilled by plotting four polythermal sections, which were passing through Mo_2C carbide of stoichiometric composition. Eutectic composition, corresponding to this section were determined by thermal analysis and controlled by microstructures of slowly cooled alloys. Afterwards, position of line of eutectic transformation $L=\gamma+\text{Mo}_2\text{C}$ was additionally defined more exactly. It was established the existence of monovariant eutectic transformation $L=\gamma+\text{Mo}_2\text{C}$, corresponding to smooth curve, being situated in nickel angle of equilibrium diagram (Fig.9). It was described by expression $\ln C_e = 6.2364 - 1.526 \ln C_{\text{Mo}}$ with dispersion of experimental data $\sigma^2 = 4.3 \cdot 10^{-4}$, where C_e and C_{Mo} are correspondingly concentrations (at%) of carbon and molybdenum in eutectic. In the alloys, having more concentration of carbon ($C_{\text{Mo}}/C_e > 2$), eutectic transformation is finished after formation of ternary eutectic transformation $L=\gamma+C+\text{Mo}_2\text{C}$ at 1265°C , which has the following composition(at.%): 76 Ni, 11.2 Mo, 12.8 C. At the other side, it is restricted by four phase equilibrium of peritectic type with participation of δ -phase (NiMo). For the first time, δ -phase appears in alloys, which are close to section IV (Fig.9). All studied sections belong to eutectic type. Section III is the most close one to quasibinary. It contains tie-line of three phase equilibrium $L=\gamma+\text{Mo}_2\text{C}$ (Fig.9).

Dependences of T_e and ΔT_e on alloy's composition are not monotonous: T_e at the point e^0 with coordinates (at. %) 74.78 Ni, 20.12 Mo, 5.1 C ($C_{\text{Mo}}/C_e = 3.945$) has maximal value equal to 1350°C and ΔT_e is equal to zero at this point. Alloy, corresponding to the point e^0 , is melted at constant temperature. It behaves as quasinonvariant eutectic. It should be noted that point e^0 is situated rather far from stoichiometric section I, below it in the composition region of alloys, enriched with molybdenum. This is confirmed by data of thermodynamic calculations (Table 2). Declination of alloy's content to one or another side from the point e^0 along the line $e'e^0e''$ is accompanied by decrease of T_e and uncrease of ΔT_e . At the same time, displacement to the side of ternary eutectic (to the point e') is accompanied by much greater decrease of T_e and increase of ΔT_e than in the case of displacement to the side of point e'' (Fig.6). This effect can be well seen at corresponding thermograms. Maximal value of ΔT_e ,

Fig. 8. Concentration dependence of the temperature (T) and temperature interval of proceeding (ΔT) of monovariant eutectic transformation $\gamma + \text{Mo}_2\text{C} \rightleftharpoons \text{L}$ in ternary system Ni-Mo-C; — experiment, - - - calculation.

Fig. 9. Fusibility diagram of ternary system Ni-Mo-C (fragment).

Fig. 8. Concentration dependence of the temperature (T) and temperature interval of proceeding (ΔT) of monovariant eutectic transformation $\gamma + \text{Mo}_2\text{C} \rightleftharpoons L$ in ternary system Ni-Mo-C; — experiment, - - - calculation.

Fig. 9. Fusibility diagram of ternary system Ni-Mo-C (fragment).

Table 1.

**Thermodynamic parameters, which are used for calculation of fusibility diagram
for Ni-Mo-C system.**

W_{NiMo}^L	W_{NiMo}^S	W_{MoC}^L	W_{NiC}^L	ΔV	ΔG_{Mo2C}^0	ΔV_{CC}^{S-L}	ΔV_{MoMo}^{S-L}	ΔV_{NiNi}^{S-L}
-25.14*	-26.23*	40.94*	0.9*	9.54*	-48.14-0.012T*	-17.16-.009T*	13.82+0.009T [46/53]	17.626+0.01T [46/53]

*- p arameters, determined from analysis of phase equilibrium in binary systems;

** - ΔG_{Mo2C}^0 is defined from table values [52], counting again for standart state from pure FCC metals

Table 2.

Coordinates of nonvariant eutectic transformations in ternary system Ni-Mo-C

calculation					experiment				
T_k, K	Ni	Mo	C		T_k, K	Ni	Mo	C	
e ⁰ 1620	74	20	6		1623	74.78	20.12	5.1	
e' 1530	76.3	9.2	14.5		1538	76.0	11.2	12.8	

Table3.

**Content of Cr, Mo or W in eutectic composite γ -NbC, which causes change in eutectic's
morphology.**

element	A	B	C
Cr	2.5	3.5	5.0
Mo	0.8	1.5	2.0
W	2.0	4.0	5.5

which is equal to 70°C, belongs to eutectic alloy of stoichiometric section Ni-Mo₂C (point C₁ at Fig. 6), in which ternary eutectic $\gamma + C + Mo_2C$ appears for the first time (Fig. 8). Stoichiometric section Ni-Mo₂C at equilibrium diagram restricts region of two phase ($\gamma + Mo_2C$) alloys after solidification. This section is not close to quasibinary as it was considered earlier [54].

Thus, composition region of alloys, which are the most favourable for directional crystallization, is situated between I and IV sections. All eutectic alloys, corresponding to this region, after solidification consist of two phases - γ -solid solution and Mo₂C carbide. The most actual are alloys, situated on the tie-line of three phase equilibrium, which is passing through point e^0 .

Eutectic alloys $\gamma + Mo_2C$ belong to the type of skeleton eutectics, in which Mo₂C carbide is the phase, leading crystallisation. In cast state alloys with compositions, close to line of eutectic transformation $L = \gamma + Mo_2C$, to the right of point C₁, have two phase structure, which is typical for eutectic alloys of transition metals with interstitial phases [75]. Besides eutectic, they contain "primary" dendrites γ -Ni as well as slightly faceted carbide crystals. Eutectic colonies are formed by fibres and lamellae of Mo₂C carbide, situated in nickel matrix (Fig. 9a). It should be noted, that facets of molybdenum carbide basic crystals, are displayed more slightly, than facets of IV-V group metal carbides in corresponding eutectics. In alloys, where crystallization results in formation of ternary eutectic $\gamma + C + Mo_2C$, graphite looks like globular or rosette, and when its content increases, it mainly takes the shape of lamellae or scales. Alloy, corresponding to the ternary eutectic, has a structure, formed by alternating lamellae of carbon and Mo₂C carbide, which are nucleated in metal matrix independently (Fig. 10b,c). In the structure of alloys, situated below section IV, besides eutectic $\gamma + Mo_2C$, there are present coarse irregular shaped δ -phase crystals (Fig. 10d), meanwhile quantity of eutectic in these alloys decreases.

Structure of Directionally Crystallized Alloys of Ni-Mo-C System.

In our previous investigations we found region of two phased $\gamma + Mo_2C$ alloys and tie-line of three phase equilibrium $L = \gamma + Mo_2C$. Alloys, belonging to this tie-line (section III at Fig. 7), are crystallized with zero interval of eutectic transformation and are the most actual for directional crystallization. For this section we fulfilled detailed investigation of directionally crystallized alloys structure and determined region of cooperative (composite) crystallization (RCC).

Fig. 10. Microstructures of the alloys of Ni-Mo-C system;
a) eutectic composition of III section (e^0), b), c) - ternary
eutectic $\gamma + C + Mo_2C$ (e'), b - SEM, d - alloy, situated below
section IV.

Within RCC the structure of alloys is characterized by regular arrangement in the matrix of carbide phase, which looks like faceted lamellae or ribbons with complex cross section (Fig.1a,b). As in other eutectics of faceted- unafected type, formation of these lamellae begins from appearance and growth of base Mo_2C crystals, which grow up to certain size, retaining their facets. Then loss of shape stability during crystal growth takes place. Branches, from which carbide phase of eutectic colony is formed afterwards, appear on its vertex (rarely at its ribs). Facets of molybdenum carbide in these alloys are displayed more slightly, than in similar eutectics with monocarbides of metals from IVA and VA groups. Lamellae of Mo_2C in eutectic alloys can form branches in their plane, forming quasifibrous parts of structure. Such branching promotes perservation of interlamella distance in directionally crystallized alloys at different fluctuation of alloy's content and crystallization rate. With increasing of crystallization rate (or decreasing of G/V_{CR}) lamella branching increases. This results in formation of quasifibrous structures. But in all cases facets of carbides and primary growth direction of phases are retained: it is $\langle 201 \rangle$ for carbide and $\langle 111 \rangle$ for nickel matrix. Let us note that there must exist connection between symmetry of primary growth direction of faceted phase and its growth shape. Really Mo_2C carbide during directional crystallization grows primary in direction $\langle 201 \rangle$, possessing symmetry axis of the second order. Evidently it causes development of lamellar shape of growth, also possessing symmetry axis of the same order.

RCC of directionally crystallized alloys has a number of peculiarities: it is assymmetric relatively to hypereutectic composition, removed to the side of hypereutectic alloys and is slightly widened with increasing of crystallization rate (Fig.1g). Such position of RCC is characteristic for faceted-nonfaceted eutectics and according to [56] is caused by essential difference between thermodynamic potentials of eutectic phases. The more is the difference, the higher is assymetry of RCC position on equilibrium diagram. From both sides of RCC there are situated so called regions of dendrite-cooperative crystallization. In these regions controlled growth is still retained and in the melt before crystallization front no dendrites are formed. Under these conditions there is formed regulare structure, in which, besides eurentic, there are present oriented dendrites of γ -solid solution (Fig.1ic) or faceted and oriented Mo_2C dendrites (Fig.1ld).

Assymetry of RCC for considered systems results in formation of different type of structure, depending on crystallization rate, in the alloys, having composition close to eutectic (in the unterval 4.0-6.5 mol.% Mo_2C). At large crystallization rates (in the interval $(16.68-22.24) \cdot 10^{-6} \text{m/s}$) in these alloys there is formed typical hypoeutectic structure, in which, besides eutectic, there are present surplus dendrites of γ -solid solution. In interval of

Fig. 11. Microstructures of directionally crystallized alloys of eutectic system γ - Mo_2C (composition in mol.%); a), b) - in the region of cooperative crystallization, 5.1 Mo_2C , b - SEM (matrix removed chemically), c) in the first region of dendrite-cooperative crystallization, 3.5 Mo_2C , d) in the second region of dendrite cooperative crystallization, 5.75 Mo_2C . Transverse section.

crystallization rates $(1.39- 11.12) \cdot 10^{-6} \text{m/s}$, depending on alloy's composition there can be formed completely eutectic structure or hypoeutectic, or hypereutectic structure with primary Mo_2C dendrites. Appearance of the last ones is characteristic for alloys, containing more than 5.5mol.% Mo_2C . It is necessary to take into account such influence of crystallization rate on alloys structure, when evaluating eutectic compositions, using cast alloys, obtained at relatively large crystallization rates.

We also studied conditions of composite structure formation in alloys, having non-zero temperature interval of eutectic transformation, and also in alloys, situated near ternary eutectic (point e' at Fig.13). This investigation showed, that in ternary system there exist two independent RCC. One of them (RCCI at Fig.13) is situated between sections I-IV, and is two phased: after directional crystallization structure of alloys in this region, as mentioned was above, consists of Mo_2C fibres or ribbons, situated in metal matrix of γ -solid solution.

In the region, adjoining to the line of monovariant eutectic transformation, change of concentration-kinetic conditions causes the change in alloy's structure, analogous to that of alloys, belonging to the previously studied section III. In the whole region of RCCI structure of alloys is characterized by the high degree of order. At little solidification rates their structure has composite type, and after exceeding certain critical value it becomes cellular. Fibres of Mo_2C in these alloys are not situated chaotically, but as oriented rows (Fig.14b). In hypereutectic alloys at low rates of crystallization besides oriented structure, there exist large faceted Mo_2C dendrites. Such alloy is outside RCCI. But with enlarging V_c , character of structure can change, because its composition gets into RCC (for different compositions the value of V_c , at which such transition takes place, is different). At last, in alloys, considerably removed from the eutectic, composite structure can not be obtained at any conditions. Boundaries of RCC behave differently, when V_c increases. From Mo_2C side boundary I looks like sloping surface, which removes with increasing of solidification rate to Mo_2C ; from γ -Ni side RCC boundary has parabolic character. Second region (RCCII at Fig.11) is situated around ternary eutectic γ -C- Mo_2C . In this region directionally crystallized alloys are three phased: besides γ -Ni and Mo_2C , there is carbon, which is crystallized as lamellae (Fig.14). For the first time, graphite as a third phase appears in alloys, corresponding to section I. It looks like separate isolated inclusions and is situated along the boundaries of eutectic colonies. When alloy's composition approaches the point of ternary eutectic, carbon content in the alloy increases, resulting in formation of new structure component - oriented ternary eutectic. It is situated between oriented two phased ($\gamma + \text{Mo}_2\text{C}$) eutectic colonies (Fig.14). Graphite in ternary eutectic looks like lamellae and scales, being chaotically distributed in regular two

Fig. 12. Polythermal section (Ni+11.87 at.% Mo)-Mo₂C with the region of cooperative crystallization (RCC); 1 - thermal analysis, 2 - alloys, belonging to RCC, 3 - alloys, outside RCC.

Fig. 13. Monovariant eutectic transformation $L \rightleftharpoons \gamma + \text{Mo}_2\text{C}$ and cooperative crystallization region (numbers show the directional crystallization rate $(V_C \cdot 10^{-6}) \text{ m/s}$).

Fig. 14. Microstructures of directionally crystallized alloys in ternary system Ni-Mo-C; a), b) - ternary eutectic (e'), c), d) - alloy from RCC 2, containing 14 at.% Mo and 8.8 at.% C; a,c - transverse section, b,d - longitudinal section.

phased structure. Such structure of ternary eutectic after directional crystallization of alloys from RCC region indicates, that carbon phase is independently nucleating and growing.

At low rates of crystallization distance between RCCI and RCCII is large. With increasing of crystallization rate these two RCC are widened to meet each other, at the same time, they are removed to the side of Mo_2C . The boundary between them passes along the section with maximal ΔT_e (70°C).

The Influence of Alloying Metals on the Structure of Eutectic Nickel with Carbides Alloys.

As stated above, solidification of $\gamma\text{-Me}'\text{C}$ type alloys starts with formation and subsequent growth of faceted $\text{Me}'\text{C}$ crystals, the nucleation sites of eutectic colony. Habit of this crystals is determined by the most slowly growing facets. Eutectic colony begins its growth from vertexes and edges of carbide crystal. According to the principle of extreme growth, colony forms in the direction of the most quickly growing facets. Such nature of eutectic alloys solidification determines interrelations between base crystal shape and morphology of eutectic colony [32]. Alloying elements may influence velocity growth ratio of different facets of carbide crystal, thus changing both habit of base carbide crystal and morphology of carbide phase in eutectic colony.

In this part we consider the results of investigation of changes in eutectic $\gamma\text{-NbC}$ alloys morphology, while they are doped with cobalt, chromium, tungsten and aluminium.

Phase Equilibrium and Structure of Cast Alloys.

The nature of eutectic transformation is one of the factors, which determine composite structure. Therefore, investigation of alloying influence on concentration-temperature parameters of eutectic transformation $L=\gamma+\text{NbC}$ has been carried out. It was established, that during alloying of this eutectic by aluminium up to 6w%, chromium up to 5w%, tungsten up to 12 w% and molybdenum up to 10w%, the same alloys' phase composition is conserved, but temperature intervals of proceeding of eutectic transformation was changing.

The displacement of $\gamma+\text{NbC}$ eutectic composition to the side of γ -solid solution is common for all alloying elements. Alloying with aluminium up to 5w% is accompanied by decreasing of NbC content in eutectic to the half (from 9w% in the system without alloying, to 4.5w% in alloyed system). Cobalt almost does not change eutectic's composition. According to increasing of alloying influence on the displacement of eutectic point to Ni - side, alloying elements may be set in a row: Co, W, Mo, Cr, Al. As quantity of alloying admixtures increases, the temperature of eutectic transformation changes non monotonously,

reaching some maximum (cobalt is an exception). This effect is more brightly expressed by doping with aluminium and tungsten, less - with cobalt and chromium. Formation of ternary eutectic, in which γ' (Ni_3Al) phase or Mo_2C are present accordingly. Eutectic transformation interval also changes to the different extent. Co and Mo almost do not influence its magnitude (Fig.15).

We need to take into account all these factors, when we want to work out complex alloyed materials of optimal composition. Such materials have maximum content of strengthening phase in eutectic, maximum temperature and minimum interval of eutectic transformation.

During volume solidification of non-alloyed eutectic $\gamma\text{-NbC}$, base crystals of NbC have cubic shape with typical habit, formed by $\{100\}$ facets (Fig.16a). Under these conditions, niobium carbide in eutectic colonies has the shape of "trefoils". Alloying with molybdenum, tungsten and chromium changes habit of base NbC crystals from hexohedral to octohedral, formed by $\{111\}$ facets (Fig.16b). Such alloying is accompanied by changes in carbide phase morphology in eutectic. Now fibres of niobium carbide become a prevalent element in eutectic structure, while trefoils are absent. Alloying with aluminium or cobalt exerts almost no influence on the structure of eutectic alloys, changing neither shape of base crystals, nor niobium carbide's morphology in eutectic colonies. Only changes in dispersity are taking place: aluminium is rather coarsening eutectic structure, while cobalt increases dispersity of eutectic.

Alloying metals can be divided into two groups according to their influence on the morphology of eutectic alloys. In the first group, there will be Cr, Mo and W, which change morphology of cast eutectic alloys. Al and Co are in the second group, for they do not change it. Metals of these groups differ in solubility in NbC also. Cr, Mo and W possess considerable solubility in it (up to 5-10w%), while Al and Co have small solubility (up to 1.5w%) [59].

Morphology of Directionally Solidified Alloys.

In cast alloys there is a tendency of morphology transformation from trefoil shape of carbide phase to fibre shape of transverse section. This tendency is considerably amplified in directionally solidified alloys. As early, alloying with Al and Co (up to 6 and up to 20w% accordingly) does not lead to the changes in NbC morphology.

Let us consider in detail the evolution of morphology of alloyed with molybdenum eutectic alloys. Mo slightly influences parameters of eutectic transformation $L=\gamma+\text{NbC}$. This allows us to observe easily changes in morphology, caused by alloying. Depending on content

Fig. 15. Influence of alloying elements on temperature (a) and temperature interval of eutectic $L \rightleftharpoons \gamma + \text{NbC}$ transformation (b).

of alloying element in directionally solidified alloys, structures of three different kinds can be formed. Transformation from one kind of structure to another takes place in a very narrow interval of alloying element content. First kind is typical for non-alloyed materials and retains under molybdenum content up to 0.8w%. In this content interval carbide phase has the shape of trefoils and hexohedron fibres, while eutectic's differentiation slightly increases comparing with that of the non-alloyed materials (Fig.16c). The second type of structure is observed in alloys, containing from 0.8 to 2.0w%Mo. In this case, lamellar shape of carbide phase is prevalent. This shape is able to branch out in its plane, forming "quasifibrous" structure (Fig.17). It is worth mentioning, that branching out of lamellae is just that very mechanism, that maintains constant alloy's composition with local changes of temperature-velocity parameters of directional solidification. Similar structures are formed in other systems also. For example, in Al-Si or Mo-ZrC [60]. The third kind of structures is present in alloys, containing more than 2.0w%Mo. Under such conditions, carbide phase looks like faceted fibres with square section (Fig.16d). Usually, only two types of niobium carbide base crystals are detected in all these alloys. These are hexohedral and octohedral types. The first is typical for alloys, containing less, than 1.5w%Mo, the second - for other alloys.

Texture-diffractometry of directionally solidified alloys has shown, that every type of structure has its own direction of primary phase growth (for niobium carbide and γ -solid solution). Directions of primary growth for both phases always coincide. For example, if carbide phase has trefoil shape, then γ -solid solution, as well as carbide phase, grows in the direction $\langle 111 \rangle$ (Fig.18a). If carbide phase is solidified in lamellar shape, then both phases in eutectic have direction of primary growth $\langle 110 \rangle$ (18b). Finally, if carbide phase is formed as fibres with square section, then both phases grow in the direction $\langle 100 \rangle$ (Fig.16d.18c). Comparing these results. one may conclude, that direction of primary growth of carbide phase determines its morphology. Indeed, during solidification in the direction $\langle 111 \rangle$ which has symmetry axes of the third order, carbide phase is growing in trefoil shape, which has symmetry axes of the third order also. If growth direction is $\langle 110 \rangle$, which has symmetry axes of the second order, carbide phase is formed in lamellae, which also have symmetry axes of the second order. In the case of growth direction $\langle 100 \rangle$ with symmetry axes of the fourth order, faceted fibres with square section are formed.

Crystal's habit is known to be determined by the most slowly growing facets. In the case of hexohedral habit. such facets are $\{100\}$, and for octahedral habit such facets are $\{111\}$.

The research of structure of directionally solidified alloys at different stages of eutectic colony's evolution has been carried out. According to our research, fibres and lamellae of niobium carbide start their growth from vertices of cube or octahedron in the direction of

Fig. 16. Different morphology of carbide phase in eutectic alloy γ -NbC: base NbC crystal in an alloy without doping (a) and in the alloy, doped with 5 mass.% Mo (b). Niobium carbide in eutectic colony in an alloy without doping (c) and in the alloy, doped with 5 mass.% Mo (d) in the directionally crystallized state. Transverse section.

Fig. 17. Morphology of niobium carbide in directionally crystallized eutectic alloy, containing from 0.8 to 1.5 mass.% Mo; a) light microscopy, b) SEM. Transverse section.

Fig. 18. Direct pole figures from NbC;
primary growth direction:
a) $\langle 111 \rangle$, b) $\langle 110 \rangle$, c) $\langle 100 \rangle$.

maximum growth velocity (accordingly $\langle 111 \rangle$ or $\langle 100 \rangle$). Their ends are faceted by planes of cube or octahedron, while their side facets - by facets $\langle 110 \rangle$ (Fig.19).

Thus, there is direct connection between symmetry of crystallographic direction of primary growth and carbide phase morphology in directionally solidified eutectics of the γ - γ' -NbC type. This determines the nature of influence, exerted by alloying metals on morphology. In this connection, experimental investigation of niobium, nickel and molybdenum distribution between solid phases of eutectic composite has been carried out. It has been shown, that niobium, being a carbide forming element, is mainly in carbide. Its content in solid solution is small (not exceeding 2.5w%). Distribution of nickel content is opposite to that of niobium: situated in solid solution, it is slightly soluted in carbide (up to 1.5w%). This is in agreement with received values of limit solubility of niobium carbide in solid solution of eutectic alloys. Contrary to niobium and nickel, molybdenum is uniformly distributed between carbide and solid solution (Fig.20). Its distribution coefficient is near unit.

Adsorption of alloying metals by the facets of carbide crystal has been also investigated. For that purpose, plane distribution of niobium and molybdenum on the grinded surface of material, alloyed with 0.95w%Mo, was studied. These distributions indicate enriching with molybdenum on the surface of growing carbide crystal, in comparison with its core (Fig.20b).

There have been carried out quantitative measurements of molybdenum concentration on the surface of carbide crystals with different habits (cubic and octahedral). These investigations have also shown that facets of $\{111\}$ type adsorb molybdenum 2.5-3 times more, than facets of $\{100\}$ type. Molybdenum concentration for facets of $\{111\}$ and $\{100\}$ types is equal to 1.17 and 0.42w%Mo accordingly.

Thus, as for our opinion, mechanism of an influence of alloying metals on eutectic composite's morphology includes the following effects. During alloying of eutectics with metals, able to solute in considerable quantities in carbide phase (metals of VA and VIA groups), selective adsorption of foreign atoms by different facets of carbide crystal is taking place. Meanwhile, velocity of facet's growth decreases to different extent proportionally to their adsorption ability and concentration of alloying metals in the melt [61,62]. For example, theoretical estimation for crystals of NaCl type (niobium carbide belongs to this type) has shown that facets $\{111\}$ possess maximum adsorption ability, facets $\{110\}$ - somewhat smaller, and even more smaller for facets $\{100\}$ [61]. This causes the following effect. Growth velocity of facets $\{111\}$ reduces more, than that of facets $\{110\}$ and $\{100\}$ during alloying. At some concentration of alloying metals, growth velocity ratio for these facets changes to the

Fig. 19. Octahedron facets of carbide vertex in eutectic alloy with 5 mass.% NbC.

Fig. 20. Distribution of Ni (a), Nb (b) and Mo (c) in eutectic composite with 0.95 at.% Mo.

contrary (comparing with that of non-alloyed materials). Dependence of growth velocity of facets {111}, {110} and {100} on concentration of alloying elements is schemetically shown at Fig.21. At this figure three concentration intervals can be distinguished. Within every of the intervals one of the facets {111}, {110} and {100} has larger growth velocity, while eutectic has accordingly different typical morphology: trefoil, lamellar or fibrous. Two other intervals, within which growth velocities of facets {100} or {111} are minimal, can be also distinguished. These two intervals determine faceting (hexohonal or octahedral) of base crystals of carbide phase during alloying. Concentration boundaries of these intervals at the eutectic composite alloying with Cr, Mo or W are presented in Table 3. Similar changes in eutectic's alloys morphology during their alloying are observed in many systems of faceted-nonfaceted class, for example, Ni-TaC [32], Ni-Al-Cr [9], Co-Cr₇C₃ [63] and so on.

Analysis of Methods and Installations for Directional Crystallization of Eutectic Alloys and Single Crystals [64-66].

Modern high productive scientific and experimental equipment for directional crystallization must satisfy the following requirements: provide high and variable temperature gradients in the melt, create stationary and homogeneous heat flow through the crystallization front, have possibility to crystallize different materials, have no problems of interaction between the melt and the material of the mould, have possibility to control visually the position and the shape of solidification front.

Thus, process of directional crystallization is determined by two groups of parameters: heat-physical characteristics of the alloy itself, and technological one, determined by specific construction of the installation. The following relation must be fulfilled between them (for mobile systems with convection) [36,67]:

$$G_c / G_L = \chi_L / \chi_c + V_c \Delta H_m / G_L \chi_L, \quad (3)$$

where G_c, G_L, χ_c, χ_L - are temperature gradients and specific thermal conduction of crystal and melt accordingly; ΔH_m - heat of melting of the alloy.

If this condition is fulfilled, the transverse gradients, causing different distortions of the solidification front are absent. According to stability criterium, the ratio G_L / V_c must exceed the ratio of temperature interval of crystallization to diffusion coefficient. Then, approximately, for known conditions, maximum crystallization rate may be evaluated:

$$V_{\max} = G_L D / \Delta T, \quad (4)$$

where ΔT is determined by the amount of admixtures in the alloy, and by deviation of alloy's content from the eutectic one.

Fig. 21. Influence of alloying on growth velocity of different facets NbC crystal in eutectic composite (scheme).

From the other hand, at large crystallization rate the decisive role may begin to play the melting heat. Maximum rate is defined as a rate, at which G_L retains positive value and front of crystallization remains being slightly convex or plane (concave shape of the front promotes to the formation of new crystallization centers, spoiling the quality of the alloy). Maximum rate is determined by the formula [68]:

$$V_{\max} = (2\alpha\chi_c / cr)^{1/2} (Z^{1/2} - Z^{-1/2}), \quad (5)$$

$$Z = \{\Delta H_m + C(T_f - T_a)\} / \{\Delta H_m + C(T_f - T_e)\}, \quad (6)$$

Here C is specific thermal conduction, T_f - heater temperature, T_a - temperature of cooling agent, T_e - crystallization temperature of eutectic.

Relations (5) and (6) show that the higher temperature conductivity coefficient is and the less radius r of the sample is, the higher is permissible crystallization rate of furnace.

Thus, crystallization rate obeys to some restrictions. Besides upper limits, which are defined by the equations (5) and (6), crystallization rate has also minimal value, which depends on temperatures fluctuations of crystallization front. These fluctuations decrease thanks to more perfect stabilization of reverse rate of crystallization front and power of heater. It is approximately equal to 3 mkm/s.

High temperature gradient is created by means of following methods: raising the difference between temperatures of heat source and cooler, decreasing the thickness of crucible walls, using cooling agents with high thermal capacity (or thermal conduction). for example, tin or indium-gallium eutectic.

There exist different methods, which allow us to realize all enumerated requirements to directional crystallization of eutectic alloys. Among them, the most wide application have found continuous methods of traverse of the sample or of heater in vertical installation. First of all, it is directional crystallization by means of Bridgmen method.

Bridgmen method. In Bridgmen installation process of heating is realized by inductor or resistance furnace. The process is carried on in vacuum or in inert atmosphere. Ceramic (or other inert to the melt) mould is set on the watercooled copper crystallizer, which is traversing down with given rate ($1.4 \cdot 10^{-6}$ - $6.9 \cdot 10^{-5}$) m/s. System of shields provides certain temperature gradient at crystallization front. These devices are characterized by low temperature gradients (50-70°C/sm). Their shortcoming is inconstancy of heat resistance between cooler and crystallization front, which is increasing, while sample is pulled out from hot zone. Besides, rate of front transference does not coincide with rate of sample's transference.

There exist several modifications of Bridgman method. For example, between shields and cooler an additional heater of little power is set up. This results in increasing of temperature gradients in the melt and their stabilization. In other modification, directional crystallization is fulfilled by plunging mould into the melt of fusible metal (tin, lead, aluminium). This fusible metal, which is displaced during plunging of mould with sample, is poured into special capacity with heating. Level of this metal is constant during crystallization. Heat condition of crystallization are close to stationary. Another modification of this method consists in heating and cooling in liquid metal, which has small volatility of vapour, of ceramic mould with a sample. This allows us to decrease thickness of mould's walls considerably and to improve heat-physical parameters of crystallization.

Common shortcoming of discussed method is presence of ceramic mould, which is interacting with the melt of alloy. This causes changes in its chemical content and spoils surface quality of article. This also complicates construction of installation, when we try to stabilize heat flow and gradients at crystallization front.

Zone melting. This method is widely used for obtaining eutectic composites. It is fulfilled by means of induction or electron beam heating. Merits of this method are: relatively high temperature gradients (up to $150^{\circ}\text{C}/\text{sm}$ at induction melting and up to $500^{\circ}\text{C}/\text{sm}$ at electron beam heating); possibility to carry on crystallization by means of "floating zone" without ceramic crucible. The last allows us to obtain composites, based on active and refractory metals. Shortcomings of this method include following facts: a) temperature maximum is observed at the center of melted zone (this promotes convection); b) there exist restriction to overheating of melted zone, because its height is conditioned by alloys' density and surface tension; c) relatively low sizes of crystallization samples, usually, their diameter is equal to 3-10 mm and their length - up to 150 mm.

Chohralsky's method. Directionally crystallized composites can be also obtained by this method. Its essential shortcoming is heightened convection in the melt near crystallization front, inconstancy of the melt's level during process of crystallization and losses of heat by sample's radiation. There are known different variants of this method. Stepanov's method has obtained wide propagation. It consists in growing from profiling diagrams and allows us to obtain profiled samples. This method is applied during growing of crystals with low density and high transparency.

Continuous and halfcontinuous methods. Methods of pulling long bars through bottom of crucible are described in [69-72]. For stabilization of crystallization front outlet orifice of a little diameter is used. Heating is fulfilled around it. High temperature gradient is created by

means of watercooled cooler for obtaining samples with little diameter. Crystallizer must have a little taper for free pulling of sample and must not be moistened by the melt.

Installations, worked out in Institute of Metal Physics NAS Ukraine. All above-stated requirements are more completely fulfilled in this complex of installations, which consists of installation for electron beam zone melting and installation for directional crystallization by means of continuous casting. The first of them is characterized by high productivity (it has efficiency up to 85%), relatively simple exploitation, possibility to crystallize alloys, which differ essentially from each other by their physical-chemical properties (for example, temperature). The second one provides minimal possible convection in the melt (this means, that crystallization front is located in lower, the most cool part of crucible). It allows us to crystallize alloys of heightened length with different temperature gradients in the melt. It is also universal and close to experimental-industrial technology.

The main part of installation for electron beam zone melting is ring electron beam heater, which consists from body, two electrostatic lenses, which deviate electron beam in such a way, that center of melted zone of the sample was situated at the level of lower edge of external electrostatic lens; ring cathode, fulfilled from tungsten wire with diameter 0.5 mm. Heater construction has been worked out to optimum one by varying its main sizes. It provides stable work of heater during no less than 160 hours.

Conclusion

Analysis of regularities of composite structure formation in eutectic alloys during directional solidification showed, that these regularities are determined by peculiarities of fusibility diagram structure of corresponding systems and by temperature-concentration parameters of eutectic transformation $L=\gamma+Me'C$. It was established, that in considered systems saddle point on fusibility diagram, which corresponds to quasinonvariant eutectic equilibrium ($\Delta T_e=0$), does not belong to according stoichiometric section metal-interstitial phase and is displaced to the side of alloying element.

Composite growth region, in which during directional solidification, there is formed highly perfect composite structure, is expanded with rate increase and removed to the side of interstitial phase. This displacement is proportional to the value of thermodynamic potential of this phase transformation. The most perfect structures are formed in the alloys, where composition corresponds to the boundary of cooperative growth region (RCC) from the base metal side. It was established, that eutectic composite's morphology is determined by symmetry of crystallographic direction of carbide phase primary growth.

Change of crystallization rate and doping alloys with solute in carbide phase elements, changes this direction and also causes the change of eutectic composite structure.

Investigation of Ni-Mo-C system was carried out. It was established, that eutectic transformation $L=\gamma+\text{Mo}_2\text{C}$ is described by a curve, corresponding to the equation: $\ln C_c = 6.236 - 1.526 \ln C_{\text{Mo}}$. Position of the region of cooperative crystallization (RCC) was determined. Directionally crystallized alloys $\gamma+\text{Mo}_2\text{C}$, which corresponds to this region, are characterized by regular structure. Optimal alloys for directional crystallization correspond to tie-line of three phase equilibrium $L=\gamma+\text{Mo}_2\text{C}$. They are characterized by the highest melting temperature (1350°C) and zero temperature interval of eutectic transformation. Region of cooperative growth along this tie-line has maximal size. Ni-Mo-C system is very actual as a basis for creation of new eutectic materials.

It has been shown, that the main shortcoming of alloys, based on titanium aluminide, is their low technological plasticity at room temperatures. The following methods lead to essential improvements in low temperature plasticity and high temperature strength of these materials. They are: production of single crystal state, formation of oriented two-phase structure by interchanging of plastic and fragile layers, performance of alloys, which are pure from oxygen, selecting optimal alloying system.

Installations, which were worked out in Institute on Metal Physics NAS Ukraine for directional crystallization of eutectic alloys and single crystals, are distinguished by high productivity and efficiency, relatively simple maintenance and possibility to solidify alloys, which differs by their physical-mechanical properties.

REFERENCES

1. J.H.Lee, J.D.Verhoeven, J.Grystal Growth, 143 (1994) 86.
2. Mater.Eng., 86 (1977) 22.
3. M.Rabinovitch, J.F.Stohr, T.Khan, Mater.et techn., (1981) 387.
4. Патент N 4292076, США (1981)
5. Патент N 2040931, Франция (1971)
6. Патент N 2441665, Франция (1980)
7. Патент N 4589937, США (1986)
8. С.Т. Кишкин, Светлов И.Л., Логунов А.В. и др., ФММ, 53 (1982) 1180.
9. Г.В.Купченко, Л.Н.Нестерович, Структура и свойства эвтектических композиционных материалов, Наука и техника, Минск, 1986, с. 200.
10. J.P.Stohr, T.Phan, Rech. Aérosp., (1980) 399.
11. О.М.Барабаш, И.В.Буря, С.П.Ошкадеров, Металлы, N 5 (1992) 92.
12. Y.W.Kim, J.Metals, 41 (1989) 24.
13. J.Wittenauer, C.Bassi, B.Walser, Scr. Met., 23 (1989) 1381.
14. R.S.Stagle, Adv. Mater. and Process, 137 (1990) 2990.
15. R.S.Mishra, D.Banorjee, Scr. met. et mater., 24 (1990) 1477.
16. W.A.Thompson, Mater. Sci. and Eng., 152 A (1992) 578.
17. M. Petters, Y.T.Lee et al., Titanium (1990) Prod. and Appl. Proc. Techn. Progtion, Ohio, 1990, p.199.
18. W.P.Hon, S.K.Wu, Mater. Sci. and Eng., 131 A (1991) 85.
19. С.И.Михайлов, С.Г.Гладунов, Г.А.Павлов и др., Авиационная промышленность, N 11 (1991) 37.
20. Cher Chunhe, Ding Youngfeng, Proc.1st Int.Conf.Met.and Mater. Sci. Tungsten, Titanium, Rare Earth and Antimony, Beijing Oxford etc., 1989, p. 948.
21. Заявка N 2217432 (Япония), Опубл. 30.08.90.
22. C. Servant, R.Penelle, Met. et etud. Scr. Rev. met., 88 (1991) 521.
23. T.Zia, B.Wang, D.Zou, H.Ma et al., Mater. Sci. and Eng., 152 A (1992) 317.
24. D.Chen, M.Es-Souni, P.A.Beaven, R.Wagner, Scr.Met., 25 (1991) 1363.
25. M.Es-Soini, R.Wagner, P.A.Beaven, Mater. Sci. and Eng., 153 A (1992) 444.
26. J.P.A.Lolvander, S.A.Count, P.Kurath et.al., Phil. Mag. Lett., 59 (1989) 289.

27. С.А.Савицкий , Г.С.Бурханов, Монокристаллы тугоплавких и редких металлов, Металлургия, М., 1972, с. 170.
28. F.Heredia, D.P.Pope, Mat. Res. Soc. Symp. Proc., 91 (1987) 213.
29. Y.Minonishi, M.H.Yoo, Phil. Mag. Lett., 61 (1990) 203.
30. Y.Minonishi, Phil. Mag., 63 A (1991) 1085.
31. А.К.Шурин, Порошковая металлургия, N 1 (1973) 50.
32. В.Курц, П.Р.Зам, Направленная кристаллизация эвтектических сплавов, Металлургия, М., 1980, с. 272.
33. К.И.Портной, Б.Н.Бабич, И.Л.Светлов, Композиционные материалы на никелевой основе , Металлургия, М., 1979, с. 274.
34. High temperature alloys for gas turbines, Ed. by D.Coutsouradis et al., Applied science publishers LTD, 1978.
35. А.В.Сторонкин, Термодинамика гетерогенных систем , Изд-во ЛГУ, ч. III 1969, с. 189.
36. Т.Я.Великанова, Сб. Диаграммы состояния в материаловедении , ИПМ АН УССР, Киев, (1980) 45.
37. В.Н.Еременко, Т.Я.Великанова, Л.В.Артюх, Сб. Диаграммы состояния в материаловедении, Наукова Думка, Киев, (1984) 28.
38. Барабаш О.М., Гриднев В.Н., Легкая Т.Н., Металлофизика, 9 (1987) 13.
39. О.М.Барабаш, Т.Н.Легкая, Сб. Стабильные и метастабильные фазы в материалах, ИПМ АН УССР, Киев, (1987) 53.
40. А.А.Смирнов, М.А.Кривоглаз, Вопросы физики металлов и металловедения, 1 N 6 (1955) 107.
41. А.А.Смирнов, М.А.Кривоглаз, Вопросы физики металлов и металловедения, 1 N 2 (1955) 311.
42. А.А.Смирнов, Молекулярно-кинетическая теория металлов, Наука, М., 1966, с. 488.
43. О.М.Барабаш, А.К.Шурин, Изв. АН СССР. Металлы, N 5 (1978) 195.
44. О.М.Барабаш, ДАН УРСР, N 11 (1978) 1037.
45. О.М.Барабаш, Сб. Диаграммы состояния металлических систем, Наука, М., (1981) 161.
46. Л. Кауфман, Х.Бернстейн, Расчет диаграмм состояния с помощью ЭВМ, Мир, М., 1972, с. 326.
47. В.Н.Еременко, Т.Я.Великанова, Л.В.Артюх, Тройные системы молибдена с углеродом и переходными металлами IVA группы, Наукова Думка, Киев, 1985 с. 296.
48. О.М.Барабаш , Р.В.Горская , Т.Н.Легкая и др. Порошковая металлургия, N 8 (1990) 67.

49. О.М.Барабаш , Р.В.Зверева , Т.Н.Легкая и др., Металлофизика, 11 N 5 (1989) 40.
50. О.М.Барабаш, Р.В.Горская, Т.Н.Легкая, Изв. АН СССР. Металлы, N 1 (1990) 82.
51. С.Т.Кишкин, И.Л.Светлов, А.В.Логунов и др., ФММ, 53 (1982) 1180.
52. Е.Фромм, Е.Гебхардт, Газы и углерод в металлах, Металлургия, М., 1980, с. 711.
53. L.Kaufman, H.Nesor, CALPHAD, 2 No 1 (1978) 55.
54. А.К.Шурин, Г.П.Дмитриева, И.Л.Светлов, Металлофизика, 8 N 2 (1986) 83.
55. О.М.Барабаш, В.Н.Гриднев, Т.Н.Легкая, Изв. АН СССР. Металлы, N 6 (1985) 211.
56. О.М.Барабаш, В.Н.Гриднев, Т.Н.Легкая, Металлофизика, 4 N 5 (1982) 20.
57. О.М.Барабаш, И.В.Буря, Т.Н.Легкая, Материалы 7-го международного симпозиума по композиционным материалам, Братислава, Словакия, 1990, с. 172.
58. О.М.Барабаш, И.В.Буря, М.Ю.Масимов и др., Металлофизика, 11 N1 (1989) 18.
59. Б.Е.Патон и др., Жаропрочность литейных никелевых сплавов и защита их от окисления, Наукова Думка, Киев, 1987, с. 254.
60. Р.Эллиот, Управление эвтектическим затвердеванием, Металлургия, М., 1987, с. 351.
61. О.М.Барабаш, Б.В.Егоров, Р.И.Барабаш, Металлофизика, 13 N 7 (1991) 9.
62. А.А.Чернов, Современная кристаллография, Наука, М., т.3 1980, с.233.
63. Патент N 40584157, США (1977).
64. Авторское свидетельство N 1746755, СССР (1992).
65. Авторское свидетельство N 1400155, СССР (1987).
66. Авторское свидетельство N 1499997, СССР (1988).
67. P.Sahm, Radex Rdsch., No 1-2 (1980) 20.
68. J.D.Livingston, H.E.Cline, E.F.Koch, R.R.Russell, Acta Met., 18 (1970) 399.
69. Патент N 543327, (Швейцария).
70. A.J.Perry, A.R.Nicoll, K.Phillips, J. Mater. Sci., 8 (1973) 1340.
71. Y.Mimura, Y.Okomura, Y.Komazama, Japanese J. of Phys. Appl., 19 (1980) 269.
72. J.D.Verhoeven, R.H.Homer, Met. Trans., 1 (1970) 3437.

CONTENT

**DIRECTIONAL SOLIDIFICATION OF Ni-BASED EUTECTIC ALLOYS AND
HIGH PURITY Ti₃Al SINGLE CRYSTALS USING AN ANNULAR
ELECTRON BEAM GUN.**

Task 2

Principle investigator Barabash O. M.

EXPERIMENTAL PROCEDURE. 2

Materials. 2

THERMAL ANALYSIS. 2

**Installation for Directional Crystallization of Eutectic Alloys and
Single Crystals by Means of Uncrucible Electron Beam Zone Melting. 3**

RESULTS OF INVESTIGATION AND THEIR DISCUSSION. 9

**Concentration-Temperature Parameters of $L \rightleftharpoons Mo_2C$ Eutectic
Transformation in Fourfold Ni-Mo-Al-C System and main
Regularities of Oriented Structure Formation 9**

**Regions of Controlled Cooperative Crystallization in the System
Ni-Mo-Al-C. 20**

**Concentration-Temperature Conditions of α phase Formation
in Ti₃Al Based Alloys. 24**

Phase Transformations of Ti₃Al Based Alloys in Solid State 25

Investigation of Fusible Diagram of Ti-Al System 30

DIRECTIONAL SOLIDIFICATION OF Ni-BASED EUTECTIC ALLOYS AND HIGH PURITY Ti_3Al SINGLE CRYSTALS USING AN ANNULAR ELECTRON BEAM GUN.

Task 2

Principle investigator Barabash O. M.

In this part we have described the results of investigation of fourfold system Ni-Mo-Al-C in the region of $L=\gamma+Mo_2C$ three-phased eutectic equilibrium as well as results of investigation of formation of DO₁₉ type structure in Ti_3Al based alloys.

In the base ternary system Ni-Mo-C eutectic transformation is monovariant and occurs in the certain temperature interval. Its peculiarity is nonmonotonous dependence of transformation temperature on content [1,2]. Existence of maximal point of this dependence, corresponding to zero temperature interval of eutectic transformation, means, that such eutectic alloy solidifies at constant temperature and possesses maximal ability to form composite structure during directional solidification. In this connection it was necessary to find out if these peculiarities of eutectic transformation are retained in Ni-Mo-C-Al system and to determine the four component eutectic alloys with little temperature interval of melting;

Purpose of this part of our investigation was to determine :

- * concentration and temperature parameters of eutectic transformation $L \leftrightarrow \gamma - Mo_2C$ in the Ni-Mo-C-Al system at different Al concentrations (2-8 w% Al);
- * influence of Al concentration on the regularities of oriented structure formation during directional solidification;
- * temperature intervals of solid/solid and solid/liquid phase transformations in Ti_3Al alloys at different Al concentrations in the interval 5-35at%.

EXPERIMENTAL PROCEDURE.

Materials.

Alloys for investigation were prepared in the laboratory electroarc furnace in the atmosphere of purified argon on the watercooled copper hearth. As charge materials there were used nickel with HO marking, high pure molybdenum, spectral pure carbon, 99.999% pure aluminium and iodided titanium.

THERMAL ANALYSIS.

Temperature of the beginning and the end of alloys melting was determined by means of installation for thermal analysis, worked out in the Institute of Metal Physics of Ukrainian National Academy of Science. This method is based on the registration of phase transformation temperature at the constant heat flow from the heater to the sample (by Stock's method). It also allows us to determine very accurately temperature of the beginning and the end of phase

transformation in the investigated samples. The scheme of the installation is shown at Fig.1. It consists of the heater (1), inside of which there is thermostat (2) with the sample in the crucible (3). Under crucible there are two temperature sensors (4) and (5), one more temperature sensor (6) is situated at the thermostat wall (2). Temperature sensor (4) is connected with self-recorder (7) for registration of sample's temperature, sensors (5) and (6) are switched on differentially. Their signals are sent to the temperature regulator (8). The velocity of heating or cooling of the sample is determined by the value of temperature difference between the sample and thermostat, which is set on the temperature regulator. Usually it is equal to $4.2 \cdot 10^{-2} \text{ }^{\circ}\text{C/s}$. Construction of the installation provides thermal stabilization of cold junctions of thermocouples at 0°C and allows us to obtain thermograms with great accuracy up to the temperature 1700°C . Precision of determination of phase transformation temperatures is equal to $\pm 5^{\circ}\text{C}$, melting interval of the samples was determined to precision $\pm 2^{\circ}\text{C}$.

For plotting the calibration diagram we have registered thermograms of pure iron ($\alpha \rightarrow \gamma$ transformation -910°C , $\gamma \rightarrow \delta$ transformation -1391°C , melting -1536°C) and also copper (983°C), nickel (1450°C) and titanium ($\alpha \rightarrow \beta$ transformation -882°C). Examples of calibration diagrams are shown at Fig.1b. Critical points were determined by intersection of tangents to the corresponding parts of thermograms. Before filling of the working chamber with inert gas, there has been reached vacuum up to the pressure 10^{-5} mPa in its volume. Survey of thermograms of nickel based alloys with weight 30g was made in crucibles from aluminum oxide in the pure helium atmosphere at the gas pressure inside the installation equal 0.09 mPa . In order to increase precision of determination of phase transformation temperature in solid state, thermal analysis of alloys based on titanium aluminide (Ti_3Al) was carried out without crucibles. The samples were situated directly on thermocouple junctions.

Structure investigations were fulfilled by means of microscope "NEOPHOT-32" JEOL, X-ray spectroscopy - by means of electron microanalyser "CAMECA"

Installation for Directional Crystallization of Eutectic Alloys and Single Crystals by Means of Uncrucible Electron Beam Zone Melting.

Directional crystallization of alloys was carried out by means of uncrucible zone melting of blanks with diameter 8mm and length 110 mm by disk electron beam. Photograph and block scheme of the installation for directional crystallization by means of electron beam zone melting are shown at Fig.2. Technical parameters of the installation are presented in Table1. This installation consists of the following main items (Fig.1b): ring vacuum watercooled chamber (1), in which electron beam heater and crystallized sample are situated (the sample is fixed up and the heater is moving upwards

Fig. 1. General view of the installation for thermal analysis (a) and examples of calibration thermograms (b) for pure nickel, iron and titanium; T - temperature, τ - time

Fig. 2. Installation for directional crystallization by means of electron beam zone melting (a) and its block-diagram (b)

during crystallization); control panel (2), where vacuum system, a device for heater transference and device for automation and control of crystallization process are situated; supply pulley (3) with one-phased electron stabilizer of the network voltage (220V), incandescing and high voltage transformers for electron beam gun supply.

The installation provides one parametric regulation of electron beam heater power by stabilizing the current of electron beam. Electric signal from positive pole of high voltage source is coming through millammeter A to the load resistance R (10 Ohm, 2Vt) to the ground. In the opposite direction through R and regulated high-precision resistance R the regulating signal is coming from stabilized source of supply. Voltage difference U, created by these currents at the resistance R is coming to the input of the amplifier Y. From the output of this amplifier the controlling signal is formed for thiristor block BT01, which is connected with the primary winding of the cathode incandescing transformer. Regulation of cathode incandescing power of the electron beam gun is performed depending on the sign and value of U.

At the same time electron beam gun is working under such conditions, that high voltage set on it does not depend on the value of electron beam stream. Heater is displaced by means of spiral pair nut-screw and worm reducer, using the direct current motor with nominal voltage 27V. Regulation and stabilization of rotation velocity of drive motor is carried in as following: from speed-voltage generator being placed on the motor shaft, the measured signal is compared with the given voltage value, the last one is proportional to given velocity of displacement. The difference of these two voltages is a controlling signal set on the impulse generator. Frequency of these impulses depends on the value and sign of controlling signal. Then these impulses are amplified to the amplitude 80V and are set on the displacing motor, defining the rate of its rotation. Such control scheme allows to change the rate of rotation in wide ranges (differing in 100 times) and to change rotation rate without essential decrease of the rotational moment at the motor shaft. Indication of heater displacement velocity is performed by means of digital voltmeter through calibration shunt of speed-voltage generator.

The main unit of the installation is the ring electron beam heater (Fig.3), consisting of frame (1), two electrostatic lens-screens (inner-(2) and outer-(3)), which deflect electron beam in such a way that the center of samples' melted zone is situated at the level of lower edge of outer screen(3)(Fig.4). Ring cathode (4), made from tungsten wire with diameter 0.5mm is suspended by means of 12 molybdenum bearings (5) on the gun's frame. Supply for the cathode incandescing is set through the two neighbour bearings. Gun's construction is made optimal by varying its main parameters such as cathode ring diameter, electrostatic screen cones' angles and diameters and provides stable and reliable work of electron beam heater during prolonged time (more than 160 hours).

Fig. 3. Ring electron-beam heater (a) and its diagram (b)

Fig. 4. Photograph of the process of eutectic alloys directional crystallization by means of electron-beam zone melting. Arrow indicates the position of crystallization front

By means of this installation we have got a series of directionally crystallized samples of eutectic alloys and single crystals based on nickel, cobalt, molybdenum, niobium and also Ti_3Al . Typical crystallization conditions of nickel based eutectic alloys are presented in Table 2.

It can be seen that it is necessary to decrease electron beam power when heater displacement velocity is increasing.

RESULTS OF INVESTIGATION AND THEIR DISCUSSION.

Concentration-Temperature Parameters of $\text{L} \leftrightarrow \text{Mo}_2\text{C}$ Eutectic Transformation in Fourfold Ni-Mo-Al-C System and main Regularities of Oriented Structure Formation

During the investigation of Ni-Mo-Al-C system we have determined five groups of alloys, differing in aluminium content. In each group aluminium content was constant and was equal to 5.0; 8.0; 10.4; 12.6 and 15.0% correspondingly. The research was fulfilled in such a way that the results of the investigation of previous group were taken into account when we determined alloys composition of the subsequent group. Total number of investigated alloys was 37, their composition is shown at Fig 5a.

It was established that in Ni-Mo-Al-C system at high temperatures there exists wide region of two-phased $\gamma + \text{Mo}_2\text{C}$ eutectic alloys with the same structure as that of eutectic alloys of base Ni-Mo-C ternary system. But when oriented structure in these alloys is formed and they are subsequently cooling, the decay of the supersaturated solid solution with the formation of γ' -particles based on Ni_3Al takes place. As a result of this process in the alloys $\gamma/\gamma' + \text{Mo}_2\text{C}$ composite structure is formed, in which in addition to fibres and lamellae of carbide phase, there are also present disperse γ' -phase particles. The same structure can be formed, using special thermal treatment. As in the most of nickel superalloys, γ' -phase content in the investigated composites is determined by aluminium content and reaches 50v% with respect to the matrix in alloys with 12.6at%Al.

Thermal analysis of the investigated alloys established the existence of a series of ($\gamma/\gamma' - \text{Mo}_2\text{C}$) eutectic alloys C ($i=0-5$) with zero melting interval. Such alloys taken as a whole are shown by smooth curve at Fig.6. Its projection on the concentration triangle of Ni-Mo-C ternary system is shown at Fig.5a. Its concentration coordinates and melting temperatures of the corresponding alloys are presented in Table 3 and at Fig.5b. The temperature change along this curve is shown at Fig.7. The curve itself is limited by points C_0 and C_5 . Point C_0 belongs to the base ternary system Ni-Mo-C and corresponds to the composition of eutectic alloy with maximal melting temperature, meanwhile point C_5 belongs to the four component alloy. Composition and melting temperature of this four component alloy are defined by the condition of contact of two liquidus surfaces: $\gamma \leftrightarrow \text{L}$ and $\text{Mo}_2\text{C} \leftrightarrow \text{L}$. The

Table 1

Technical data of the electron-beam melting installation

N	Parameter and units of measurement	Value
1.	Total powerb(kw)	2
	including the electron beam	1.0
2.	Size of crystallized samples (mm)	
	diameter	2-10
	length	60-130
3.	Source of heating	ring
4.	Accelerating voltage (kv)	
	operating no more than	12
	idle motion no more than	16
5.	Operating atmosphere	
	vacuum (Pa)	$6.7 \cdot 10^{-4}$
6.	Displacement velocity of melted zone (m/s)	
	in thq range	$5.6 \cdot 10^{-6}$ - $4.2 \cdot 10^{-2}$
7.	Temperature gradient at the crystallization front in the melt with sample's diameter 8mm ($^{\circ}\text{C}/\text{sm}$)	$0.1 T_m$

Table 2

Eutectic alloy of Ni-Mo₂C system containing
20.12 at.% Mo, 5.1 at.% C, 74.78 at.% Ni. Sample's
diameter - 8 mm, zone height - 8 mm

V_c m/s $\cdot 10^{-6}$	U - electron beam, kv	I - electron beam, ma	I - incandescing current in primary circuit of incandescing transformer a
0.11	10	28.5	1.35
0.22	10	28.3	1.33
0.33	10	28.0	1.30
0.44	10	27.7	1.30
0.55	10	27.3	1.28
0.66	10	26.8	1.28
0.88	10	26.8	1.25

Fig. 5. The curve of $L \rightleftharpoons \gamma + Mo_2C$ eutectic transformation occurring at constant temperature in the fourfold system (projection on concentration triangle Ni-Mo-C) (a) and eutectic alloys compositions (b); darkened symbols correspond to eutectic alloys with zero melting intervals; digits show aluminium content, % (at.): 1 - 0, 2 - 5, 3 - 8, 4 - 10.4, 5 - 12.6, 6 - 15

Fig. 6. The surface, formed by tie-lines of ternary eutectic equilibrium $L \rightleftharpoons \gamma+Mo_2C$ in Ni-Mo-Al-C system

Table 3

(continuation)

1	2	3	4	5	6	7
30.	57.58	20.80	12.62	9.0	unknown	C ₅
31.	48.92	26.463	12.62	12.0	unknown	
32.	46.03	28.35	12.62	13.0	unknown	
33.	76.3	6.8	13.05	3.4	1350 - 1365	
34.	77.0	6.0	14.0	3.0	unknown	
35.	75.0	5.0	15.0	5.0	1350 - 1355	
36.	70.0	5.0	15.0	10.0	1325 - 1330	
37.	73.982	8.518	15.0	2.5	1357 - 1360	

Table 4

Concentration-temperature parameters of $L \rightleftharpoons \gamma + \text{Mo}_2\text{C}$
eutectic transformation in fourfold Ni-Mo-Al-C system

C _i	Eutectic alloy composition , % (at).				Eutectic transformation temperature, °C	Interval eutectic transformation, °C
	Ni	Mo	Al	C		
C ₀	74.78	20.12	0.0	5.1	1350	0
C ₁	74.30	16.40	5.0	4.3	1365	0
C ₂	75.51	13.09	8.0	3.4	1370	0
C ₃	75.6	11.0	10.4	3.0	1372	0
C ₄	76.36	8.52	12.62	2.5	1375	0
C ₅	75.0	5.0	15.0	5.0	1330	0

Fig. 7. Aluminium influence on the temperature of three phased eutectic equilibrium $L \rightleftharpoons \gamma + \text{Mo}_2\text{C}$ in Ni-Mo-Al-C system

melting temperature of such alloy corresponds to the absolute temperature maximum of eutectic equilibrium $L \leftrightarrow \gamma + Mo_2C$ in the fourfold system.

As it follows from the obtained data, that increase of aluminium content results not only in the decrease of carbide phase in eutectic, but also in the displacement of alloy's content to the stoichiometric section Ni-Mo₂C (ratio between molybdenum and carbon content in the alloys is tending to the stoichiometric carbide composition). Thus, carbide phase content changes from 16v% in eutectic alloy without aluminium doping to 8v% in alloys, doped with 12.6at% Al. The ratio between molybdenum and carbon concentrations under these conditions changes from 3.9 to 3.4 correspondingly. Melting temperature of γ/γ' -Mo₂C eutectic alloys also changes proportionally to aluminium content and increases from 1350°C for alloys without aluminium doping to 1375°C for alloys, doped with 12.6at% Al.

Thermograms of eutectic alloys with different aluminium content are shown at Fig.8. It should be noted, that content deviation from optimal one to the direction of Mo or C in the region of each alloy group causes the decrease of eutectic transformation temperature and expansion of temperature interval of its proceeding. For example, at Fig.8(c,d) there are shown thermograms of alloys with 8% Al, situated to the right and to the left of eutectic composition. It can be seen, that for these alloys temperature decrease of the beginning of eutectic transformation to 1365°C takes place and there appears temperature interval. Simultaneous increase of aluminium and carbon content leads to the appearance of ternary $\gamma + C + Mo_2C$ eutectic. Its structure is shown at Fig.9. Such structure is accompanied by decreasing of melting (crystallization) temperature of alloys (descending part of the temperature curve at Fig.7 - point C₃). Melting temperature of this ternary eutectic is equal to 1330°C, moreover it is melting at constant temperature.

Existence of this ternary eutectic indicates, that concentration dependence of fourfold $\gamma + Mo_2C + C \leftrightarrow L$ eutectic transformation temperature in the system Ni-Mo-C-Al is not monotonous and has maximum. Position of this maximum exactly corresponds to the above-stated ternary eutectic composition.

Data on quantitative microprobe analysis together with the results of thermal analysis allowed us to determine the direction of three-phased $L \leftrightarrow \gamma + Mo_2C$ eutectic equilibrium tie-line (conoda) in this system. Let us note that according to these data Al solubility in carbide phase is small (less than 0.04 at %).

Equations of tie-lines (conoda) for three-phased equilibrium $L \leftrightarrow \gamma + Mo_2C$ which passes through eutectic alloys with 5.0; 8.0; 10.4; 12.6 at% Al look like:

$$C_{Mo} = 1.332C_C - 2.332C_{Al} + 22.341;$$

$$C_{Mo} = 1.203C_C - 2.203C_{Al} + 26.636;$$

$$C_{Mo} = 1.05C_C - 2.05C_{Al} + 31.76,$$

where C_C , C_{Mo} , C_{Al} - are concentrations (at%) of carbon, molybdenum and aluminium correspondingly.

Fig. 8. Thermograms of the alloys of Ni-Mo-Al-C system:
(copies); a - alloy C_1 , b - alloy C_2

Fig. 8. (continuation)
c - alloy N 13, d - alloy N 14

Fig. 8. (continuation)
e - alloy C_3 , f - alloy C_4

Fig. 9. Structure of ternary eutectic $\gamma + \text{Mo}_2\text{C} + \text{C}$

The set of such tie-lines in tetrahedron of fourfold system forms lined surface nmp, dividing its volume into two parts (Fig.6). In each of these parts the vertex of tie-line (conoda) triangles $L \leftrightarrow \gamma + \text{Mo}_2\text{C}$, which define the composition of the melt, are directed to one side from lined surface. Moreover, transition from one type of tie-line triangles to another occurs by "fastening" them into straight line. Normal $\mathbf{n}$ to one of these tie-lines, situated in the plane, tangent to this lined surface, gives the direction of temperature gradient in considered region of tetrahedron. Perpendicular to this normal plane is isothermal and defines the position of tie-line triangles in the neighbourhood of local temperature maximums of eutectic transformation. This means, that there are no triangles, situated on the tangent surfaces to the region nmp. Such position of lined surface in the tetrahedron of fourfold system allows us to triangulate this system with sufficient reliability on the tie-lines of eutectic equilibrium and to present it as a set of quasiternary sections with common base-Mo-C rib.

Eutectic transformation $L \leftrightarrow \gamma + \text{Mo}_2\text{C}$, situated in the plane of each quasiternary section, possesses all peculiarities which are characteristic for ternary system Ni-Mo-C. For example, in each section there is its own tangent point of two liquidus isotherms $\gamma \leftrightarrow L$ and $L \leftrightarrow \text{Mo}_2\text{C}$. Eutectic alloy (C_1), corresponding to this point possesses maximal temperature and zero melting temperature interval. Ensemble of sets of such curves forms funnel-shaped surface of three-phased eutectic equilibrium in the volume of concentration tetrahedron, and set of C_1 points forms smooth curve on its surface. Thus, eutectic alloys, situated on the curve $C_0 C_5$, are two-phased, have almost zero melting intervals and are most actual for production of composite materials on its basis by means of directional crystallization.

Regions of Controlled Cooperative Crystallization in the System Ni-Mo-Al-C.

Cooperative crystallization region (CCR) was defined for a section, drawn along the tie-line of three-phased eutectic equilibrium. This tie-line contains eutectic alloy with 12.6at% Al, as it corresponds to the absolute temperature maximum of three-phased equilibrium $L \leftrightarrow \gamma + \text{Mo}_2\text{C}$ in fourfold Ni-Mo-Al-C system. Compositions of the researched alloys and conditions of their directional solidification are shown at Fig.10. Using the results of thermal analysis and optical metallography of this alloy's structure we determined polythermal section of fusible diagram and found the position of controlled crystallization region. Outside of this region it is not possible to obtain regular structure. In its turn, controlled crystallization region consists of three subregions. In each of them its own type of structure is formed: in two of them in alloy's structure in addition to oriented eutectic there are present oriented dendrites of γ -Ni or Mo_2C carbide. Between these two subregions the cooperative crystallization region (CCR) is situated. It is characterized by formation of completely

Fig. 10. Polythermal sections of fusible diagram of fourfold Ni-Mo-Al-C system, carried out through corresponding tie-lines, which contain eutectic alloys of C_0 composition (a) and C_4 (b) and cooperative crystallization regions (CCR);

○ - thermal analysis, ● - alloys belonging to CCR,
 ○ - alloys outside CCR

"quasieutectic" structure (Fig.11). In its own turn, CCR is also divided into two subregions:

- region of composite growth, within which alloys are solidified with plane front;
- region of cellular solidification.

In the first region of dendrite-cooperative crystallization from nickel side (Fig.10) nickel based γ -solid solution is the phase, that originates and leads the alloy's crystallization. This phase is crystallized as nickel dendrites, oriented in the direction [001] with the main axis parallel to sample's axis. Size of these dendrites and extent of their sprouting into the melt decreases as alloy's composition approaches the boundary of CCR. Right at the CCR boundary phases that originate and lead the alloy's crystallization substitute. Molybdenum carbide begins to play now this role. Under these conditions crystallization of alloy begins from formation and subsequent growth of carbide crystals, from which eutectic colonies themselves are developing afterwards. These eutectic colonies form composite structure of an alloy. The increase of crystallization rate causes slight expansion of CCR relatively to eutectic composition (Fig.10). The boundary of this region from nickel side coincides at low temperatures with the projection of the line ET (eutectic transformation). Alloys, situated at this boundary, crystallize with the most stability and with the least quantity of defects. Such high stability may be explained by the fact that, inevitably occurring fluctuations of alloys' composition and of the velocity of displacement of solidification front do not take the alloys outside of CCR.

As was stated above, within the CCR alloys possess regular oriented two phased ($\gamma + \text{Mo}_2\text{C}$)-structure, which was formed directly during directional solidification. Then, during following cooling to 1250°C Ni_3Al based γ' -phase is separated from γ -solid solution and the alloy acquires three-phased $\gamma/\gamma' + \text{Mo}_2\text{C}$ structure. It consists of γ -matrix with disperse γ' -phase particles and molybdenum carbide looking like faceted lamellae or fibres and bands (Fig.11 b,c). Lamellae of carbide phase are able to disintegrate in their plane, thus they keep constant alloy's composition and form quasifibrous parts of structure. When crystallization rate is increased higher than 2.0sm/h, in these alloys there occurs the loss of stability of the plane front of crystallization and cellular structure is developing (Fig.11d), which decreases the extent of perfectness of composite structure.

Comparing the obtained results with concentration-temperature parameters of the existence of eutectic equilibrium in ternary Ni-Mo-C system we can see, that doping with aluminium brings to the decrease of carbide phase volume part in the eutectic and to the increase of it's melting temperature. Such effect can be understood, if we accept, that $L \leftrightarrow \text{Mo}_2\text{C}$ liquidus surface in fourfold system has a shape of stretched paraboloid, being turned by it's large axis inside Ni-Mo-Al-C tetrahedron. Liquidus $L \leftrightarrow \gamma$ -Ni looks like convex surface, and with temperature decrease this surface adjoins to Ni-Mo-Al ternary system, because the differences in the values of concentration coordinates of metal components

Fig. 11. The structure of eutectic alloys in the region of cooperative crystallization; a - obtained on the conditions of plane crystallization front; b -, c- selective etching: b - the matrix is removed, c - carbide fibres are removed; d - obtained in the conditions of cellular front

(C_{Mo}^L , C_{Al}^L) and of carbon C_C^L increase. At such arrangement of the surfaces their touching will take place at higher temperatures and it will correspond to the alloys' compositions with lower carbide phase content and will displace to carbon side.

Using thermodynamic analysis we have shown, that the formation of $L \leftrightarrow Mo_2C$ liquidus surface in the shape of stretched paraboloid will take place after doping the eutectic alloy with the elements, having negligible solubility in carbide phase. If, at the same time, alloying element will possess significant solubility in Ni-based γ -solid solution, than in such system the existence of bivariant two phased eutectic alloys with zero melting (crystallization) interval is possible.

As a result of the investigation of directionally crystallized alloys it was established, that doping with aluminium does not cause the decrease of the stability of the plane front of solidification. That's why interval of crystallization rates, at which the formation of composite structure takes place, is the same as for the alloys, corresponding to the base Ni-Mo-C ternary system. Region of composite growth at the equilibrium diagram becomes more symmetric relatively eutectic composition. It indicates, that doping with aluminium decreases anomalousness of γ - Mo_2C eutectic alloys, thus moving them to the side of normal eutectic type according to their classification.

Concentration-Temperature Conditions of Phase Formation in Ti_3Al Based Alloys.

Intensive investigations of these alloys based on the Ti-AL system intermetallics (carried out in many centers on materials science) showed, that they are very actual as high temperature aircraft materials. These investigations also showed their main shortage-fragility at room temperatures and as a result of it - low corresponding to manufacturing requirements. But ability of such materials for plastic deformation may be improved. So in particular, to the present moment, for Ti_3Al based alloys it is established that their plasticity during extension may be increased to the level 2-4%.

It should be noted that possibilities for improvement of plasticity properties of such alloys are not settled. One of such methods for increasing plasticity level of intermetallics is their producing in single crystal state. Also we may expect, that for these alloys increase of plasticity properties can be achieved by the decrease of distant order degree and the tetragonal degree of crystal structure

All this especially refers to alloys based on Ti_3Al intermetallic, and makes it very actual to work out methods for obtaining high pure single crystals based on this intermetallic as to determine concentration-temperature conditions of the formation of DO_{19} type superstructure (α_2 -phase).

There are known several variants of Ti-Al equilibrium diagram [4-8]. The main difference between them is in the absence of coincidence among the data

about Ti_3Al intermetallic formation mechanism. In the articles [3-5] it is written, that it is formed according to peritectic reaction, and in [6,7] they say, that it is formed due to α -phase ordering according to the first kind phase transformation. That's why it is necessary to make the positions of phase regions in this part of Ti-Al equilibrium diagram more accurate.

In this part we shall describe the results of our investigation of the alloys enriched with titanium and containing up to 40% (at)Al.

Phase Transformations of Ti_3Al Based Alloys in Solid State

We have investigated 8 alloys with different aluminium content (Table 5). Compositions of all alloys were controlled by means of X-ray fluorescence analysis. To increase the reliability of the results and to elucidate the possibility of contamination of the alloys with oxygen and nitrogen we fulfilled multiple (no less, than 3 times) thermography of the alloys. The obtained thermograms are shown at Fig.1b. It can be seen, that all thermograms of the first and following heatings coincide between each other. It indicates, that there is no contamination of the alloys with interstitial element and that there is high recurrence of the results. At all thermograms we can rather distinctly see inflections, which are connected with $\alpha \rightarrow \beta$ transformation occurring during heating. It can be noticed the little (5°C) interval of the transformation in iodide titanium, which is perhaps caused by its insufficient purity (99,96%) relatively substitutional elements. For comparison: in the close to considered one temperature interval $\alpha \rightarrow \gamma$ transformation in high pure iron takes place at constant temperature (910°C) (corresponding thermograms are shown at Fig.1b)

At the thermograms there are also seen inflections connected with $\alpha_2 \rightarrow \alpha$ transformation, their intensity is decreasing at the increase of aluminium content. At the thermograms of the alloys, corresponding to two-phased ($\alpha_2 + \alpha$) - region, they are practically unrevealed. With the increase of aluminium content $\alpha_2 + \alpha$ temperature increases, reaching maximal value for the alloy, corresponding to stoichiometric composition of Ti_3Al intermetallic, and then it again decreases. For comparison at Fig.12 and 13 there are presented four thermograms for the alloys with 20,0; 24,0; 25,0 and 28,0%(at)Al. It should be noted, that phase transformation in the alloy with 25, 0%(at)Al takes place not at constant temperature as it should be according to the theory of phase transformations, but in certain temperature interval (about 25°C).

The observed effect can be connected with the fact, that disordering of the alloy occurs according to diffusion mechanism of aluminium atoms redistribution on crystal lattice sites. That's why it is characterized by relatively large times of relaxation and requires rather low heating velocities. But the decrease of heating rate during thermography to $1^\circ/\text{min}$ and less, decreases very essentially the information we can get from thermograms. That's why thermography of all alloys was carried out at relatively large heating velocities.

Table 5

Alloy's composition and temperatures of phase transformation
in Ti-Al system

N	Al	Ti	Phase transformation temperature, °C					
			$\alpha_2 \Rightarrow \alpha$		$\alpha \Rightarrow \beta$		$\beta \Rightarrow L$	
	% (at).		start	end	start	end	start	end
1.	0	100	—	—	882	887	1668	1668
2.	5.0	95.0	702	731	948	966	—	—
3.	15.0	85.0	945	954	1069	1113	1683	1688
4.	19.6	80.4	981	1024	1107	1128	1688	1691
5.	24.1	75.9	1107	1145	1163	1170	—	—
6.	25.0	75.0	1103	1127	1146	1159	—	—
7.	28.0	72.0	1063	1123	1166	1185	1641	1662
8.	35.0	65.0	998	1069	1158	1170	—	—

Fig. 12. Thermogram of Ti based alloy with 19.6 at.% Al - thermogram obtained without melting - (copy)

Fig. 13. Thermograms of titanium based alloys
(copies) a - alloy with 25 at.% Al (a)

Fig. 13. (continuation)
b - alloy with 28 at.%

It could lead to the appearance of the phase transformation intervals at corresponding thermograms. That's why at Fig.14 presenting this part of the diagram, $\alpha_2 \rightarrow \alpha$ transformation in the alloy with 25,0at%Al is shown occurring at constant temperature.

It should be emphasized, that at all thermograms of the alloys, two effects are observed: one of them at high temperatures is connected with $\alpha \rightarrow \beta$ transformation; the second at low temperatures is caused by $\alpha \rightarrow \alpha_2$ disordering processes. The presence of this effect indicates, that disordering process occurs according to first type of phase transformations.

All the obtained data allow us to give our variant of equilibrium diagram in the enriched with ^{titanium} region (Fig.14). It mainly coincides with the one, given in the work [8] (Fig.14b). Comparing them, we can find some distinctions: according to our investigation data the disordering process takes place at lower temperatures; the region of ordering is displaced to titanium side, and maximum at the curve of ordering directly corresponds to stoichiometric composition of Ti_3Al intermetallic. Minimal interval of $\alpha \rightarrow \beta$ transformation also corresponds to this composition. Two phased $\alpha + \beta$ region looks like sigar. It is monotonously increasing to the side of alloys with higher aluminium content. It also is situated in the region of lower temperatures.

Investigation of Fusible Diagram of Ti-Al System

We have carried out this investigation in order to determine melting temperature intervals of the alloys in the region of Ti_3Al intermetallic existence. To increase the accuracy of the experiment the special attention was paid to the crucible's materials. We have tested crucibles made from BeO ; stabilized hafnium oxide and yttrium oxide. The last one were prepared from the workpieces, obtained by hot pressing of the powder. The best results were obtained by means of yttrium oxide crucibles, in which the interaction between the crucible material and the alloy was minimal. Low thermal stability of this crucibles required small rates of heating and cooling of the samples in the temperature interval $500-1300^\circ C$. As a result of thermography of the alloys we have established on the fusible diagram of Ti-Al system the existence of maximum with coordinates $1705^\circ C$ and 19,6at%Al (corresponding thermogram is shown at Fig.15a). This alloy is melting at constant temperature (according to thermography data it's melting temperature interval is less, than $2^\circ C$). The alloys, having the compositions to the right and to the left of this maximum are melted at lower temperatures and have essential melting temperature intervals. As an example at Fig.15b,c there are presented thermograms of two alloys, containing 15 and 28at%Al correspondingly. Temperatures of the beginning and of the end of their melting are equal correspondingly $1683-1688$ and $1641-1662^\circ C$ ($\Delta T = 5$ and $21^\circ C$).

Fusible diagram, which was constructed by these data is presented at Fig.16. It is satisfactorily confirming to the results of work [5], where there was

Fig. 14. The part of the equilibrium diagram Ti-Al;
(phase transformations in solid state)

Fig. 15. Thermograms of titanium based alloys (copies): alloy with 19.6 at.% Al (a), alloy with 15 at.% Al (b)

Fig. 15. (continuation)
alloy with 28 at.% Al (c)

Fig. 16. The part of fusible diagram of Ti-Al
system in the region enriched with titanium

fulfilled thermodynamic calculation of this part of the diagram. But our experimental values of liquidus and solidus temperatures are 20°C less, than those presented in [7].

As a result of our investigation let us list the main results;

1. Doping with aluminium of Ni-Mo-Al-C system does not cause the decrease of stability of the plane front of crystallization. That's why interval of crystallization rates, at which the formation of composite structure takes place is the same as for eutectic alloys corresponding to base Ni-Mo-C ternary system.

2. Doping with aluminium makes the region of composite growth on the equilibrium diagram more symmetric relatively eutectic composition. It indicates, that eutectic γ/γ' -Mo₂C alloys become less anomalous. According to eutectic classification they are displaced to the side of normal ones.

3. By means of absolute thermal analysis in the titanium enriched part of Ti-Al diagram there were determined the temperatures of the beginning and of the end of phase transformation with the participation of liquid and solid β , α and α_2 -phases.

Nonmonotonous character of fusible diagram and of the curves of ordering $\alpha \rightarrow \alpha_2$ was established. In contrast to them fusible diagram in the region of $\alpha \rightarrow \beta$ transformation looks like sigar. The temperature of this transformation monotonously increases with the increase of aluminium content in the alloys.

4. The position of maximum at fusible diagram is determined. It has the following coordinates: 1705°C and 19,8at%Al. At the curves of $\alpha \rightarrow \alpha_2$ ordering maximum coordinates are equal: 1115°C and 25at%Al. This alloy corresponds to minimal value of the general temperature interval of $\beta \leftrightarrow \alpha \leftrightarrow \alpha_2$ transformation.

5. According to thermography data the most optimum for single crystal production there are the alloys, in which the composition corresponds to the maximums at the curves of $L \leftrightarrow \beta$ and $\alpha \leftrightarrow \alpha_2$ phase transformations.

REFERENCES

1. O.M.Barabash, R.V.Gorskaya, T.N.Legkaya etc., Powder metallurgy, N 8 (1990) 67 (in Russian).
2. O.M.Barabash, R.V.Gorskaya, T.N.Legkaya etc., Izvestiya Academy of Science USSR. Metals, N 1 (1990) 82 (in Russian).
3. I.I.Kornilov, Titanium, Nauka, M., 1972.
4. U.Tsvikker, Titanium and its alloys, Metallurgy, M., 1976 (in Russian).
5. Titanium metallography / editors S.G.Glazunov and B.A.Kolachev. Metallurgy, M., 1980 (in Russian).
6. Y.-W.Kim, J. of Metals, 41 (1989) 24.
7. J.P.Gros, B.Sundman, I.Ausara, Scr.Met., 22 (1988) 1587.
8. K.Kaltenbach, S.Cama, D.G.Pinatti etc., Z.Metallk., 80 (1989) 535.

Project Title: Purification of Molten metals by Application of Electric Fields
Principal Investigator: A. V. Kaybichev
Institute of Metallurgy
Ekaterinburg, Russia
AM-7662

CLAUSE 1 - STATEMENT OF WORK

Tasks:

The Contractor shall:

- 1. Provide a report detailing the theory and experimental set-up plus a compilation of previously determined results on molten metals by application of electric fields.**
- 2. Estimate the electron and ion current in the interelectrode space in He gas at one atmosphere from Ni-1 W/0 Ti -[S] melts for experiments with changing polarity. Conduct experiments to verify the calculations using Ni-1 W/0 - [S] melts to remove [S] from the melt. Report the results.**

URAL DIVISION OF RUSSIAN ACADEMY OF SCIENCES

INSTITUTE OF METALLURGY

PURIFICATION OF MOLTEN METALS BY APPLICATION OF ELECTRIC FIELD

REPORT 1

THE THEORY AND EXPERIMENTAL SET-UP PLUS A COMPILATION OF PREVIOUS
DETERMINED RESULTS ON MOLTEN METALS PURIFICATION BY APPLICATION
OF ELECTRIC FIELD

Contractors:

Sandia National Laborato-
ries, Albuquerque, USA
Institute of Metallurgy,
Ural Division of Russian
Academy of Sciences, Eka-
terinburg, Russia

Principal Investigator:

A.V.Kaibichev

A.V. Kaibichev

Ekaterinburg 1995

CONTENT

1.1. The present state of the question.....	3
1.2. Atoms and molecules bonding with metal surface.....	4
1.3. The calculation of evaporating field strength for metals.....	6
1.4. The calculation of evaporating field strength for alloys.....	8
1.5. The impact action of gas molecules on metal surface.	9
1.6. The influence of gases on metals evaporation in electric field.....	12
1.7. The cathode sputtering.....	14
1.8. The movement and the mobility of ions in gases and metals vapours.....	15
1.9. The influence of electric field on liquid metals....	17
Conclusion.....	19
References.....	20

PURIFICATION OF MOLTEN METALS BY APPLICATION OF ELECTRIC FIELD

1.1. The present state of the question

The electric field causes electron and ion emission.

The electron emission from solid metals is well-known phenomenon [1]. Its development needs some certain conditions: electrode must be covered with special coating to decrease work function, cathode must be heated up to high temperature, deep vacuum is necessary to provide free motion of electrons in the interelectrodes space.

Ion emission was discovered relatively not long ago [2-4]. The high voltage ($5\div 30$ kV) applied to solid metal specimen gives a rise to field evaporation. It is thermally activated process. The energy of activation may be set to zero at any temperature by increase of electric field strength. It gives the opportunity for evaporation of metals in the form of ions. The cathode doesn't emit electrons here, therefore it is used at low temperatures and may be manufactured from the material with high work function.

The ion transfer in inert gas medium at low pressures ($10^{-2}\div 1$ torr) results in cathode sputtering. This process takes place on negatively charged metal surfaces at the voltage about some tens kV [5]. The metal transfer in this case is provided by gas discharge and is explained by cathode bombardment with positive ions of inert gas and by energy transmission from accelerating ion to target atoms [6]. When single atom of cathode accepts the energy of displacement (>25 eV) it becomes able to leave its site in crystal lattice and to transmit energy to adjacent atoms during subsequent elastic impacts. The excessive energy of the ion after one's impact and penetration into metal is in its turn consumed for atoms excitation. Finally the displaced atoms appear which are significantly removed from equilibrium positions and can sometimes leave the cathode causing its sputtering. In contrast to field evaporation cathode sputtering takes place at about ten times lower voltage [7] and is preferable in gas medium disposed to ionization. The use of highly purified inert gases creates the opportunity for substantial rise of electric field strength before their ionization occurs and for stimulation of metals evapora-

tion by field. Therefore the gas medium composition plays an important role in the development of any kind of emission. The presence of small amounts of easy ionized impurities may change qualitatively the elements mass transfer direction.

The mass transfer is directed from cathode to anode during sputtering and is oppositely directed during field evaporation. In both cases the maximum mass transfer with full suppression of electron emission is possible. The mass transfer direction might be adjusted by changing of electric current polarity, electric field strength, temperature, composition and pressure of gases above melt.

The ion form and surface activity of elements in metal melts, the presence of charge at metal-gas interface allow to suppose mass transfer across phase boundaries to be strongly affected by the application of electric field. So one might expect the surface active elements removal from metal melts in electric field to be effective.

1.2. Atoms and molecules bonding with metal surface

The interparticular interactions on metal surface are typically determined by three kinds of forces: Van-der-Vaals forces (physical adsorption), exchange (homeopolar) forces and heteropolar (coulomb) forces [8].

The Van-der-Vaals forces represent the most weak bonding of atoms and molecules with metal surface and are determined by orientation of electric dipoles of adsorbed particles, attraction of neutral atoms due to dipole moments fluctuations and by arising of electrostatic induction.

The homeopolar forces are more significant and act during weak chemical adsorption when the electron clouds of adsorbed atom and metal overlap. The atom-metal bond is ensured by serving electrons with uncoupled spins.

The heteropolar (coulomb) forces characterize strong bonding and are ensured by the transition of electron from one atom to another. This transition leads to formation of ion layer which induces the oppositely charged layer on the metal surface at the distance d . The increase of degree of metal surface covering with

adsorbate might give rise to attraction forces connected with cross-interactions between adsorbed ion and the image formed by the nearest adsorbed atom. If the metal is the acceptor of electrons, the energy of image forces at low degree of metal surface covering is given by [8]:

$$E^+ = -(I - \varphi)e + e^2/4d, \quad (1.2.1)$$

and if the metal is the donor of electrons, this energy is equal to:

$$E^- = (S - \varphi)e + e^2/4d, \quad (1.2.2)$$

where I - first ionization potential, S - affinity of atom to electron, φ - work function, e - electron charge.

The condition of electron transfer from adsorbed atom to metal may be written as $e\varphi > eI$, and the condition of ion adsorption looks as follows:

$$E_u + e\varphi > eI + E_a, \quad (1.2.3)$$

where E_u and E_a - ion and atom adsorption energies correspondingly.

The conditions of electrons transfer at metal-adsorbate interface show that adsorption processes proceed with release of significant energy. The only exception is physical adsorption.

Fig. 1.2.1 shows the change of valent electron energy level at 0 K as the function of the distance x from metal surface [9]. The valent electron level of separate atom, eI , at the infinite distance from the surface is broaden into the band of levels $L(E)$ in the gap between equilibrium distance x_p and critical distance of recharge x_k under the influence of metal Fermi energy E_0 . The charge of adsorbed atoms on the metal surface will be positive if $L(E)$ levels are located above E_0 , and will be negative if $L(E)$ levels are located below E_0 . The adsorbed atoms doesn't recharge if the levels coincide with E_0 . Such behaviour is connected with self-dependent tunneling of electrons through activational barrier to lower energy levels.

Figure 1.2.1. The change of valent electron energy level during adsorption

Figure 1.2.2. The circular cycle of adatom removal from the point x_k near metal surface

The ionization potential of adsorbed atom I^i differs from the potential of isolated atom I and is determined from Born-Haber circular cycle (fig. 1.2.2) [10]. The system acquires additional energy Q_a for separation and removal of adsorbed atom from the point x_k into infinity with its subsequent ionization eI there. The ion transfer from infinity to the point x_k is accompanied by energy loss equal to negative work of ion removal $-Q_u$ and the ion neutralization proceeds with the release of energy:

$$I^i = I + \frac{1}{e} (Q_a - Q_u). \quad (1.2.4)$$

The desorption of atomic particles (ions, atoms, molecules) from the surface layer needs energy supply not less the energy of bonding with the surface. The influence of electric field energy on atomic particles removal will be discussed in this report.

1.3. The calculation of evaporating field strength for metals

The influence of electric field on atomic particles in metal surface layer was described in [11] using classical electrostatics. Mechanical strains σ (kg/mm^2) generated in the surface layer under the action of electric field F ($\text{V/\AA}$) are estimated from the following expression:

$$\sigma = 45,1467 F^2. \quad (1.3.1)$$

At any high metal strength it is possible to develop bigger rupturing strains σ by rising of electric field strength. This gives the opportunity for atomic particles removal from the metal surface.

The atomic particles transfer (in the form of positive ions) from the metal surface in vacuum and in rarefied helium atmosphere under the action of high voltage (5-30 kV) was observed comparatively not long ago in the experiments [12-14]. For pure metals such phenomenon is known as field evaporation from anode. The field evaporation means also the evaporation of impurities and solute atoms in electric field.

There are two approaches to the explanation of ion evaporation from metal surface in electric field. Some authors [12-23] connect the ions removal with their direct evaporation through resultant potential barrier formed under the action of mirror image forces and applied electric field. Such cases are described by the image potential model [12-18] based on the balance of energy losses. The charge exchange model is used in its turn when charge exchange is the limiting stage of ion formation [19-24].

The evaporating field strength F_n for the ions with the charge divisible by n , the work function ϕ , the sum of ionization potentials ΣI_n , the electron charge e and the atom sublimation energy Q_a is calculated in the model of image potential using following expression [24]:

$$F_n = (Q_a + \Sigma I_n - n\phi)^2 / n^3 e^3. \quad (1.3.2)$$

The next expression was suggested [24] for calculation of evaporating field strength F_n on the base of charge exchange model:

$$F_n = (Q_a + \Sigma I_n - n\phi - 3,6n^2/r) / nr, \quad (1.3.4)$$

where r - radius of the atoms with single bond.

The applicability of both models was discussed in [23]. In particular it was shown that the applicability of the models for description of field evaporation at the value of energy barrier for thermal activation Q much less than the heat of neutral particles evaporation Q_0 ($Q \ll Q_0$) is determined by the ratio:

$$(\Sigma I_n - n\phi) / Q_a \quad (1.3.4)$$

When this ratio is less than 3 the image potential model is recognized [23] to be more preferable. When the ratio is higher than 3 the field evaporation is better described by the charge exchange model.

The results of field strength F_1 , F_2 and F_3 calculations for correspondingly charged metal ions are given in [17,24]. These

results are in a good agreement with experimental data for the evaporation of ions with $n=2$ and, in some cases, with $n=1$. The minimum evaporation strength is mainly typical for twice-charged ions though the significant influence of polarization on field evaporation at low temperatures was experimentally observed [28]. The evaporating fields for the majority of refractory metals at 0 K change from 4 to 5 V/Å and vary in common from 1.6 to 5 V/Å. The ionization of helium requires the strength 3.5 V/Å at 77 K [29] and about 4.9 V/Å at 5 K. So the evaporation of almost all metals becomes possible in the atmosphere of pure helium. The speed of tungsten evaporation in vacuum reached 10^9 layers per sec. after the application of stationary voltage and high-voltage nanosecond pulses [22]. If such tendency stays true for metal melts it gives the opportunity for the decrease of surface active elements content down to nine orders of magnitude.

1.4. The calculation of evaporating field strength for alloys

The presence of foreign impurities and alloying elements in metals has an influence on field evaporation. The evaporation of infinitely dilute alloys was described in [17]. This paper was focused exceptionally on direct energetic bonding between solute atoms and adjacent solvent atoms. The interactions between solute elements were neglected. The influence of small contents of impurity elements on their heat of evaporation is taken into account [17] using impurities partial molar enthalpies $\Delta\bar{H}^\infty$ and heats $Q_{\text{пл}}$ of melting and for gases - using atomic energies of dissociation E :

$$Q_A = Q_{\text{пл}} - \Delta\bar{H}^\infty \quad (1.4.1)$$

$$Q_A = E - \Delta\bar{H}^\infty \quad (1.4.2)$$

The condition of evaporation of two-atoms molecular ion MeA , which is the compound of metal Me with non-metal impurity A , is given [17] as:

$$Q_{\text{MeA}} - (E_A - \Delta H^\infty) < \sum_I I_A - \sum_I I_{\text{MeA}}. \quad (1.4.3)$$

where Q_{MeA} - the energy of molecule sublimation from metal lattice; $\sum_I I_A$ - total ionization potential of non-metal impurity; $\sum_I I_{\text{MeA}}$ - total ionization potential of metal-impurity compound.

The estimation of molecular complexes evaporation by field using equation (1.4.3) is difficult due to the absence of necessary data. There is the lack of information on sublimation energies and ionization potentials for MeA molecules. The energy of sublimation Q_{MeA} is evaluated [17] from simple oxides pressure values (4-5 eV) and the molecular ions ionization potentials are assumed to be close to ones of corresponding gases. According to this data the evaporation of non-metal impurities in the form of molecular ions is impossible because the significant decrease of energy consumption when the atomic ions are changed with molecular ones seems to be improbable. However there is the possibility for the evaporation of oxygen molecular ions for which the heat of sublimation is less than the heat of formation. In the case of hydrides the dissociation take place before evaporation.

Experimental data on tungsten field evaporation are explained using assumption about the existence of desorption complexes W-N, W-O [30].

1.5. The impact action of gas molecules on metal surface

The action of gas molecules on metal surface is displayed when deep vacuum ($\ll 10^{-6}$ torr) is changed with low vacuum (10^{-5} - 10^{-2} torr) by injection of inert gas. This is indicated by decrease of evaporating field strength [31].

The injection of neon instead of helium into vacuum promoted field evaporation. Neon atoms doesn't ionized in the region of strong electric field [31]. The average kinetic energy of the latter atoms at polarization coefficient α :

$$\frac{mV^2}{2} \approx \left(\frac{2}{3}\right)kT + \left(\frac{1}{2}\right)\alpha F^2 \quad (1.5.1)$$

in the case of collision with the surface in normal direction is transferred to removed metal atoms with weight M in maximum quantitative ratio $4mM/(m + M)^2$. Neon being five times heavier as compared with helium transfers more energy to surface atoms and promotes their evaporation by field.

The maximum exchanging energy of gas atom collision with metal surface atom is equal to accommodation coefficient a [32]:

$$a = \frac{E_0 - E_1}{E_0 - E_c} = \lim \frac{T_0 - T_1}{T_0 - T_c}, \quad (1.5.2)$$

where E_0 , T_0 - initial kinetic energy and temperature of approaching gas atom; E_c , T_c - initial kinetic energy and temperature of atom to be removed; E_1 , T_1 - initial kinetic energy and temperature of gas atom after collision.

The average value of accommodation coefficient $\bar{a}$ taking into account all angles of collision is two times smaller than the maximum value:

$$\bar{a} = \frac{2mM}{(M+m)^2} \quad (1.5.3)$$

In common case of hard spheres interaction maximum exchanging energy E_m for collision of particles with atomic masses m and M is equal to:

$$E_m = \frac{4Mm}{(M+m)^2} \left[(E_0 - E_c) + \frac{(M-m)}{(Mm)^{1/2}} (E_0 E_c)^{1/2} \right] \quad (1.5.4)$$

If one assume initial kinetic energy of striking atom E_c to be equal to zero he will have:

$$E_m = \frac{4Mm}{(M+m)^2} E_0 \quad (1.5.5)$$

The relative decrease of evaporating field strength $\Delta F/F$ un-

der the action of present gas atoms collisions was found out [18] for the case of evaporation at $T=0$:

$$\frac{-\Delta F}{F} = \frac{2kT^*}{Q_0} \ln \frac{\nu^*}{K_e}, \quad (1.5.6)$$

where T^* - effective temperature, ν^* - collisions frequency (it is calculated [18] from gas flow and cross-section of trapping on the surface neglecting the losses resulted from partial ionization), K_e - the speed of metals evaporation, Q_0 - the minimum of metal atom potential energy.

Effective temperature T^* is determined according to Maxwell-Boltzmann distribution function from the metal temperature T_{Me} (not equal to 0 K), the temperature T_g of gas atoms approaching to the metal and the average accommodation coefficient $\bar{a}$ [33]:

$$T^* = \bar{a}T_g + (1-\bar{a})T_{Me} \quad (1.5.7)$$

According to (1.5.6) the increase of effective temperature T^* and collisions frequency ν^* at metal atom potential energy Q_0 and constant speed K_e of field evaporation reduces electric field strength. This dependence was confirmed experimentally [31]. For tungsten, molybdenum and platinum in the rarefied mixture of helium and neon $10^{-4} \div 2 \cdot 10^{-3}$ torr it was found that:

$$-\Delta F/F \sim F^{3/2} \quad (1.5.8)$$

The above-mentioned information is the evidence of field evaporation promotion by collisions of inert gases. Therefore the large opportunities are hidden in the use of ion bombardment. So the mass-spectrometric analysis of the products of platinum target with 0.001% Ca impurity bombardment by inert gases ions gave the same intensity of Pt^+ и Ca^+ ions beams [34]. This indicates the possibility of impurities selective removal from surfaces and especially from liquid metals.

The analysis of inert gases impact action on field evapora-

tion is focused only on lower pressures. The region of atmosphere pressure was not discussed although the growth of inert gases pressure by 4-5 orders of magnitude must change evaporating field strength. It is desirable to verify this hypothesis.

1.6. The influence of gases on metals evaporation in electric field

The lowering of deep vacuum in system by injection of inert and chemically active gases mixture results in the sharp decrease of evaporating field strength. This decrease of strength is significantly bigger than in the atmosphere of pure inert gas [24]. Such strong influence can't be caused by collisions only, therefore it is explained by direct participation of chemically active gas in the process of evaporation. Maximum contribution is achieved when chemically active gas adsorption on metal surface with significant release of energy proceeds simultaneously with evaporation by field (within the time of one atom oscillation). In the given case there is no sufficient time for dissipation of atom's heat of adsorption H_a and this heat must have essential influence on evaporation. Joint influence of adsorption heat and electric field on metal evaporation is known as field etching.

Predominant evaporation of the particles in the form of metal-gas complexes MeG is conditioned by lower evaporating field as compared with the evaporation of metal Me and gas G ions [24]. The following expression was obtained [35] for approximate estimation of the opportunity of molecular complex MeG predominant evaporation assuming ions charge equality to 1 and the absence of ions polarization:

$$|Q_a + \Sigma I_n| > |Q_a' + \Sigma I_n| < |H_a + E_d + \Sigma I_n''|, \quad (1.6.1)$$

where Q_a , Q_a' - sublimation energy of ions Me and MeG ; ΣI_n , $\Sigma I_n'$ and $\Sigma I_n''$ - total ionization potentials of atom Me and molecules MeG and G correspondingly; H_a and E_d - adsorption heat and dissociation energy of gas molecules.

Hydrogen and nitrogen additions to inert gases are commonly

used as chemically active gases. For example, the autoion current in the presence of hydrogen in helium was 10-20 times higher than in the case of full ionization of all hydrogen molecules [36, 37]. This phenomenon was explained by polarized molecules attraction in non-uniform electric field and points out the necessity of taking into account gas polarizability.

The introduction of small amounts of hydrogen in the mixture with helium appreciably lowers evaporating field strength for greater part of metals and promotes ones evaporation [37-39]. This is explained by the influence of field on formation of hydride compounds in surface layer of metal which are highly disposed to evaporation as compared with metal atoms. The formation of Be hydrides in the case of Be evaporation by field at the temperature of liquid hydrogen was confirmed by mass-spectrometric investigations. In the absence of hydrogen only ions Be^{++} were observed. The growth of hydrogen content up to 10^{-3} torr led to Be evaporation only in the form of BeH^+ . The mixture of Be^{++} and BeH^+ was observed at hydrogen pressure 10^{-6} torr. Therefore the assumption about charges equality (1.6.1) seems to be rather arbitrary as there is the possibility of simultaneous evaporation of Be^{++} ($n=2$) and BeH^+ ($n=1$). The hydrides formation and the decrease of evaporating field strength were observed for Fe, Ni and Cu. The hydrogen injection favoured the process of Zn evaporation. However the hydrides were not found out probably due ones fast decomposition in electric field. The change of hydrogen partial pressure from 10^{-8} to 10^{-4} torr resulted in the decrease of Nb field evaporation voltage from 20 down to 10 kV [30]. All the metals under study demonstrated acceleration of ones evaporation by field in the presence of hydrogen though the individual speeds of evaporation were different. The composition of gas atmosphere most favourable for evaporation was also not the same. So neither pure hydrogen nor hydrogen-helium mixture assisted tungsten evaporation in electric field but such promotion of evaporation was observed in neon-hydrogen mixture. The most interesting feature of pure hydrogen usage as the filling gas is the practical absence of cathode sputtering [40]. Positively charged ion hydrides were revealed by mass-spectrometry in the processes of Si and Cu field evaporation [41].

Nitrogen is chemically active gas. Its traces have strong corrosion influence on metal in electric field [42]. Mass-spectrometric analysis of evaporation products [40, 43] showed the presence of multiple charged molecular oxides and nitrides of evaporated metals CuO^+ , NiO^+ , FeO^{2+} , FeN_2^{2+} , WO_3^{3+} , WN_2^{4+} . The presence of multiple charged molecular ions of metals with active gas in electric field is the evidence of their minimum potential energy as compared with metals ions. Therefore molecular complexes evaporation requires minimum energy consumption and is predominant.

1.7. The cathode sputtering

The application of electric field in rarefied inert gases (10^{-2} -1 torr) results in cathode sputtering of metals. Metals sputtering is caused here by negative charge at the voltage of some tens kV [5]. Metals transfer is conditioned by energy transmission from striking atoms to target atoms. When single atom of cathode accepts the energy of displacement (>25 eV) it leaves its site in crystal lattice and becomes able to transmit energy to adjacent atoms during subsequent elastic impacts. Finally the formation of displaced atoms able to leave cathode becomes possible. The cathode sputtering is accompanied by the release of heat energy and ionization energy. This release is usually estimated with the help of cathode sputtering factor N which is equal to the ratio of sputtered atoms number n_a to falling atoms number n_p :

$$N = n_a/n_p \quad (1.7.1)$$

The cathode sputtering factor depends on the masses of bombarding ions M and target atoms m :

$$N = \text{const} \frac{Mm}{(M+m)^2} \quad (1.7.2)$$

Its maximum value is achieved at equal masses M and m and is not higher than 0.25.

The cathode sputtering was discussed in details in monographs [5,6]. The cathode material transfer is conditioned mainly by gas discharge. Electric fields application is recommended [44] for cleaning of monocrystals surface.

1.8. The movement and the mobility of ions in gases and metals vapours

The removal of ions from metals surface depends on conditions of ions transfer in surrounding space. The speed of ions movement is determined by concentration, diffusivity and concentration gradient [45,46]. It becomes constant in the direction of electric field if ions acceleration in the periods between collisions with gas molecules is counterbalanced by ones braking during collisions. When the ions average energy is higher than the heat energy of gas molecules due to increase of electric field strength, the mobility of ions K is not constant. In the last case it becomes the function of the ratio of electric field strength to numerical density of gas molecules N . This function defines the excess of ions energy in the field above the heat movement. The ions energy distribution substantially differs here from Maxwell distribution and is unable to be definitely calculated using existing theories [45]. As the coefficients of mobility K^- and diffusion D^- of electrons owing to small mass of electron are some orders of magnitude higher as compared with K^+ and D^+ of ions at the same electric field strength, two versions of the movement are possible. The first one takes place at charged particles density about 10^7 - 10^8 cm^{-3} . It is typical for deep vacuum. One may neglect here the interaction between negatively and positively charged particles. The second case is more typical for high degrees of ionization. The coulomb interaction of electrons with positive ions plays here an important role in the arising electric field. Different mobilities of ions and electrons generate space charge. The latter creates electric field which promotes more uniform density of oppositely charged particles by means of ions acceleration and electrons deceleration. As the result the speeds of oppositely charged particles motions become the same as the ambipolar diffusion coefficient D_a describing the displacement of

particles with both signs has also the same value:

$$D_a = \frac{D^+K^- + D^-K^+}{K^+ + K^-} \quad (1.8.1)$$

The only exception is the region adjacent to electrodes and commensurable with Debye screening radius where the polarity is supported by applied electric field.

The major part of experimental data on mobility coefficients K , diffusivity D and drift speed V_d was obtained at the pressures up to 10^{-1} torr. At the higher pressures the injection of ions into mass-spectrometer becomes difficult. At the atmospheric pressure in the drift tube mass-spectrometer needs small outlet orifice and high-speed ions pumping out. But even such design does not exclude the formation of molecular groups around the ions in expanding gas stream in mass-spectrometer leading to deterioration the spectrum. The values of the ratio of electric field strength F to molecules number N cover the interval $0.3 \div 5000$ Td (Townsend $F/N = 10^{-17}$ V·cm²). The range of higher values of F/N is experimentally limited by system's electric short circuit. The average ions energy can reach here the value of 10 eV where non-elastic collisions become significant.

Experimental data on ions mobilities in helium, hydrogen, argon, neon, nitrogen, oxygen, carbon monoxide and in own vapours of metals extrapolated to zero field are given in the monographs [45, 46]. The highest mobility of ions is observed in helium and hydrogen and is significantly lower in other gases. The variation of gases ions mobility in their own medium covers the range of values from 31.8 to 1.41 cm²/V·s where the most high value belongs to proton. The range of metals ions mobility variation is more wide: 21.5÷0.075 cm²/V·s. The lowest values belong to metals ions in their own vapours. In such environment the mobilities are, as a rule, two orders of magnitude lower than in helium. It allows to expect the study of metal melts purification by electric field in helium atmosphere to be effective.

The influence of temperature on mobility of sodium and caesium ions up to 500 K was demonstrated in [47]. The mobility of sodium ions increased from 17.3 cm²/V·s (92 K) to 23 cm²/V·s (477

K) and the one of caesium ions was practically constant. Small changes of mobilities with temperature allow qualitatively to carry out further investigations on the base of the data given in [45, 46].

1.9. The influence of electric field on liquid metals

We estimated the possibility of impurities removal from liquid metals in the atmosphere of highly purified helium using low-current modes. All the experiments were carried out in resistance furnace (fig. 1.9.1) with tubular graphite heater (2) containing gas-tight alumina casing. The mass changes of metal melts were determined by thermogravimetry. The influence of polarity and circuit voltage was studied during isothermal exposure. The constant emission current was set by changing of potential difference between liquid metals in the BeO crucible (3) and cylindrical Mo screen (5) using universal power source UPS-1. The crucible (3) was suspended on W wire (8) inside hermetically sealed alumina casing (4). Its upper end was closed by water-cooled lid with inlets and rubber tightenings. Mo-glass column was sealed by rubber tightening in the central inlet orifice of the lid through which Mo hanger of the crucible was introduced into the furnace. The extension of spring - 0.01 g/mm allowed to measure mass change about 10^{-5} g by cathetometer KM-9 with resolution 0.001 mm. The temperature was measured by tungsten-rhenium thermocouple the hot junction of which was located at the same level as crucible (3). Constant values of circuit voltage and evaporation speed during isothermal exposure were the evidences of high degree of purification.

Fe, Si, Al, Cu and Ag melts were studied in the experiments (fig. 1.9.2-1.9.4). The application of electric field using molten metal as cathode and molybdenum electrode with opposite polarity promoted evaporation of Fe, Al, Cu, Ag. The reversing of polarity resulted in the returning of Fe, Cu, Ag into the melt. By contrast to above mentioned metals Si was evaporated from the melt under the action of positive polarity and returned back under the action of negative polarity. These results display different influence of electric field on liquid metals evaporation.

Figure 1.9.1. The scheme of experimental installation for thermogravimetry in electric field

1 - resistance furnace; 2 - tubular graphite heater; 3 - metal melt under applied electric charge; 4 - gas-tight alumina casing; 5 - Mo screen (ϕ 40 mm); 6 - water-cooled cover with inlets and rubber tightening; 7 - Mo glass column; 8 - W wire spring balance

Experimental mass change in electric field was compared with the data on ion transfer of metals in helium calculated according to Faraday's first law:

$$m = \frac{1}{96500} \cdot \frac{A}{n} \cdot I\tau, \quad (1.9.1)$$

where m - mass change, g; A - atom mass; n - ion charge; I - electric current, A; τ - time, s.

The comparison of results pointed on different ion contribution of elements into transfer of current. Silicon and copper vapours have practically pure ion conductivity in helium. The fraction of ion conductivity is enough high for Ag vapours and is low for Fe vapours. The ion conductivity of vapours of some elements in electric field and the difference between interelectrodes potentials for evaporating elements (fig. 1.9.2-1.9.4) indicate the possibility of liquid metals purification in electric field.

The mass transfer of elements (Fe, Si, Al, Cu) in the interelectrodes space under the application of positive and negative polarities of the melt is not the same. This difference is probably caused by certain chemical activity of metals and ones possible recharging in electric field. For better reproducibility of results on mass transfer we had carried out an experiment dedicated to evaluation of electric field action in helium on such chemically inert metal as silver (fig 1.9.4). In this case positive polarity of liquid silver is characterized by mass growth and negative polarity - by mass loss. The speed of mass change is almost constant in various periods due to high purity of liquid silver.

Periodic exposure of positively charged liquid silver at 1485°C in the electric field with emission current 200 mA in both cases was accompanied by mass growth and by significant increase of applied voltage. The voltage increased at the first period from 200 to 390 V. This is explained by removal of the mixture of silver ions with growing molybdenum content from molybdenum cathode. The repeated exposure of liquid silver under positive polarity instead of negative polarity proceeded as well with

Figure 1.9.2. The influence of melt polarity and isothermal exposure in helium on Fe and Si mass and circuit voltage changes

1 - mass change, $\Delta P \cdot 10^{-2} \text{ g/cm}^2$; 2 - circuit voltage, V; 3 - time, min; 4 - mA

Figure 1.9.3. The influence of melt polarity and isotherma exposure in helium on liquid Al and Cu mass and circuit voltage changes
 1 - mass change, $\Delta\rho \cdot 10^{-2} \text{ g/cm}^2$; 2 - circuit voltage, V; 3 - time, min; 4 - mA; 5 - Al; 6 - Cu

Figure 1.9.4. The influence of melt polarity and isothermal exposure in helium on liquid Ag mass and circuit voltage changes
 1 - mass change, $\Delta P \cdot 10^{-2} \text{ g/cm}^2$; 2 - circuit voltage, V; 3 - time, min; 4 - mA

the increase of voltage up to 400 V. The speed of mass growth increased from $1,55 \cdot 10^{-3}$ g/(cm²·min) to $4.4 \cdot 10^{-3}$ g/(cm²·min). The lower value belongs to the first period and the higher value - to the second one. Sufficient amounts of the vapours of silver and its impurities with low charge and evaporating fields strength had probably precipitated on the surface of molybdenum electrode as the result of preliminary purification of silver. The higher speed of mass growth was conditioned by electric transfer of these depositions.

The evaporation of silver took place under negative polarity with extremum change of the voltage. This change was especially sharp during the first isothermal exposure. At the beginning the voltage grew from 150 up to 210 V and then decreased down to 190 V. The bend of mass loss curve is observed at the point corresponding to maximum voltage. This bend may be resulted from the change of evaporating ions composition. The average speed of evaporation is equal to $8,17 \cdot 10^{-3}$ g/(cm²·min). Its inconstancy and the change of voltage are caused by removal of impurities from the melt together with silver ions. Repeated isothermal exposure of silver under negative polarity was accompanied by somewhat large mass loss - $1 \cdot 10^{-2}$ g/(cm²·min). Mass change as well as voltage change (200 → 190 V) are not high. These changes are probably the evidence of high degree of liquid silver purification. The influence of polarity on mass transfer increases with the temperature.

Conclusion

The influence of electric field on surface phenomena at solid metal-vacuum or inert gas interface at low temperatures and pressures was established theoretically and experimentally. The cleaning of monocrystals surface up to atom purity is known quite well. However there is the lack of data on liquid metal purification in electric field.

The ion form and the surface activity of elements in metal melts, the presence of charge at metal-gas interface allow to expect the removal of surface-active impurities from metals by application of electric field to be effective.

References

1. Фоменко В.С. Эмиссионные свойства материалов. Справочник. - Киев: Наукова думка, 1970, 146 с.
2. Chalin L.M., Biondi M.A. Mobilities of Mercury Ions in Helium, Neon and Argon.- Phys. Rev. 1957, v.107, No 5, p. 1219-1221.
3. Kovar F.R. Mobility of Mercury Ions in Mercury Vapor.- Phys. Rev. 1964, v.133, No 3, A, p. 681-685.
4. Biondi M.A. Processes Involving Ions and Metastable Atoms in Mercury Afterglows.- Phys. Rev. 1957, v.90, No 5, p. 730-737.
5. Акишин А.И. Ионная бомбардировка в вакууме. М.-Л.: Госэнергоиздат, 1963, 142 с., ил.
6. Плешивцев Н.В. Катодное распыление.- М., Атомиздат, 1968, 343 с., ил.
7. Field-Ion Microscopy. Edited by John J.Hren and S.Ranganathan. Plenum Press - New-York, 1968.
8. Kaminsky M. Atomic and Ionic Impact Phenomena on Metal Surfaces. Springer-Verlag, Berlin - Heidelberg - New-York, 1965.
9. Зандберг Э.Я., Ионов Н.И. Поверхностная ионизация.- М., Наука, 1969, 432 с., ил.
10. Добрецов Л.Н., Гомоюнов М.В. Эмиссионная электроника.- М., Наука, 1966, 564 с., ил.
11. Парселл Э. Электричество и магнетизм.- М., Наука, 1975, 438 с., ил.
12. Muller E.W. Kurze Originalmitteilungen.- Naturwissensch. 1941, v.29, s. 533-534.
13. Muller E.W. Field Desorption.- Phys. Rev. 1956, v.102, No 3, p. 618-624.
14. Мюллер Э.В. Автоионизация и автоионная микроскопия.- УФН, 1962, 37, с. 481-552.
15. Brandon D.G. The Resolution of Atomic Structure: Recent Advances in the Theory and Development of the Field Ion Microscope.- Brit. J. Appl. Phys. 1963, v.14, p. 474-484.
16. Brandon D.G. The Structure of Field-Evaporated Surfaces.- Surface Sci., 1964, No 3, p. 1-18.
17. Brandon D.G. The Field Evaporation of Dilute Alloys.- Surface

- Sci., 1966, No 5, p. 137-146.
18. Brandon D.G. On Field Evaporation.- Phil. Mag. 1966, v.14, p. 803-820.
 19. Gomer R. Field Desorption.- J. Chem. Phys. 1959, v.31, No 2, p. 341-345.
 20. Gomer R., Swanson W. Theory of Field Desorption.- J. Chem. Phys. 1963, v.38, p. 1613-1620.
 21. Swanson L.W., Gomer R. Field Desorption of Carbon Monoxide from Tungsten.- J. Chem. Phys. 1963, v.39, No 11, p. 2813-2836.
 22. Tsong T.T., Muller E.W. Field Evaporation Rates of Tungsten.- Phys. Status Solidi. (a), 1970, A1, No 3, p. 513-533.
 23. Брэндон Д.Г. Испарение полев.- В кн. Автоионная микроскопия.- М.: Мир, 1971, с. 34-58.
 24. Muller E.W., Tsong T.T. Field Ion Microscopy. American Elsevier Publishing Company, Inc., New-York, 1969.
 25. Vesely M., Ehrlich G. Field Evaporation: Model and Experiment.- Surface Sci. 1973, v.34, p. 547-560.
 26. Muller E.W., Young R.D. Determination of Field Strength for Field Evaporation and Ionization in the Field Ion Microscope.- J. Appl. Phys. 1961, v.32, No 11, p. 2425-2428.
 27. Nakamura S. Field Evaporation of Samples in Field Ion Microscope.- Electron Microscopy. 1966, v.1, Tokyo. Maruzen Co., Ltd., 1966, p. 243-244.
 28. Vanselow R., Schmidt W.A. Feldverdampfung von Platin bei hohen Temperaturen im Ultrahochvakuum und Gegenwart von Sauerstoff: Massenspektrometrische Analys der Oberflächenkomplexe.- Z. Naturforsch. 1966, v.21a, No 10, s. 1690-1696.
 29. Southon M.J., Brandon D.G. Current-Voltage Characteristics of the Helium Field-Ion Microscope.- Phil. Mag. 1963, v.8, No 38, p. 579-591.
 30. Mulson J.F., Muller E.W. Corrosion of Tungsten and Iridium by Field Desorption of Nitrogen and Carbon Monoxide.- J. Chem. Phys. 1963, v.38, No 11, p. 2615-2619.
 31. Nishikawa O., Muller E.W. Operation of the Field Ion Microscope with Neon.- J. Appl. Phys. 1964, v.35, No 10, p. 2806-2812.
 32. Knudsen M. Die Molekulare Wärmeleitung der Gase und der Akko-

- modations Koeffizient.- Ann. Phys. 1911, v.34, s. 593-656.
33. Goodman F.O. On the Theory of Accommodation Coefficients.- J. Phys. Chem. Solids 1965, v.26, No 1, p. 85-105.
 34. Bradley R.C., Arking A.A., Beers D.S. Secondary Positive Ion-Emission from Platinum.- J. Chem. Phys. 1960, v.33, No 3, p. 764-769.
 35. Brandon D.G., Wald M. The Direct Observation of Lattice Defects by Field Ion Microscopy.- Phil. Mag. 1961, v.6, No 68, p. 1035-1044.
 36. Muller E.W., Bahadur K. Field Ionization of Gases at a Metal Surface and the Resolution of the Field Ion Microscope.- Phys. Rev. 1956, v.102, No 3, p. 624-631.
 37. Muller E.W., Nakamura S., Nishikawa O., Melane S.B. Gas-Surface Interactions and Field-Ion Microscopy of Nonrefractory Metals.- J. Appl. Phys. 1965, v.36, No 8, p. 2496-2503.
 38. Muller E.W., Erwin W. Hydrogen Promotion on Field Ionization and Rearrangemnt of Surface Charge.- Surface Sci. 1967, v.7, No 3, p. 462-473.
 39. Мюллер Э.В. Автоионная микроскопия.- УФН. 1967, т.92, N 2, с. 293-320.
 40. Muller E.W. Field Emission and Sputtering of Thoriated Tungsten.- Z. Physik. 1937, v.106, No 12, s. 132-140.
 41. Barofsky D.F., Muller E.W. Mass Spectrometric Analysis of Low Temperature Field Evaporation.- Surface Sci. 1968, v.10, No 2, p. 177-196.
 42. Muller E.W. Field Emission Microscopy of Clean Surfaces with Electrons and Positive Ions.- Ann. N.Y. Acad. Sci. 1963, v.101, No 3, p.585-598.
 43. Muller E.W., Panitz J., McLane S.B. The Atom-Probe Field Ion Microscope.- Rev. Scient. Instrum. 1968, v.39, No 1, p. 83-86.
 44. Farnsworth H.E. Atomically Clean Surfaces.- Dechema-Monogr. 1975, p. 1537-1548.
 45. McDaniel E.W., Mason E.A. The Mobility and Diffusion of Ions in Gases.- John Wiley and Sons, New-York - London - Sydney - Toronto, 1973.
 46. Huxley L.G.H., Crompton R.W. The Diffusion and Drift of Electrons in Gases.- A Wiley-Interscience Publication John Wiley

and Sons, New-York - London - Sydney - Toronto, 1974.

47. Pearce A.F. Variations of Mobility of Gaseous Ions with Temperature. II. Cesium and Sodium Ions in Helium.- Proc. Roy. Soc. (London). 1936, A-155, p. 490-498.

Project Title: Effect of Volatile Alloy Components on the Vacuum Arc Remelting Process

Principal Investigator: Felix Shved

Research and Development Institute of Metallurgy

Chelyabinsk, Russia

AM-7663

CLAUSE 1 - STATEMENT OF WORK

Tasks:

The Contractor shall:

1. Produce an industrial sized electrode of a suitable alloy without volatile alloy components. Suitable material would be a superalloy base or tool steel. Produce and provide a report that details the base chemistry.
2. Vacuum arc remelt the electrode under standard conditions of melt current and leak rate. Allow process to come to steady-state and make successive additions of volatile alloy components to the molten pool. The alloy components of interest are magnesium and manganese. Measure the arc characteristics during and after each addition. Allow the arc to return to steady-state between additions.

Analyze the data and derive the coefficients predicting voltage from furnace setting, including a coefficient of conductivity for each condition evaluated. Provide a report detailing the data, observations, results and conclusions.

REPORT № 1

Project Title: Effect of Volatile Alloy Components on the Vacuum Arc Remelting Process (AM-7663)

Abstract

Corresponding to the Task 1 of the Project an industrial size electrode of a nickel base superalloy is produced and prepared to double experimental remelt. The choice of such procedure is explained. Report details the base chemistry of the electrode.

INTRODUCTION.

Investigations, made at Chelyabinsk Scientific & Research Institute of Metallurgy and also at Sandia National Laboratories, revealed, that some important properties of the arc discharge such as the sum of cathode and anode drops and specific electric resistance of the arc column are dependent on the chemistry of the material remelted and of furnace atmosphere.

For example, moving from steel to the Ni-base alloys, one can notice that $U_k + U_a$ decreases and current coefficient of specific resistance (CCSR) increases. When some quantity of carbon oxide is present in the furnace atmosphere the CCSR for Fe-Ni-base alloy is decreased, and the same is influence of manganese content in the low and middle alloyed constructional steel.

The aim of this work is to get detailed quantitative data on the influence of volatile components (magnesium and manganese) on the arc discharge characteristics at VAR. The variable content of these components in a consumable electrode is guaranteed by the double remelt of one the same electrode with the addition at the first remelt to the upper half of the ingot of Mg and Mn. As for the lower part of this ingot serving as electrode for the second remelt, the volatiles, and especially magnesium content in it will be at the minimal level, not attainable at VIM with magnesia crucible.

VOLUME OF WORK.

1. A consumable electrode is produced of Ni-base superalloy of CrNi62MoNbCoTiAl grade, melted in VIM by standard technology with the prescribed by this technology magnesium addition.

Two ring gutters are turned at the distance of 60 and 80% from the bottom of electrode (see Fig.).

The turnings, obtained at the making of gutters, are used for chemical analysis of Mg content in the base material.

For keeping in the gutter of the materials, which are placed in it a strip of nickel or some other metallic material may be welded around the electrode as it is shown on Fig.

2. Chemical composition of electrode (weight %):

C	Mn	Si	S	P	Cr	Ni	Mo	Ti	Al	Co	Nb	Cu	W	V	Fe	B
0.04	0.04	0.12	0.002	0.007	13.5	0.04	4.9	2.7	2.5	9.9	2.6	0.02	0.02	0.03	0.6	0.009

In the gutter 1 close to the beginning of remelt a portion of Ni-Mg alloy with 16% Mg is placed. The quantity of alloy is calculated to give medium Mg content in the upper part of ingot of 0.03%. In the gutter 2 a metallic Mn addition (0.3% of the rest of electrode weight) is placed.

The particles size of materials added - 1÷5 mm.

3. The consumable electrode is remelted to the mold 400 mm dia. with the standart start procedure and transition to the steady parameters 4.5 kA, 23÷23.5 V. The arc gap at the beginning stage of the melt - 10÷15 mm.

After steady-state of the process is achieved 4 - 5 short circuit experiments (SCE) are made at the arc current 4.5; 6.0 and 8.0 kA and arc gap of 10÷20 mm. Besides that, 4 SCE's are made at arc current 4.5 and 8.0 kA after gutters with Mg and Mn are remelted (2 SCE's after each addition). The remelt of the gutters is carried out at the stationary current 4.5 kA.

4. The first remelt VAR ingot of 390 mm dia. is turned to the diam. of 370÷375 mm with the simultaneous selection of samples for Mg и Mn content analysys at 2 points of the lower part and at 6 points of the upper part of the ingot.

The ingot is remelted in the mold of 450 mm dia. at the current of 5.0÷9.0 kA with the set of SCE's, which is adjusted to the chemical analysis results.

5. A Short Sirquit Experiment Procedure.

The furnace is equipped by 4-channel device for simultaneous registra-tion of the arc current, arc voltage, ram position and vacuum.

The source of signal for ram position is variable resistance, which movable element is tightly connected to one of ram drive moving parts. After steady-state of the process is achieved (all parameters do not change at least for 10 min), the target arc voltage is manually lowered to the level of 5÷10 V. After this the consumable electrode automatically is going down with a great speed until it touches to the surface of the pool. After short delay electro-d is automatically raised by 10÷15 mm. Target voltage is again manually restored at the working level.

6. As a result of experiments the following parameters will be derived

Parameter		ARC heat/ experi- ment	Approximate content **	
			Mg	Mn
Cathode and anode voltage falls sum	Current coeffic. of specific electric resistance	1/1÷4	standard	low
		1/5,6	high	low
		1/7,8	rather high	high
		2/1÷4	extra low	extra low
		2/5,6	rather high	extra low
		2/7,8	close to standard	high

** The actual Mg and Mn contents are checked by analysis

Experimental data obtained will be statistically analysed and coefficients, characterizing influence of the Mg and Mn influence on the arc properties, will be derived.

Project Title: Melting, Refining and Casting of Ti-based Alloys in an Electron Beam Furnace with Electromagnetic Stirring.
Principal Investigator: Segey V. Ladokhin
Institute of Foundry Problems
Kiev, Ukraine
AM-7664

CLAUSE 1 - STATEMENT OF WORK

Tasks:

The Contractor shall:

1. Provide a report detailing previous work in the area of Melting, refining and casting of Ti-based alloys in an electron-beam furnace with electromagnetic stirring. Include a general description of the process, why it is unique, its advantages and data illustrating these points. Also include a description of any mathematical modeling used to describe the stirring fields and flows in the hearth.
2. Perform experiments under different conditions of electromagnetic stirring (including no stirring) on a Ti alloy containing a volatile alloy component. Characterize the evaporation of Ti-base material and the volatile alloy component under different conditions of stirring. Also characterize the energy consumption and time of melting. Provide a detailed report describing the experimental procedures and results of the experiments performed.
3. Demonstrate the capability to produce a multicomponent Ti alloy by casting Ti alloy parts of a composition to be specified by Sandia, and delivering the cast parts to Sandia for evaluation after casting. The materials and molds for this task will be supplied by Sandia. In addition to the cast parts, provide a detailed report describing the experimental procedures and results of the experiments performed.
4. Investigate the ability of electromagnetically stirred EB melting to purify material. Ti alloy material that has been contaminated with intermetallic inclusions will be provided by Sandia. Bars shall be cast and returned to Sandia for evaluation. The experiments shall be performed under conditions where the stirring circulates the material through the hot zone to dissolve inclusions. In addition to the cast parts, provide a detailed report describing the experimental procedures and results of the experiments performed.

Electromagnetic Stirring of Melt at the Electron-Beam Skull Melting

(Report of Task 1, Contract No. AM-7664)

Abstract

Skull crucibles with the electromagnetic stirring (EMS) systems and electron-beam (EB) casting installations including those based on standard vacuum induction and vacuum arc furnaces have been developed. Non-stationary EB heating parameters of the melting with EMS have been analysed and refinement processes at this type of heating have been discussed as well. Some specific technological methods of metals and alloys melting and casting, the usage of which is possible mostly in case of EMS action on the melt, have been described. It has been shown that EMS application 3-4 times increases the melt volume in the crucible, 10-20% reduces the specific electric energy consumption, and 20-30 % cuts metal losses through evaporation.

Introduction.

The melt stirring during technological processes has always been a problem of interest for specialists in chemistry, metallurgy and casting production, since the efficient melt stirring causes the intensification of the mass- and heat-transfer and the development of various technologies on its basis.[1, 2].

For the electron-beam skull melting (EBSM) this problem first became important in the early 1970-s, when the task to produce rather massive castings from refractory metals and alloys arose [3, 4]. At that time the equipment and technologies allowed to obtain castings of several kg and only from pure metals or simple alloys. The attempts to solve this problem through increasing skull crucible diameter and creating local heating zones on the surface heated [5] were not successful, since the melt mass increase in the crucible was insignificant, and the selective character

of the volatile elements evaporation further complicated the multi-component alloys melting. Moreover, the energy consumption and metal losses through evaporation grew due to the crucible diameter increase thus changing the economic data for the worse.

It was concluded that to overcome these disadvantages the melt in the crucible had to be stirred during heating and EMS seemed the most adequate for EBSM [6].

However, the EMS systems not only complicate the skull crucibles construction but also require technological solutions allowing to avoid the electron beam deflection from the heating zone due to the electromagnetic fields of the EMS systems. Besides, EB heating becomes increasingly non-stationary which is considered undesirable in the technology [6,7], and this requires special analysis of such heating and related refinement. At the same time, EMS allows to implement such EB melting and casting methods, which are either difficult or impossible to use without melt stirring.

In this report the development of skull crucibles with the EMS systems and the EB casting installations with the crucibles of this type is described, the heating and refinement peculiarities at the non-stationary EB action on the melt are analysed, the technological methods of metals and alloys melting and casting relevant to EMS of the melt are presented.

It should be noted that for this report the literature published in the former USSR have been mostly used, since any data on the EMS use during skull melting in the USA or other developed countries where the EB technologies are rather widely used have not been found.

1. The equipment for the EB skull melting with EMS

The most important area of the equipment development for EBSM with EMS is the construction of skull crucibles with EMS systems. Now the crucibles allowing to obtain up to 300 kg of melt for Ni- and Zr-based alloys, 200 kg for Ti-based alloys and 120 kg for Nb-based alloys have been created.

In all cases the EMS systems consist of coils and magnetic cores covering the crucible walls or both the walls and the bottom.. The number of coils and cores, their location on the crucible and energy supply are determined by the size of the crucible, its geometry and the metal melted [8]. The schemes of some skull crucibles with wall and bottom-wall location of the EMS systems and different methods of pouring are given in Fig.1. In practice *a*, *b*, and *c* variants are used. In Fig. 2 and 3 the examples of operating crucibles of type *a* and *b* are shown,. They were constructed for melting and casting of Zr, and Nb respectively.

Not only melting crucibles, but also other vessels for melt refining may be equipped with the EMS systems, for example those for cold-hearth EB process [9]. In Fig.4 and 5 the scheme of the gutter with the EMS system and its general view in the EB furnace melting chamber are shown, respectively. In this case the gutter was developed for the steel refinement in the flow with liquid metal charge at the comparatively low productivity of the process. Due to this its size parameters are rather small: length 1000 mm, width 250 mm, height 110 mm [10]. Such constructions may be equipped only with the wall-bottom EMS systems, since the limited height of the gutter does not allow to place the necessary amount of coils and cores around the walls. The gutters with the EMS systems can be used not only for melt refinement in the flow, but also for alloys melting, i.e. skull melting. It should be mentioned that flat ingots (slabs) can be produced in such gutters using cold charge as well [9,11]. Such slab is shown in Fig.6.

The most important characteristics of the EB melting with EMS are the speed and direction of the melt flow under the influence of the electro-magnetic fields of the EMS system. They were investigated in numerous works, for example [12-19], but any reliable analytical approaches to estimate these characteristics haven't yet been developed. Therefore, for practical purposes the values of flows speed and direction of circulation, obtained experimentally with model melts (mostly mercury, gallium and tin), are used. The example is given in Fig.7. Here the data from article [16] on the speed distribution and mercury circulation in the model skull crucible of diameter 300 mm with the wall-bottom EMS system are presented. These results together with other literature data allow to conclude that depending on the conditions of the experiment the crucible size and its walls thickness, the melt movement speed on the pool surface is about 0,3-0,4 m/sec and possibly never exceeds 1.0 m/sec. These data correlate with the results obtained for other vessels of similar size, in particular, induction furnace crucibles [20] and continuous casting crucibles [21].

The crucibles with the EMS systems are of high operating qualities and allow to conduct over 500 meltings. With correct exploitation, preventing the electron beam from contact with crucible walls, the number of meltings may increase to 1000 and more. Depending on the metal melted, crucible parameters, the metal and the melt temperature, the cooling water expenditure is 15-60 litre/min, while the temperature difference of water at the entrance and exit is 5-50K.

The crucibles with the EMS systems require the EB installations of specific construction. One of the most important requirements is to place the gun above the crucible on the same axis [22]. Such location allows to avoid the electron beam deflection from the heating zone under the influence of magnetic fields of the EMS system. However, this may complicate the gun exploitation. According to the tests conducted,

the axial gun with two level pumping system and water cooling the cathode holder seems the most appropriate. Such guns were developed by von Ardenne (Germany) [5], the Russian Electrotechnical Institute (Russia) [23], the Institute of Foundry Problems (Ukraine) [24]. Unfortunately, the well known Leybold guns [25] haven't yet been tested in our Institute because it's impossible to buy them.

Other important issues concern the development of the appropriate methods of metal pouring into the mold, mechanisms for charge loading and castings unloading without destruction of melting chambers leakproofness, construction of equipment for condensate collection, pool thermal scrinning, etc [22].

There are two directions of the EB installations development: new constructions and standard vacuum induction and vacuum arc furnaces reconstruction into the EB installations. The installations of the first type are used mostly for specific casting production and are characterised with high both productivity and the EB heating power. In Fig.8 the example of such installation with the EB heating power 600 kW for Nb-based alloys melting and casting is shown. It was assembled at one of the enterprises in Russia.

significant inve The installations of the second type are used mostly for the improved quality castings production in vacuum induction and vacuum arc furnaces. For such reconstruction the induction crucible is replaced with the skull crucible containing the EMS system, the charge loading mechanism is replaced with the EB gun and relocated (in vacuum induction furnaces this mechanism is usually placed above the crucible), the vacuum and watching systems are modernized. Usually the furnaces are not noticeably changed and can be reversed back, if necessary. Now some vacuum furnaces VDL-4, UPPF-3M and ISV-004, which are widely used in Russian and Ukrainian plants, have been reconstructed into the EB installations. In Fig. 9 such EB installation based on standard vacuum arc furnace is shown. The advantage of this method of the EB casting installations construction is its quickness and stments reduction.

2. The EB heating and refinement of metals and alloys with EMS

The EMS noticeably changes the heating conditions compared to the conventional EB melting, since the electromagnetic field of the EMS system eliminates the electron beam scanning along the surface heated. Under these conditions the movement of the surface heated and

the beam is determined by the melt movement speed under the influence of magnetic field. But since this speed is low, the zone of local overheating is formed on the pool surface. This zone determines the peculiarities of the refinement processes.

The principal scheme of the EB melt overheating zone with possible temperature distribution along the focal spot diameter is shown in Fig.10 [26]. Actually, the picture represents physical models of the EBSM processes, when the melt is heated with the electron beam of the power P scanning the surface heated with the velocity v . The shaded parts are the electron hindering zones in the melt and nonmetallic inclusion in it.

It is assumed that the power density in the focal spot zone does not reach the values of the "explosive boiling of the substance" [27], while the energy release along the electron path δ_e is uniform. During the beam action on the pool surface the heat penetrates into the melt. The temperature T is distributed uniformly along the focal spot diameter, so is the temperature T_e outside the heating zone. The transition from T_e to T occurs as jump on the spot border.

Analysing the admixture atoms evaporation we assume that the velocity of evaporation from the melt surface outside the focal spot with the area $S - s$ equals w_p^0 . From the focal spot area s the admixture evaporation goes with the velocity w_p^1 . The total admixture evaporation velocity is $w_p = w_p^0 + w_p^1$.

In the zone of the beam action on the metal surface the nonmetallic inclusion of the diameter $2r$ appears and $2r < 2a$ where $2a$ is the focal spot diameter. The average electron path into the admixture substance is δ_e' , with $\delta_e' < \delta_e$.

The metal thickness on the inclusion surface is significantly lower than δ_e . The inclusion heating temperature in the beam action zone is T' and is distributed uniformly. The transition from T to T' occurs also as jump on the inclusion border. The energy release along the electron path in the inclusion is uniform.

Analysing gas bulbs elimination it is assumed that there is a bulb of the diameter $2R_r$ in the overheating zone. Its size is determined by the minimum thermodynamic potential.

It should be emphasized that the real temperature distribution along the pool surface differs from that described above. In real conditions the temperature transitions do not occur as jump on the focal spot and nonmetallic inclusion border, but are continual though rather abrupt. Due to this the transition as jump seems more appropriate in models in order to simplify the analysis. Another assumption concerns the energy release along the electron path in the metal and inclusion. In reality it is not uniform and reaches its maximum at some distance from the surface [27]. However, taking into consideration $2a \gg \delta_e, \delta_e'$ for the models proposed, the

assumption of its uniform character does not seem to cause any significant error in the calculations.

Within the model described the melt heating temperature T in the focal spot zone can be calculated on the basis of the following. The time of the beam heating in each fixed point of the surface is $\tau \approx 2a/v$. During this time the heat penetrates up to

$$\delta \approx (\lambda \tau / C_v)^{1/2} \approx (2a\lambda / v C_v)^{1/2} \quad (1)$$

where λ is the effective thermal conductivity, C_v is the heat capacity per unit of melt volume.

Taking into consideration the beam movement velocity the surface heated is

$$s \approx v \tau 2a \approx 4a^2 \quad (2)$$

while the volume heated is

$$V \approx s \delta \approx (2a)^{5/2} (\lambda / v C_v)^{1/2} \quad (3)$$

Then the energy balance in the heating zone is

$$C_v (2a)^{5/2} (\lambda / v C_v)^{1/2} (T - T_0) \approx P \cdot 2a / v \quad (4)$$

where P is the electron beam power.

It follows from the equation (4) that

$$T \approx T_0 + P / (2a)^{3/2} (v \lambda C_v)^{1/2} \quad (5)$$

Equation (5) is correct, if

$$\lambda / 2a C_v < v < 2a \lambda / C_v \delta_0^2 \quad (6)$$

This is always observed in practice only after the first portion of liquid metal appears in the heating zone [26].

The melt heating temperature value obtained allows to calculate the admixtures evaporation velocity [26, 28]. According to the physical model described above, the evaporation from the focal zone will significantly influence the metal refinement from the admixture, provided

$$s \omega_p' \geq s \omega_p^0 \quad (7)$$

Since in general the total admixture evaporation speed is

$$\omega_p = \mathcal{D} C \exp(-u / \kappa T_e), \quad (8)$$

in the model admitted

$$\omega_p = \mathcal{D} C [(S - s) \exp(-u / \kappa T_0) + s \exp(-u / \kappa T)] \quad (9)$$

where $\mathcal{D}$ is the constant for the given component evaporated, C is the admixture concentration, u is the admixture evaporation activation energy per one atom (molecule), κ is the Boltzmann constant.

At $s \ll S$ the analysis makes sense only if

$$\exp(-u / \kappa T) \gg \exp(-u / \kappa T_0) \quad (10)$$

In this case

$$\omega_p \approx \mathcal{D} C [S \exp(-u / \kappa T_0) + s \exp(-u / \kappa T)] \quad (11)$$

Introducing the equations (2) and (5) into (11) we obtain

$$\omega_p \approx \mathcal{D} C \left\{ S \exp(-u / \kappa T_0) + 4a^2 \exp \left[- \frac{u (v \lambda C_v)^{1/2} (2a)^{3/2}}{\kappa T_0 (v \lambda C_v)^{1/2} (2a)^{3/2} + \kappa P} \right] \right\} \quad (12)$$

The w_p is maximum, if

$$a = a_c = (4\kappa\rho/3u)^{2/3} (v\lambda c_v)^{-1/3} / 2 \quad (13)$$

the criteria of the equation (13) applicability are

$$v > v_c = 3u\lambda^2 / 4\kappa\rho c_v, \quad u > \kappa T_c \quad (14)$$

So the analysis of the heating and refinement processes shows that the use of the focused electron beams at the EB melting allows to achieve the maximum admixtures evaporation velocity. In principle, these conditions may be calculated theoretically before the melt. However, the data on the admixtures evaporation activation energy should be known for such calculation.

The formation of the focal spot of optimum size, allowing to achieve the maximum evaporation velocity, depends on the fact, that the focal spot radius reduction causes the temperature increase in the beam action zone, and according to the exponential law the evaporation velocity speed per area unit grows too. On the other hand, the focal spot area of higher temperature reduces with the radius reduction, according to the quadratic equation. Under the definite combination of both competing factors the maximum evaporation velocity can be reached.

The local overheating zone promotes nonmetallics and gas bulbs elimination. In particular, if nonmetallics and slag on the pool surface are under the direct action of the electron beam, their explosive evaporation is possible. The explosive evaporation occurs, if [26]

$$\rho > \epsilon_g N 2a \delta_c \quad (15)$$

where ϵ_g is the heat of dissociation per one inclusion molecule,

N is the number of molecules per inclusion volume unit. The expression (15) is correct, if

$$v > 2a\lambda'/c_v' \gamma^2 \quad (16)$$

where γ is the nonmetallic inclusion radius, λ' and c_v' are the heat conductivity and the thermal heat capacity of the inclusion volume unit, respectively.

There are good conditions in the overheating zone for insoluble gas bulbs growth and their exhaust to furnace atmosphere. The bulbs of gas, solubility of which depends on the temperature increase, disappear dissolving in the melt in the overheating zone. The equations (17) and (18) describe the bulbs maximum size of insoluble and soluble gas, respectively:

$$R_f < \left(\frac{3}{m_f}\right)^{1/2} \frac{a(\kappa T)^{3/2}}{v\sigma_c d_f^2} \quad (17)$$

$$R_r < \frac{(9a D_r k T C_{pa})^{2/3}}{2(v^2 \sigma_c \rho_a v_a^2)^{1/3}} \quad (18)$$

where m_r is gas molecule mass, d_r is gas molecule diameter, σ_c is specific surface energy, D_r is gas diffusion ratio, C_{pa} is two atom gas solubility limit at the atmosphere pressure P_a , v_a is metal atomic volume.

Analysing the EBSM processes it is necessary to estimate the duration and circulating factors for the melt in the overheating zone that can be done roughly according to the following equations:

$$\tau_o \approx W \left(\frac{C_v}{\lambda v} \right)^{1/2} / (2a)^{3/2} \quad (19)$$

$$n_c \approx (2a)^{3/2} \left(\frac{\lambda v}{C_v} \right)^{1/2} \tau_n / W \quad (20)$$

where W is the melt volume in the crucible, τ_n is the total refinement time for the given volume at the EB heating. In principle, these equations may be used for the qualitative analysis of the EBSM processes. However, it's not taken into consideration the EB treatment of the metal at the stage when the liquid metal pool is forming though it can affect the melt and castings properties.

3. Technological peculiarities of the EB metals and alloys melting and casting with EMS

The technology of EBSM with EMS is characterised with step-by-step heating power increase similar to the EB melting without EMS. However, due to the larger mass of the metal melted, the duration of the separate melting stages, first of all heating and melting, increases. In Fig.11 the EB heating power regimes are given for the Zr melting in 2 litres crucible with the wall EMS system [31]. It is obvious, that EMS more than 3 times increases the melt mass in the crucible, though the melting time grows nearly twice (curves 1 and 2). The specific electric energy consumption reduces despite the additional consumption by the EMS system. This is due to the noticeable increase of the mass melted.

To reduce the duration of melting with EMS the EB installations must be equipped with more powerful vacuum pumps. In such case the EB maximum power is easier to achieve, and the total time of the melting significantly reduces, which is obvious from Fig.11.

The experimental data [8, 14, 31, 32] prove that in general EMS allows to increase the melt volume 3-4 times, reduces the specific electric energy consumption 10-20%, and 20-30% - the metal loss through evaporation.

The advantage of EMS is the possibility of multi-component alloys melting, including those with volatile elements. The addition of such elements into the cold charge does not seem efficient, since they almost completely evaporate in the course of melting. EMS makes it possible to introduce these elements directly into the melt before melt pouring from the crucible. Due to this the losses are significantly reduced and the required composition of alloys may be obtained. The efficiency of this technological procedure was tested by Cr introduction into Ni-based alloys, Al, Cr and Mn into Ti-based alloys, and V into Nb-based alloys.

EMS also allows to use some other technological procedures, which are impossible without stirring. One of them is the melt circulation reversing in the course of melting. It permits to control the depth of the liquid metal pool being formed and the skull thickness on the crucible walls.

The intensive melt stirring and reversing allow to melt charge including production wastes, such as scrap, cast parts revert, shaving, etc. In principle, the wastes in the charge may reach 100%, i.e. using EMS alloys melting is possible without addition of virgin alloys. The recycling of the waste is practically unlimited, since the procedure described above allows to compensate the volatile elements losses. This is probably the advantage of EBSM with EMS compared to the well known EB cold hearth remelting [33]. The example of technological possibilities of the procedures described is given in Fig.12, where castings of different kind produced in the EB installations only from production wastes are shown.

The quick melting of metal after its complete solidification in the crucible is also possible with EMS. This have resulted in new melting technology development, based on the intended solidification of liquid metal in the crucible. As this takes place, nonmetallic and slag inclusions are pushed up on the surface where they are eliminated by the low power electron beam heating without solid metal melting. This allows to avoid the evaporation of some components of alloys, i.e. their chemical composition change, as well as to eliminate nonmetallic and slag inclusions. After the complete elimination of slag from the pool surface the high power EB heating and the EMS system are switched on

to melt metal in the crucible. This procedure may be repeated several times.

Due to the efficient melt stirring under the influence of electromagnetic fields the melt can be poured through the hole in the crucible bottom. The melt stirring makes it possible to avoid the instability of pouring and to prevent the penetration of slag into the mould. Moreover, the metal of the casting head can be heated by the electron beam through the hole in the crucible bottom thus improving the casting quality. Now this method is used mostly for massive casting production, in particular for massive Zr castings presented in Fig.12.

Conclusion.

The analysis of the modern EB skull melting with EMS, as well as the last reviews on the EB technologies [33-35] show that refractory metals and alloys will be the main objects of the EB metallurgical and casting technologies. There is the tendency of the wider usage of EB for Ti and Ti-based alloys melting and casting which proves the significance and actuality of the project presented.

At the same time it may be concluded that there is a growing interest to studies of the EB melting and refinement of Ni-based superalloys. This is due to the necessity of further improvement of their quality, since other melting and refinement methods (vacuum induction melting, vacuum arc remelting, electroslag refining) can not fulfil the necessary requirements [36, 37].

However, the most important shortcomings of the EB technologies, mainly the high electric energy consumption, metal losses through evaporation, the lower productivity compared to other methods of refinement, expensive and complicated equipment, limit their practical application.

The possibilities of EBSM with EMS to compensate these negative factors are shown in this report. However, in case of superalloys melting and casting the combination of induction and EB melting seems more effective [38]. Such method has not yet been used because of the lack of the necessary equipment. The report shows the possibility to develop the combined skull-ceramic crucibles with the EMS systems, allowing the simultaneous induction and EB heating. It may be assumed that such combined heating will reduce the melting time and specific electric energy consumption. However, there is a possibility of the interaction of melt with ceramics during melting in the combined crucibles, which may affect the quality of alloys melted. There are many other problems of the combined melting: the ratio of the induction to EB heating, the optimum electrical frequency at the induction heating, the skull formation in the combined crucibles, etc.

In this connection it seems important to develop combined skull-ceramic crucibles and technologies of superalloys melting with EB or combined induction-EB heating. Taking into consideration the complexity of such works requiring both standard and new technological equipment, as well as special research, we propose to start initial investigation before this project on the Ti-based alloys melting and casting is completed. This will save time.

References

1. Levich V.G., *Physico-chemical hydrodynamics.*, (Moscow: Fizmatgiz, 1959),(Russian).
2. Grigorjan V.A., Beljanchikov A.N., Stomakhin A.J., *Theoretical basis of electric steel melting*, (Moscow: Metallurgija, 1979) , (Russian).
3. Uljanov V.L., Litein. pr-vo, (1972) No 8,pp. 3-4, (Russian).
4. Uljanov V.L., Litein. pr-vo, (1972) No 10,pp. 13-15, (Russian).
5. Schiller S., Heisig U., Panzer S., *Electronenstrahltechnologie*, (Dresden:Forshungsinst, Manfred von Ardenne, 1976).
6. Movchan B.A., Tikhonovskii A.L., Kurapov Yu.A., *Electron-beam melting and refining of metals and alloys*, (Kiev: Nauk. Dumka, 1973), (Russian).
7. Kalugin A.S., *Electron-beam melting of metals*, (Moscow: Metallurgija, 1980), (Russian).
8. Didyk B.S. et.al., Spec.elektrometallurgija, (1986) No 61, pp.38-43, (Russian).
9. Ladokhin S.V., *Development of electron-beam technology with liquid metal charge*, (Kiev: IPL,1980), (Russian).
10. Ladokhin S.V., Shishkarjev E.Je., Spec.elektrometallurgija, (1980) No 43, pp.63-69, (Russian).
11. Paton B.Je. et.al., Spec.elektrometallurgija, (1981) No 47, pp.63-67, (Russian).
12. Panasjuk L.S. et.al., In: *Refractory metals casting*, (Kiev: IPL,1970), pp.76-87, (Russian).
13. Mikelson A.E. et.al., In: *Refractory metals casting*, (Kiev: IPL,1970), pp.92-101, (Russian).
14. Didyk B.S., Vinogradskii I.N., In: *Refractory metals casting*, (Kiev: IPL, 1974), pp.57-65, (Russian).
15. Javich V.Je., In: *Casting processes automation and mechanization*, (Kiev: IPL, 1972), pp.255-260, (Russian).
16. Mikelson A.E. et.al., In: *Casting processes automation*, (Kiev: IPL, 1973),pp.46-51, (Russian).
17. Tir L.L., Stolov M.J., *Electromagnetic equipment for the control of melt circulation in electric furnaces* , (Moscow: Metallurgija, 1975), (Russian).
18. Revin M.G., Krivonischenko I.A., In: *UPI reports*, (Sverdlovsk: UPI,1967),pp. 38-48, (Russian).
19. Pakhuchii A.A., In: *Refractory metals casting*, (Kiev: IPL, 1974), pp.133-185, (Russian).
20. Moore D.J., Hunt J.C.R., In: *Liquid-Metal Flows and Magnetohydrodyn.*, 3rd Int. Semin. MHD Flows and Turbulence Sor., ((N.Y.1983) pp.359-373.
21. Gibbins P.C., Steel Times, (1985) 213, No 6, pp.284-287.

22. Ladokhin S.V. In: *The morden methods of alloys casting and cyustallisation*, (Kiev: IPL,1983), pp.127-134, (Russian).
23. Electron axial gun of type EPA-300-04.2.TU16-681.078-85.
24. Jakovlev V.T. et. al., In: *Refractory metals casting* ,(Kiev: IPL,1974), pp.9-11, (Russian).
25. Electron-beam technology in vacuum metallurgy, (Erlensee: Leybold Durferriit GmbH).
26. Ladokhin S.V., Kornjushin Yu.V., *The EB skull melting of metals and alloys*, (Kiev: Nauk.Dumka,1988), (Russian).
27. Rykalin N.N.,Zujev I.V., Uglov A.A. , *The electron-beam treatment of materials*, (Moscow: Mashinostrojenije,1978), (Russian).
28. Ladokhin S.V., Kornjushin Yu.V., *Izv. AN SSSR.Metally.*,(1986) No 4, pp.42-45, (Russian).
29. Kornjushin Yu.V., Ladokhin S.V., *Izv. AN SSSR.Metally*, (1987) No 4, pp.48-51, (Russian).
30. Ladokhin S.V., Lapshuk T.V., Anikin Yu.F., In: *The melting and refining of the casting alloys*, (Kiev: IPL,1990), pp.48-53, (Russian).
31. Ladokhin S.V., Anikin Yu.F., In: *MHD in metallurgy and casting production.*, (Kiev: IPL,1981), pp.52-57, (Russian).
32. Levitskii N.I., Miroshnichenko V.I., Jakovlev V.T., In: *The melting and refining of the casting alloys*, (Kiev: IPL,1990), pp.53-61, (Russian).
33. Bakish R., JOM , (1992) No 6, pp.37-39.
34. Bakish R., JOM , (1993) No 6, pp.61-63.
35. Ladokhin S.V.,Shmigidin V.G., *Metall i litje Ukrainy*, (1995) No 3, (Russian), in press.
36. Loria E.A., JOM, (1993) No 6, pp.33-36.
37. Anikin Yu.F. et.al., *Probl. spec.elektrometallurgii*, (1993) No 3, pp.40- 43.,(Russian).
38. Tir L.L., Fomin N. I., *The morden methods of induction melting*, (Moscow: Energija, 1975), (Russian).

Principal Investigator, Dr.Sc.

Sergey V. Ladokhin.

January 20 , 1995

Fig. 1. Schemes of skull crucibles with EMS systems
a - wall EMS system, *b* - wall-bottom EMS system, *c* - wall EMS system and bottom pouring, *d* - crucible with inclined walls and wall EMS system, *e* - crucible with walls made of magnetic cores.
 1 - water cooled wall, 2 - melt, 3 - skull, 4 - coil, 5 - magnetic core, 6 - hole in crucible bottom, 7 - water cooled lid.

Fig. 2. The skull crucible with wall EMS system
The crucible for Zr and Zr-alloys melting and casting. The melt mass reaches up to 60 kg. The melt pouring trough crucible tilting.

Fig. 3. The skull crucible with wall-bottom EMS system
The crucible for Nb and Nb-alloys melting and casting. The melt mass reaches up to 40 kg. The melt pouring through crucible tilting.

Fig. 4. Scheme of cold-hearth gutter with EMS system
1 - bottom coil, 2 - bottom core, 3 - water cooled bottom, 4 - water cooled walls, 5 - wall coil, 6 - wall core.

Fig. 5. The cold-hearth gutter in the EB installation chamber

Fig. 6. The cold-hearth gutter with formed slab after EB melting
The slab is obtained by remelting stainless steel scrap.

Fig. 7. The distribution of melt flows speed in the model skull crucible of 300 mm diameter (from [16])
Mercury as a model metal is used. The scale : 1mm = 20mm/sec.

Fig.8. The EB casting installation with 4 mold chambers
The EB power is 600 kW. The installation is constructed for Nb castings production.

Fig. 9. The EB casting installation based on a standard vacuum arc furnace

The EB power is 300 kW. The installation is used for Zr castings production.

Fig 11. The EB power regimes at Zr melting in the skull crucible
 1 - melting without EMS, 2 - melting with EMS, 3 - melting with EMS
 and additional gas pumping out a melting chamber.
 The crucible diameter is 200 mm. The numbers near arrows mean melts
 mass in kg.

Fig. 12. The castings produced in the EB installations with EMS
1-4 - Zr-alloys castings, 5-10 - Ti-alloys castings, 11 - Nb-alloy
casting, 12-15 - blades made of Ni-based superalloys, 16-21 - Cu castings,
22 - superalloy bar for remelting, 23 - carbon mold for Ti-alloy blades
casting.

Experimental Research of the Electromagnetic Stirring Effect on the Electron Beam Skull Melting of Titanium and Its Alloys

(Report of Task 2, Contract No. AM-7664)

Abstract

Technological equipment and experimental techniques for the melts have been described. The results of Ti-based alloys production with the electro-magnetic stirring (EMS) have been given. The EMS at the electron beam skull melting (EBSM) have been shown to facilitate the melting of alloys containing volatile elements as well as to reduce the specific consumption of the electric energy and to increase the melt mass produced in skull crucible.

Introduction

The earlier investigations, which were reported in the 1st stage of this Contract, have shown the EBSM with the EMS to influence both technological characteristics of the process and the multi-component alloys production. According to the programme, this work describes the experimental meltings of multi-component Ti-based alloys in the skull installation. The experimental research has been focused on the volatile elements behaviour, since these elements determine the required composition of alloys produced in the EB installations.

The equipment and materials melted were chosen in order to allow the further use of the results obtained at industrial enterprises of Ukraine and Russia as well. In particular, this has determined the use of titanium scrap, chips, stampings as charge for melting and the use of electron-beam installation on the basis of standart vacuum induction furnace as melting equipment.

Technological equipment, materials melted and methods of work

For the experiments the EB casting installation constructed on the basis of the vacuum induction furnace of ISV-004 type [1] was used. The scheme of this installation is shown in Fig. 1. Its main technological characteristics are the following:

1. Melting camera volume - $2,2 \text{ m}^3$.
2. The number of the EB guns - one.
3. Maximum gun power - 200 kW.
4. Operating pressure in the melting chambers - 0,13 Pa.
5. Operating pressure in the gun cathode camera - $1,3 \times 10^{-2}$ Pa.
6. General water expenditure for the installation cooling - $10,0 \text{ m}^3/\text{hour}$, including that for the crucible cooling - $2,4 \text{ m}^3/\text{hour}$.
7. The time of the operating gas pressure in the melting chamber reaches two hours.

From the technological point of view, the operation of the installation is periodical, i.e. it is opened after each melting for a new charge and new casting moulds assembling. The periodical character of works reduces the productivity of the installation, however, it is of no importance during the experimental research.

The peculiarity of the installation construction is that the EB gun and the melting crucible are placed on the same axis (ref. the report on the Task 1 of the Contract).

The skull crucible used is equipped with the bottom-side EMS system. The efficiency of such EMS system has been proved in a series of earlier experiments[2]. The scheme of the crucible is shown in Fig. 2. The volume of the crucible is 14 litres, while its useful volume is 10 litres, allowing to obtain up to 30 kg of Ti melt (without the skull mass). The EMS system coils are fed with currents of industrial frequency at the voltage of 20-30 V and the current power of 630-765 A. The metal is poured out by the crucible tilting during 4 to 10 sec, depending on the casting produced.

The cylindrical carbon moulds of 130 mm in diameter are used.

For the experiments the alloy VT20 containing Al, Mo, V and Zr was used. This alloy is multi-component and contains volatile elements, as well as may be practically used in both deformed and cast state[3]. Since the alloy VT20 is rather expensive, the alloy VT1, i.e. technical Ti, was used for additional investigation focused mostly on the dependence of the melt mass and specific energy consumption on the conditions of the process. For the VT20 production stamp wastes were used as a charge, while for VT1 - scrap and chips.

The investigation was based on a series of experimental meltings focused on the following parameters:

- mass and quality of materials charged including the Al addition;
- the duration of separate melting steps and the total time of melting;
- the pressure of gases in the melting chamber and in the EB gun cathode chamber;
- the EB heating power and its regulation in the course of melting;
- the current voltage and power in the EMS system coils, as well as the time of the EMS system operation;
- the cooling water consumption and temperature;
- the melt mass and temperature.

Al is added two minutes before the melt pouring from the crucible by drip melting. This process usually takes not more than one minute.

The temperature is measured by the W-Re thermocouples with protective graphite cap. Before the temperature is measured, i.e. before the thermocouple is submerged into the melt, the thermocouple is heated above the metal surface during not less than three minutes outside the electron beam spot zone. The depth of thermocouple submergence into the melt is 40-50 mm, while the distance between the thermocouple and the crucible wall is about 60 mm.

The samples for chemical analysis are taken from different zones of the ingot.

Experimental meltings and their results

It has been noted that the alloy VT20 was chosen for main experiments while the alloy VT1 was used in additional ones. All experimental meltings with the VT1 were done earlier, i.e. before the Contract No. AM-7664 was made, in the crucible shown in Fig. 2. The data obtained were used for the meltings with the alloy VT20.

The optimal regimes of the EB heating power regulation at fixed VT1 pouring, the effect of the exposure time at the given maximal heating power on the melt mass, and the relationship between the specific electric energy consumption and the VT1 melt mass are given in Fig. 3,4 and 5, respectively. On the basis of these data for the experimental meltings with the VT20 the following parameters were chosen: the charge mass - 15 kg, the maximum EB heating power - 140-150 kW, the melting time - nearly 25 min. It was planned to have 6 meltings with the VT20, of which three were with the addition of a volatile element (Al), and other three - without.

In Table 1 the parameters of all experimental VT20 meltings are given. The principal purpose of the experiment was the assessment of the composition correction possibility through the volatile element addition during the melting. The other important task was to investigate the EMS effect on the technological parameters of the process, namely, the melt mass and specific energy consumption.

Table 1. The technological parameters of the EBSM of the alloy VT20

No of melt	EMS operational time, min.	Al addition mass, kg	Heating time at maximal power, min.	Melt mass, kg	Specific electric energy consumption kW.hr/kg
1	14	0	8	13.2	2.82
2	15	0	9	13.7	2.74
3	15	0	9	13.5	2.80
4	14	0.3	10	13.8	2.82
5	15	0.3	11	13.2	2.88
6	0	0.3	10	6.8	4.57

Note 1: The melts No 3 and 4 were carried out at the melt stirring from the crucible walls towards its centre. In the other melts the stirring direction was opposite.

Note 2: The difference between the mass of charge (15kg) and the mass of the melt poured is due to the fact, that a part of the liquid metal is solidified on the crucible walls and the pouring spout during the pouring. .

Note 3: The cooling water consumption was 40 l/min, the input and output temperature difference of 15-17 K.

Analysing the data from Table 1, it should be taken into consideration that the melt mass during the melting without the EMS is in fact maximal for the crucible used. The attempts to increase the mass poured by means of higher EB heating power and/or higher charge mass have not been successful. At the same time, during the melting with the EMS the melt mass may be increased up to 30 kg. Therefore, with this type of the crucible the melt mass at the EMS 4 times exceeds that without the EMS. This corresponds with other data about the effect of stirring on the EBSM [4].

The total electric energy consumption on the EB heating during the experiments was 30,9 - 31,5 kW.hours, while on the electro-magnetic stirring - 6,4 - 7,5 kW.hours. The reduction of the specific energy consumption resulted from the melt mass increase.

During the experimental meltings the effect of the stirring direction - from the crucible walls to its centre and to the opposite - has not been proved important. However, this effect was noticeable during Ni-based superalloys melting in the skull crucible with the side stirring system. It may be assumed, that this is the result of the insufficient height of the crucible with the combined bottom-side EMS system used in these experiments.

The integral temperature of the melt in the crucible before its pouring out is 1700 - 1720°C. Variation of metal losses through evaporation is from 2.2% till 3.5%.

The most important requirement is the chemical composition of the alloy melted. In Table 2 the results of the chemical analysis of the samples from different meltings compared to those of the initial metal and according to State requirements are given.

Table 2. Chemical composition of the alloy VT20 produced by the EBSM(mass %)

No of melting	Melting conditions	Al	Mo	V	Zr
	State cond.	5.5-7.5	0.5-2.0	0.8-1.8	1.5-2.5
	initial	6.2	1.6	1.5	2.0
1	without addition	4.8	1.62	1.4	1.9
2	the same	4.63	1.64	1.32	1.9
3	the same	4.65	1.67	1.36	1.8
4	with addition	6.17	1.62	1.41	2.09
5	the same	6.08	1.71	1.62	1.97
6	the same	4.95	2.09	2.37	2.12

Note: The chemical analysis of metal from different zones of the same ingot have proved that in all cases the difference in the content of chemical elements was within the analysis error limits.

According to the data from Table 2, the volatile element may be introduced to the Ti-based alloy during the melting, if necessary. The EBSM with the electro-magnetic stirring allows to do it quite easily. Without stirring the addition becomes less efficient due to metal losses through evaporation.

For the technology of the volatile element introduction to the melt, it is important to determine the necessary time of the melt exposure to the EB heating after the addition. In our experiments it was one minute. In other cases it may reach a few minutes and usually must be verified by additional test meltings.

Some peculiarities of the scull formation at the EBSM with the EMS and its effect on the alloy melted should also be mentioned. In our case, at the melting crucible size shown in Fig.2 and cooling water consumption and temperature - in Table 1, the scull thickness is 8-10 mm and its mass - about 15 kg. This means, that at the maximum melt mass of 30 kg, the initial charge should be not less than 45 kg, and the following charges should correspond to the melt mass required. Such scull does not seem to influence the chemical composition of the liquid metal bath, though in the initial studies of the EBSM [5] it was assumed that the scull melt would allow to control the composition of the alloys melted.

Conclusion

The studies described have revealed the principal peculiarities of the multi-component Ti-based alloys melting in the EB skull installations. It has been shown, that the addition of the volatile element to the alloy before the melt pouring out of the crucible may compensate its losses through evaporation. However, in practice this method may be realised only with the intensive melt stirring in the crucible. For the EBSM the EMS has proved the most efficient method of stirring. The important advantages of the EMS are also the increase of the melt mass and the reduction of the electric energy consumption.

In general, the investigations have proved that the EBSM with the EMS is the most effective casting technology compared to other EB melting technologies. Taking into consideration the good prospects of the Ti casting [6,7], this technology seems to become most widely used in the nearest future, first of all for Ti-based alloys melting and casting.

References

1. "Development of EB Casting Production Technology with Titanium Wastes Utilization" (Report No. 2048, Institute of Foundry Problems, Kiev, 1991).
2. Didyk B.S. et al., "Crucibles for Electron Beam Skull Melting", Spec. elektrometallurgia, No. 61 (1986), 38-43 (Russian).
3. Bibikov E.L. et al., Titanium Alloys. Titanium Alloys Casting Production (Moscow: Metallurgia, 1983), 296 (Russian).
4. Ladokhin S.V., "EB Melting and Casting Technology Modernization", Litein. pr-vo, No.3 (1985), 28-30 (Russian).
5. Dovbnja V.D. , "Alloys Composition Change During EB Skull Melting", Refractory metals casting, No.1 (1970), 58-75 (Russian).
6. Ward W. Minkler, "Titanium's 37 Year", J. Metals, No.3 (1987), 9.
7. Rodney R. Boyer, "Aerospace Applications of Beta Titanium Alloys", J. Metals, No.7 (1994), 20-23.

Principal Investigator, Dr. Sc.

Sergey V. Ladokhin

April 25, 1995

Fig.1. Scheme of electron-beam casting installation on the basis of vacuum induction furnace ISV-004.

1 - mounting; 2 - crucible tilting mechanism; 3 - skull crucible with EMS system; 4 - melting (vacuum) chamber; 5 - vacuum pumps; 6 - EB gun.

Fig.2. Scheme of skull crucible with side-bottom EMS system.
 1 - crucible bottom with branch pipe; 2 - bottom core; 3 - coil; 4 - wall (side) core; 5 - wall (side) coil; 6 - crucible wall; 7 - pouring spout; 8 - top flange.

Fig.3. Optimal regimes of EB power regulation at fixed pouring melt mass.

The numbers near arrows mean melts mass. Stroke lines mean EB heating with EMS.

Fig.4. Effect of the heating time at the given maximum EB power on the pouring melt mass.
1 - EB power 180 kW; 2 - 140 kW; 3 - 80 kW.

Fig.5. Relationship between the specific energy expenditure and the pouring melt mass.

Project Title: Electron Beam Spray Casting of Dense Metal and Ceramic Coatings.

Principal Investigator: Nikolai Trigub

Paton Electric Welding Institute

Kiev, Ukraine

AM-7665

CLAUSE 1 - STATEMENT OF WORK

Tasks:

The Contractor shall:

- 1) Provide a detailed report discussing the electron beam spray casting technique, the types of materials that may be sprayed and the types of substrates that can be coated, and the advantages of coating parts using this method as opposed to other techniques. Include data from previous experiments and investigations that demonstrate the mechanical and chemical properties of spray cast materials, as well as their microstructures. Include a discussion of relevant theory as well as any models that have been developed describing the process. Discuss potential industrial applications of spray cast materials.
- 2) Perform investigations into the influence of substrate temperature and coating speed on the mechanical properties Al/Al₂O₃ and Ti/Fe parts. Determine coating hardness, density and uniformity, and evaluate its adhesive qualities. Prepare and provide a report detailing the results of the investigation described above, and provide spray cast samples of Al/Al₂O₃ and Ti/Fe to Sandia for evaluation.
- 3) Develop a model that describes the bonding interface in metal/metal oxide composite components, and provide a report on the results of the model development.

Electron Beam Spray Casting of Dense Metal and Ceramic Coatings.

1. Technique and facilities.

1.1 Process scheme.

The essence of electron beam (EB) spray casting is the directed melt spray generation by centrifugal atomisation of liquid metal from rotating consumable billet (2) surface in conditions of its heating by EB (1) and melt droplets deposition on a substrate (3 of Fig.1).

1.2 Installation.

For the realization of process an experimental installation E121 was created (Fig.2).

As a heat source in installation two axial EB guns were used, each of 60 kW power. The power of supply source was 400 kW, output voltage was 25 kV.

Each gun was rigged with high-productive vacuum unit H-160, which allowed to hold pressure not higher than 7.5×10^{-3} Pa during all the technological cycle if pressure in the technological chamber was not higher than 0.067 Pa. This technological steps provided high stability of the process technological parameters and results reproduction.

In the technological chamber of installation two technological units were arranged. First unit was intended for the rotation of consumable billet around horizontal or vertical axis. The frequency of rotation was regulated continuously or step-by-step within the range of $0 \dots 5000 \text{ min}^{-1}$. Second unit provided displacement of the substrate with respect to spray. The unit as to design was a system of movable carriages, which were arranged on different levels with respect to general support frame. By means of simple rearranging of carriages it was possible to deposit spray both on rotated body surface and on plate-parallel substrates at horizontal or vertical position. By unit design provided an ability of simultaneous displacement of substrate in longitudinal and transversal directions with respect to spray axis in the range $0.008 \dots 8 \text{ m/min}$ and its rotation around horizontal or vertical axis with frequency $10 \dots 60 \text{ min}^{-1}$.

The control of electrical drives can be accomplished in manual regime from autonomous control unit or from numerical

programming control device, thus providing the producing of casted billets or coatings with required surface profile or required geometrical size in automatic regime.

The dimensions of vacuum technological chamber (2000 mm dia., 1500 mm height) and units design allowed to atomise consumable billets with 100 kg mass and to deposit melt on rotated body surface up to 500 mm dia., 500 mm length and plate-parallel - 500x500x200 mm.

1.3 Technique.

The technological scheme of dense deposit producing from sprayed melt was quite simple and realized as follows. The consumable billet made as rotated body was fixed in a holder of rotation unit; the substrate of required size was placed in capture of the substrate moving technological unit. Technological chamber was evacuated. After reaching pressure in chamber not higher than 0.067 Pa and in guns 7.5×10^{-3} Pa consumable billet rotation drive was turned on and the power was supplied to the EB guns. The surface of consumable billet was heated by one gun, the substrate was heated by another. In the conditions of optimal technological parameters the spray of small droplets was created. The spray of melt was deposited on the substrate surface, liquid metal droplets spreaded and solidified with thin layer formation. With layer-by-layer deposition the billet or coating of required geometrical size and shape was formed. During deposition of melt on substrate constant temperature close to solidus temperature of deposited material was maintained sufficient for a reliable adhesion between the layers of spreaded melt droplets. The uniformity of temperature field was provided by programming distribution of EB gun power on the substrate.

The analysis of technique regimes of spray forming showed that under definite values of EB power optimal for specific metal on the surface of rotating billet in the region of beam focal spot melted metal of small volume was created, which under the action of centrifugal forces at accelerations of 250 g and higher was removed as the directed spray of small droplets in a diametral billet plane $20-22^\circ$ and axial plane $1-2^\circ$ and droplet velocities about 15 m/s. The direction of spray was simply regulated by location of EB focal spot on the billet surface. The granulometric

composition and its homogeneity mainly were determined by consumable billet frequency of rotation. In the investigated range of rotating frequencies $1000-2500 \text{ min}^{-1}$ the droplets size was varied between 100 and $1000 \mu\text{m}$.

2. Materials.

As materials used both for the substrate and for the consumable billet any industrial metal may practically be used, including refractory; Ni, Al, Ti - based alloys; steels.

There following requirement for consumable billet material were specified: the billet had not to be destroyed when rotated with frequency of the order of 1000 min^{-1} and to cause cracks in heating up to 0.5-0.6 melting temperature. For reaching material interreaction with substrate (if it is required) the melting temperature had to be lower than melting temperature of billet material.

Moreover, nonmetallic substrate can also be used.

3. Properties.

3.1 Mechanical properties.

Mechanical properties of materials produced by the method of EB spray casting were examined on example of superalloy (composition in mass % C:0.10-0.16; W:9.5-11; Cr:7.5-9.0; Ni-base; Co:14.1-17.0; Al:4.85-5.10; Ti:2.0-2.7) dense deposit $100 \times 100 \times 200 \text{ mm}$ produced with substrate temperature 1530 K. Obtained average results of elasticity limit, destruction limit, relative elongation and density were shown at the Table 1.

In addition, at the table for comparison corresponding values were given for the same alloy produced by the EB cold hearth remelting method. It was essentially to mention solid characteristics of the alloy produced by the EB spray casting rised on 15-20% after appropriate thermomechanical treatment.

T A B L E 1

Condition	σ_B MPa	$\sigma_{0.2}$ MPa	δ %	a_k J/sm ²	ρ gr/sm ³
EB cold hearth casted	965	830	16	43	8.50
EB spray casted	1150	920	13	65	8.53

The experiments of Al deposition on Al_2O_3 substrate also were done. In this case examination were not done but solidity of connection was attractive demonstrated at the Fig.3 from which it was clear a destruction was not on the bound but on the ceramic layer.

3.2 Diffusion penetration.

Diffusion interreaction of superalloy (composition in mass % C:0.07; Cr:13.0-16.0; Ni-base; Mo:2.8-3.2; Ti:2.35-2.75) in form of layer about 10 mm thick with nickel substract at the temperature 1480 K was investigated. The depth of diffusion penetration of elements from the alloy to nickel at given temperature was: Al-50 μ m, Cr-28 μ m, Ti-46 μ m. The higher was temperature the deeper was diffusion penetration.

3.3 Crystalline structures size.

Investigated materials and alloys (superalloys, stainless steels, aluminium) produced by the EB spray casting had equiaxed small grained or dendritic structure. At the Fig.4 alteration of sprayed alloy was represented depending on initial temperature of substrate the alloy was deposited on.

Materials produced by EB spray casting distingnished in high grade of dendritic uniformity. Investigations of dendritic nonuniformity in the suprealloy (see 3.1) were done. The liquation coefficient was not higer than 1.2 for all elements. 3.4. Loss of added elements.

The values of chemical elements loss in alloy by evaporation during EB spray casting were determined. The amounts of losses were numerically calculated with using Langmuir and diffusion mechanisms of evaporation. As an example stainless

steel was taken (composition in mass % C:0.08; Mn:2.0; Cr:17-19; Ni:9.0-11). The contents of Mn was altered on 31% and contents of Cr - on 1.5%. The laboratory analysis confirmed the calculations.

In comparison with other vacuum techniques low losses by evaporation were determined by such factors as small surface of liquid metal (the total surface of liquid droplets and surface of liquid bulk on expend billet was of the order of 10^{-3} m^2) and small extraheating under melting temperature (not higher than 50K).

4. Theoretical basis.

The process of EB spray casting was quite difficult for the theoretical consideration of physical processes took place during its different steps. It was necessary to involve such branches of physics as heat transfer, hydrodynamics, surface phenomena, radiation, kinetics and other. For the numerical calculation it was necessary to use the methods of mathematical modelling.

The mathematical model of heat transfer took place during solidification of spreading droplets on a substrate was created for the temperature fields in the metal-substrate system and initial velocities of quenching in the solidifying metal calculation/ 1 /. The elaborations allowed to describe from the physical point of view the process steps of EB spray casting and to make numerical calculations.

4.1. The processes took place during consumable billet melting.

To the side surface of cylindrical billet electron beam was directed with the cross section square of the order of 10^{-4} m^2 and surface power of the order of 10^8 W/m^2 . The beam energy was partially consumed for the billet heating (about 80%) and the rest went out to the space as a scattered electrons. The melted bulk of the material (metal) with dimension 0.3-0.5 rad was created under the action of the beam at stable heating regime on the side surface of consumable billet along circular generating line. Rotating billet provided to melted metal the acceleration of the order of 1000 m/s^2 and it was removed in a form of droplets spray along the tangent to the billet surface perpendicularly to the rotation axis with velocity of the order of 10 m/s .

Droplets size without hydrodynamics consideration was

determined by surface tension σ , melt density ρ and expend billet radius R and rotation frequency n in accordance with formula

$$\frac{1}{\pi n \sqrt{\frac{\sigma}{\rho R}}}$$

At the installation (1.2) experiment for the droplet size determination was made with sprayed steel quenched in a bulk filled with an oil. The results showed the droplets size lied in the interval between 10 μm and 3 mm (Fig.5).

After investigation of separate solidified droplets of superalloy (3.2) on nickel substrate (Fig.6) it was determined that at the statistic ensemble of droplets two sizes dominated: 0.3 and 0.9 mm. Such bimodal nature of distribution was explained by droplet-satellite creation during droplet isolation from expend billet surface / 2 /.

The time of droplet situation at the beam action zone was equal to value of the order of 10^{-3} s. During this period droplet had time to be overheated only about 1.5 K, that was why futher calculation suppose the droplet left billet with the temperature of liquid state transformation.

4.2 Shape formation and cooling of droplets during fly in vaquum from billet to substrate.

In accordance with / 3 / the shape and state of droplets depended on correlation of that parameters as droplet oscillation time, oscillations attenuation time constant, time of droplet cooling to solidification beginning, whole time of crystallisation heat removing and time of droplets moving from heating zone to the barrier (substrate). After the calculation of this parameters according to conventional procedure applied to given process following characteristic values were obtained:

- oscillation time 2.5×10^{-5} s;
- oscillations attenuation time 5×10^{-5} s;
- the time to beginning of solidification 10^{-1} s;
- the time of moving 2×10^{-2} s.

Parameters correlation showed the droplet had right circle form on substrate and was in solid-liquid state with temperature closed to liquidus temperature wich carried out experiments confirmed (Fig.6)

4.3 Droplet spreading, quenching and solidification on the substrate.

After the droplet arrived on the substrate it spreaded and solidified simultaneously. At the moment of surface touching at the point of touching compression wave created which spreaded with sound velocity. Inside compression zone superfluous pressure 10^8 Pa created. After compression wave passed kinetic pressure began to act on on droplet equal to

$$\rho V^2,$$

where ρ - droplet material density, V - droplet velocity. If numerically expressed kinetic pressure was equal to value of the order of 10^5 Pa and acted on whole droplet bulk during whole spreading time that equal to 10^{-4} s.

The spreading might be stopped by two factors determined by initial temperature of substrate heating:

- a) the energy of spreaded droplet surface tension became greater then kinetic energy supplied to the droplet by rotated billet;
- b) the temperature on the periphery of spreading droplet became lower than the temperature of droplet material solidification.

In the second case, as authors / 4 / reffered, at the droplet periphery characteristic barrier created consisted of liquid material influx covered solidified one.

To determine the influence of initial substrate temperature on the droplet spreading character the experiment was carried out with single droplets deposition on a substrates at a different temperatures. Nickel discs 10 mm thick were used as a substrates and the superalloy (3.2) was used as a sprayed. During single droplets deposition substrate was feeded in one move to the steady melt spray with the velocity 0.04 m/s. Substrates temperature was varied in a range from 1200 to 1550 K (superalloy solidus temperature). At low substrate temperatures characteristic breaker created (Fig.6a) which at higher temperature smothed (Fig.6b) and after reaching alloy solidification temperature drorlets consolidated in a merged film (Fig.6c). During material structure formation produced by sprayed casting method side breaker played negative role because uniform layers spreading violated and different thickness at a central droplet part and at a periphery led to different quenching velocities of alloy. For the effect of

breaker creation avoiding the substrate temperature during technological process must be approached to the sprayed alloy solidus temperature.

For the contact temperature on droplet-substrate bound determined as depending on substrate initial temperature according to model / 1 / calculations were made for the substrate temperatures range 900...1550 K. Calculations results were supplied as a thermal cycles at the Fig.7. Temperature rising at the metal-substrate contact zone took place mainly because hidden crystallisation heat outcome at the interval 1550...1650 K. If substrate preliminary heated over 1500 K, as it evidently from the graph, the temperature became higher than solidus, i.e melting of the highest layer of substrate took place. The analysis of temperature field in metal-substrate system showed the melting depth rised with substrate initial heating rising but not higher than 20 μm .

All the above mentioned calculations had a great deal with droplets spreading on deposited layer of sprayed material.

The quenching velocities calculated according to / 1 / were characteristic for EB spray casting and were equal to $10^4 \dots 10^5 \text{ K/s}$, and the quantity of quenching velocity rised with initial substrate heating falling. Such a high quenching velocities led to characteristic uniform small grained structure of materials (Fig.8).

With the help of optical electron microscope and microrentgenspectral analysator the structure of superalloy (3.1) was investigated obtained with substrate initial temperatures 1175 and 1375 K. It was determined that structure of alloy produced by EB spray casting in comparison with casted structure obtained as a result of conventional EB remelting differed by morphology of structural consistents and their size. Grain size in the alloy specimen 25-30 times smaller than in specimen of EB remelting. Carbide generation with a "strokes" configuration in EB melting structures replaced by large arbitrary placed generations of cubic and block configuration. In addition, larger carbides were situated on grain boundaries and smaller were situated statistically uniform in the grain body.

Deposition temperature rising from 1175 to 1375 K promoted

to structure components formation with higher dispersion, more uniform in size and character of situation carbide phases, significantly low porosity and defectivity. The main phases presented in the alloy produced from sprayed melt were γ -phase and γ' -phase. Carbides MC were situated inside grains and at the bounds.

Carbides of complex composition, nitrides and carbonitrides were displayed in alloy. The amount of dispersed generations in alloy produced from sprayed melt differed from EB remelting alloy more than one order. If deposition temperature was equal to 1175 K γ' -phase formed with bimodal and spherical structures, and spherical was wished.

5. Advantages.

The advantages of given technique compared with another determined by following factors:

5.1 The process took place in vacuum (1.2). Vacuum as a rule was more pure environment than inert and other gases. For example, authors / 5 / stated that vacuum at a pressure 0.133 Pa was million times pure concerning aggressive gases than pure argon produced by industry.

Nitrogen or others inert gases were used in Osprey process as a protective environment. Thanks to it microporosity generated by gas bubbles catching and separation bound between separate spreaded droplets observed in produced material. According to / 6 / the porosity in Al-based alloy specimens was equal to 8-12% near the substrate. In the case of EB spraying one could see such picture only in regimes with insufficient heating of the substrate (when substrate temperature 200-300 K low than melting temperature of sprayed material).

For the plasma and flame deposition techniques such shortages as for Osprey presented.

5.2 High velocity of liquid droplets in spray (1.3). Such velocity allowed to obtain high quenching velocities (3.3,4). High velocity of droplets gave an achievement for the method in shape of small grained structure compared with VADER technique and "Leybold Gereus" EB technique in which metal dropped on a substrate under action of gravity. The advantages in properties were said by data represented in table 1.

5.3 Relatively high productivity of the method compared to so cold rapid quenching methods: gun, flatten, spinning and other. All of this methods provided the productivity no more than 1 kg/h while spray casting method provided the productivity of the order of 10-100 kg/h depending on applied technique.

6. Potential industrial application.

Enumerated advantages of EB spray casting method allowed to produce wide spectrum of goods with mass up to 100 kg and linear size up to 500 mm (Fig.9a,b). The characteristic features of the billets were structure usual for rapid quenching (3.3,4); close accordance of billet with unit shape (Fig.9c); consumable material chemical composition keeping (3.4)

6.2 Coating. The method allowed to produce coatings 1 mm thick and more which might be along with the substrate considered as bimetals. Units coating by the method was allowed them to carry recovering function in expensive units weared out, to remove casted defects, to improve surface layer properties (Fig.9d), to economise material (Fig.9e). For the material of coating the same material might be used (in case of recovering or defects removing), with improved properties or more cheap. The coatings characterised by solid interreaction with substrate and uniform small microstructure. The shortage of the method was impossibility to produce coating less then 1 mm thick.

6.3 Composite materials. Composites of metal ceramics type (Al-Al₂O₃) and fiber type composites (steel fibers-aluminium matrix) were produced by EB spraying method. Experiments for coating of steel tube by titanium layer were done (Fig.9f). In addition, it was possible to produce multilayer materials and grained composites by spraying from two or more consumable billets simultaneously.

Pictures and photos.

1. The scheme of EB spray casting.
2. E121 installation.
3. Aluminium - aluminium oxide specimen after bend examination.
4. Superalloy microstructure ($\times 120$) at different substrate temperatures: a-1200K, b-1470K, c-1530K.
5. Granulometric composition of melt spray.
6. Superalloy separate droplets on nickel substrate ($\times 10$) at different substrate temperatures: a-1100K, b-1450K, c-1530K.
7. Thermocycles (T,t) at material - substrate bound.
8. Superalloy microstructure ($\times 660$).
9. Goods examples produced by EB spray casting:
 - a - 200 mm diameter superalloy ring,
 - b - 60 mm diameter titanium tubes after mechanical treatment,
 - c - superalloy profile ($\times 0.9$),
 - d - engine unit (35 mm diameter) original and after coating with instrumental high-speed steel layer,
 - e - extruder coated with low-carbon steel layer ($\times 0.5$),
 - f - bimetallic titanium - steel tube.

Fig. 1.

Half tone
14/3/15

Photo 2.

Photo 3.

Photo 4. (a).

Photo 4. (b).

Photo 4. (c).

$\phi \leq 1 \text{ mm}$

$\phi 1 \div 2 \text{ mm}$

$\phi 2 \div 3 \text{ mm}$

$\phi 3 \div 5 \text{ mm}$

Photo 5.

Photo 6. (a).

Photo 6. (b).

Photo 6. (c).

Fig. 7.

Photo 8.

Photo 9. (a).

Photo 9. (b).

Photo 9. (c).

Photo 9. (d).

Photo 9. (c).

Photo 9. (d).

Photo 9. (e).

Photo 9. (f).

Project Title: Characterization of a Metal Vapor Buring on Nickel-Magnesium Cathode.

Principal Investigator: Yuri Korolev
High Current Electronics Institute
Tomsk, Russia
AM-7666

CLAUSE 1 - STATEMENT OF WORK

Tasks:

The Contractor shall:

1. Produce and provide to Sandia a report that describes the design and construction of an apparatus providing a 1cm diameter Ni cathode over a larger diameter Ni cathode. The design of the apparatus shall provide for the apparatus to sustain a 100amp arc for a sufficient duration such that steady state conditions are achieved. The design shall also provide for diagnostics when (at least) one electrode has a molten surface. Pressures in the vacuum chamber due to metal vapor shall be up to 0.1 Torr.

The Contractor shall submit the report described above to Sandia for approval. If Sandia has any comments, questions, or changes the Contractor shall make any necessary alterations and resubmit the report. Subsequent work shall commence only after Sandia and the Contractor have agreed about the design described in Task 1.

In each of Tasks 2 through 4, a set of data shall be obtained for pure Ni electrodes and for Ni-1 W/0 Mg alloy electrodes.

2. Provide a report of the results of measurements (experiments) with two solid (unmelted) electrodes at gaps of 5mm and 20mm. Measurements shall include:

- (a) electrode temperature
- (b) electron density
- (c) estimates of thermal and directed velocity of ions

These measurements shall sample a point in the flare region and a point in the positive column for the 20mm gap.

3. Provide a report of the results of measurements (experiments) with at least one molten electrode, consisting of the same data set as Task 2. Arc duration to the point of a study state of the plasma parameters, shall also be provided.

4. Provide a report of the results of measurements (experiments) with at least one molten cathode, consisting of the same data set as Task 2. Also provide the

duration up to the first arc that is short circuited by a falling droplet of molten metal.

5. Provide a final report that: (1) compares the results of Tasks 2,3, and 4, and (2) describes a theoretical model of the steady state cathode spot in the presence of at least one molten electrode, containing a comparison with an experiment performed.

Russian Academy of Sciences
Siberian Division
High Current Electronics Institute

Scientific Report

**Characterization of a Metal Vapor Burning
on Nickel-Magnesium Cathode**

(Report No 1, Contract AM-7666)

Principal Investigator:
Prof. Yuri Korolev

Tomsk, January 1995

1. Introduction

1.1. General requirements for experimental arrangement

The objectives of this work are to develop the plasma diagnostic techniques for vacuum discharges in the arc furnaces and the theoretical models for arc. In order to solve these problems it is necessary to design an experimental setup closely approximating the conditions in an actual arc furnace. A principle of such a furnace operation is illustrated in Fig. 1.

The bulk cylindrical cathode with the flat operating surface 20 cm in diameter is inserted into the water-cooling vessel being the anode of discharge chamber. The electrode system is arranged vertically and the cathode is placed at the upper part of the construction, as shown in Fig. 1. In the course of arcing the bulk cathode, in the points where the cathode spots are attached, melts and the drops of liquid metal flow down the anode vessel thereby ensuring the cathode overmelting. Nickel and Ni + 1 % Mg alloy are the most of interest cathode materials for the present work.

A typical gas pressure range in an initial stage of the arc operation is from 10^{-2} to 10^{-1} Torr with gap spacing from 0.5 to 2 cm. During the arcing the pressure, or exactly to say the heavy particle density, can be increased since an evaporation of the electrodes occurs. Under these conditions with the total discharge current of 2 kA and discharge operating voltage of 24 V from 20 to 30 cathode spots exist on the flat surface simultaneously. Thus the current onto a "single" cathode spot is about 100 A.

The prerequisites for operation of the similar "single" spot have to be provided in our experimental setup and the experimental arrangement have to offer a possibility to carry out the plasma diagnostic with a spatial and temporal resolution.

Before proceeding the description of the experimental setup and procedure let turn our attention to the vacuum discharge modes in furnace.

1.2. The features of a high-current vacuum arc on cold cathode

As noted above, one of the goals of this work is a diagnostic of arc plasma. In majority of cases a plasma-forming medium in arc discharge is a cathode vapor, therefore the properties of the cathode spots govern the plasma parameters in great extent. The cathode spot can not be treated as a steady-state object since the spot passes through various stages of development after its initiation. Hence, we have to expect that the diagnostic data will differ from one to another depending on the instant in which the measurements are taken. In other words, the results of measurements may depend on

spatial and temporal resolution of apparatus applied. In this connection we shall in brief describe the main features of vacuum arc cathode spots and determine the subject of investigation in more details.

A vacuum arc, like an arc in gas, may be initiated by moving current-carrying contacts apart or as a result of breakdown of vacuum gaps at late breakdown stages. The first technique of arc initiation is used in so-called vacuum opening switches (vacuum current interrupters). The principle of operation of such a switch is as follows. When contacts are closed, they carry a current of commercial frequency. If there appears an overloading in current, the electrodes are rapidly moved apart to a distance of 1 to 2 cm. In the gap formed, an arc with a typical current of up to 10^4 A is initiated. The vacuum arc, however, has the property to extinguish spontaneously at a low current. Therefore, at the instant when the current becomes zero, the circuit opens and the load is switched off from the power supply. The demand for this type of devices is a potent impetus to the study of the arc [1].

In the other arc initiation technique, either a self-breakdown of the vacuum gap is accomplished, or a discharge is ignited at the cathode by forcibly initiating a cathode spot. This technique is widely used in vacuum spark gaps.

As a rule, a vacuum arc operates in the constricted cathode spot mode. At high currents, well discernible anode spots also appear. They are formed almost always at the anode end facing the cathode, unlike the cathode spots which are very movable and may dispose to the side surfaces of the cathode. Anode spots supply the anode material vapor to the gap and may modify the discharge properties. However, by initiating a discharge in a large gap or using a specially shaped anode, e.g. hollow anode, one may attain conditions such that the power dissipated per unit area be insufficient for anode spots to appear. Just such conditions for the discharge operation without anode spots will be discussed below, since a great deal of experimental data for this case [1, 2] offer an opportunity to make preliminary estimates. It should be noted that in the direct-arc-furnaces the anode surface is liquid. Then even though the arc current uniformly flows to the anode and anode spot is absent, the vapor of the anode material may exert some effect on arc characteristics. An elucidation of this effect is one of the goals for present work.

Let us first consider an idealized model of the cathode spot invoking Fig. 2. Here, on the surface of a solid cathode a molten metal layer as if residing in a sort of tub is present. This layer provides the thermionic emission current, j_{em} , and the flux of evaporating atoms, j_a , into a gap. The necessary cathode temperature, T_c , is maintained by ion bombardment of the cathode. The ions are accelerated in a cathode layer of length l_c across which the cathode voltage V_c falls. The electrons emitted from the cathode are also

accelerated in the layer and, when arriving at the plasma region, they have the energy eV_c , since the distance l_c is shorter than the electron free path for any type of collision. In other words, the cathode potential fall region is a sort of vacuum diode with ion neutralization. The electric field at the cathode is described by McCown's equation.

In a steady state, all parameters of the cathode layer are time-independent, i.e. it is meant that the values of T_c, j_{em}, j_a, l_c , and V_c as well as the characteristics of the cathode plasma and the ion flux onto the cathode are constant. In the process of arc operation, the cathode material is expended (the cathode erodes). The material is removed from the gap, including onto the anode and the discharge chamber walls, in the form of atoms and ions. The cathode therewith supplies just such an amount of vapor, which is necessary to maintain a given current density at the cathode with a certain size of the molten metal zone.

It should be stressed once more that the above model describes an idealized pattern and it is convenient for a theoretical treatment of the process. If a situation close to that described, i.e. a quasi-steady state, would take place for a certain measurable time interval, the vacuum arc could be considered a convenient object for investigation. The term "convenient" is used in relation to the actual situation which is far from the above idealized pattern.

In particular, we call attention to the following circumstance. During the operation of an arc discharge, the gap resistance is generally much lower than the ballast resistance of the circuit. Therefore, the discharge current is restricted by the ballast resistance and, in many modes, it is invariable in time. In some sense, this fact gave rise to the tendency to classify the arc discharge with the stationary discharges, i.e. discharges for which a certain current voltage characteristic exists and a certain current corresponds to a given operating voltage. Nevertheless, these exterior indications are far from testifiable to the fact that the processes at the metal surface, in the cathode layer, and in the cathode plasma are steady-state. By and large a constant current onto the anode may be provided, but the cathode spot "lives its own life". It moves over the surface, dividing into cells or component parts; some cells die, some appear, and so the current density at each point of the cathode surface is varying in time.

Thus, the processes occurring in the cathode spot of a constricted arc are far from the idealized pattern shown in Fig. 2. This presents substantial problems for both the experimental study and the development of theoretical models of the cathode spot. Therefore, no universally accepted concept on the whole set of properties of the cathode spot exists. The discussion of some or other phenomena accompanying the operation of an arc discharge on a cold electrode is being continued in the literature. Recently, however, a

1. Introduction

variety of the vacuum arc has been discovered, where the actual processes very closely fit to the stationary spot model. This is the so-called arc with diffuse current attachment at the evaporating cathode. It is generally initiated with the use of an external heater; the cathode material is placed into a high-melting-point crucible and heated to its melting point. Thus produced molten metal bath serves as a cathode. Once a discharge has been initiated, the external heater can be switched off in some cases, since the cathode heating will be entirely provided by ion bombardment. Typically, the crucible is from one to a few centimeters in size. Correspondingly, the area of this peculiar kind of cathode spot is from one to a few square centimeters and current density from 10 to 1000 A/cm². For this diffuse arc, there exist reliable technique for measuring the required parameters in the cathode spot region.

Therefore, to gain a better understanding of the processes occurring in a nonstationary cathode spot, we first dwell on the model of an arc with diffuse cathode spot. This model has been suggested in our papers [3, 4] where the detail mathematical description and the comparison with the experiments are presented. Here we shall only illustrate the main idea of the model directed to Fig. 3.

In constructing a theoretical models of the cathode spot of a vacuum arc, some suppositions are generally used, which have already assumed the significance of postulates, although none of them have been confirmed by direct measurements. These postulates are as follows.

- The cathode fall voltage cannot exceed the arc operating voltage, i.e. the potential increases monotonically in the direction from the cathode to anode.
- The length of the cathode layer is small and this layer is collisionless for the electrons that have started from the cathode. Consequently, charged particles are not generated in the cathode layer.
- The ion current onto the cathode is provided from the plasma of the cathode flare, i.e. from the l_c boundary (Fig. 2). This current cannot exceed the classical Bohm current from the plasma. Consequently, the ion current at the cathode, as distinct from a glow discharge, constitutes a negligibly small part of the total discharge current, and the total discharge current is close to emission current.

We believe that these suppositions are inadequate. Therefore, we give in the present section a description of the cathode layer model which assumes that the potential distribution along the gap is nonmonotonic. The general considerations that allow us to construct such a model are reduced to the fact that the cathode flare plasma is charged positively due to the extraction of electrons from this plasma and the diffusion motion of electrons toward the anode. This results in an increase in cathode fall voltage and

appearance of a potential maximum at the cathode region boundary. The idea of a potential hump appearing under conditions like these was first offered by Plyutto, but this viewpoint was not further developed.

As it was shown in Refs. 3 and 4, the potential hump model allows a self-consistent interpretation of a diversity of experimental data obtained for arcs with diffuse cathode spots. The potential distribution along the discharge axis is shown schematically in Fig. 3. Here the cathode is set at point $x = 0$. The outer boundary of the cathode plasma corresponds to coordinate x_m . The rest of the gap, $(d - x_m)$, may then be called a vacuum diode with ion neutralization or positive column. The cathode voltage falls on length l_c and, as shown in Fig. 3, it may exceed the discharge operating voltage, V_a . Note that the scale on the X -axis is not linear. The distance l_c is very small: it is much less than the dimension of the flare, $(x_m - l_c)$.

In the process of arc operation, a flux of neutral atoms j_a is evaporated from the cathode. If an atom has been ionized within the length l_c , it returns back onto the cathode in the form of an ion. Such ions constitute the current $j_i(0)$ at the cathode. It is clear that the ion current cannot exceed j_a . If the ionization of atoms occurs between the points l_c and x_1 , the ions produced are accelerated in the region where the characteristic $V(x)$ has a negative slope, thereby constituting an ion flux onto the anode.

The relation between the cathode vapor density and the distance x_m is such that the electron free path for ionization either compares with x_m or exceeds it. Therefore, the presence of the potential hump region, $0x_m$, is important for keeping the ionization degree in the cathode flare high. This region is a potential trap for the electrons having started from the cathode and lost in collisions an energy greater than eV_m . They remain inside the potential well and, owing to their oscillating motion, provide for efficient plasma generation inside the cathode flare. These conditions are similar to some extent to those in a low-pressure glow discharge with a hollow cathode.

Although the length l_c is far smaller as compared to all free paths, nevertheless, ionization of atoms may occur in this region. The ionization is produced not by the electrons that have started from the cathode, but the energetic thermal electrons from the cathode flare plasma, which may fly into the potential barrier region $0l_c$. Clearly, the probability of ionization is the higher, the higher the plasma temperature and the longer the time of flight of the atoms through the cathode layer. These energetic electrons also provide the back electron current onto the cathode, j_{eb} . Thus, the total current density at the cathode is given by

$$j(0) = j_{em} + j_i(0) - j_{eb}, \quad (1.1)$$

1. Introduction

where j_{em} is the thermionic current density enhanced by the Schottky effect.

In the cross section x_m , the same current density is provided by the components appearing in the following equation:

$$j(0) = j(x_m) = \lambda j_{em} + j_{ep} - j_i(x_m), \quad (1.2)$$

where λ is the fraction of the thermionic current constituted by electrons which have started from the cathode and have not lost their energy in collisions within the length x_m ; j_{ep} is the current of plasma electrons, whose energy is high enough for they were able to overcome the potential barrier $e(V_c - V_m)$; and $j_i(x_m)$ is the current of ions which have been generated within the length $(x_1 - l_c)$ and reached the anode.

Thus, on the one hand, there exists a channel for the cathode material vapor to come to the plasma and, on the other hand, a channel for its rapid going away toward the cathode and anode in the form of ions with velocities of the order of 10^7 cm/s. Owing to the balance between these processes, a certain size of the cathode flare is established.

In the model described, the region of potential minimum near the point x_m is a potential trap for ions. The build-up of ions in this region as well as the ion flow toward the anode allows efficient neutralization of the electron space charge in the region $(d - x_m)$, identified by us with a vacuum diode. As a result, the high current density is provided through this "vacuum diode" with a low voltage $(V_a - V_m)$ across it, and thereby a low arc operating voltage is available.

We believe that the above representation may with any corrections be applied to the vacuum arc with the constricted cathode spot that is the subject of present paper.

Let us consider now the principal properties of a vacuum arc with a constricted cathode spot. One of the peculiarities of the operation of an arc discharge in vacuum is that the spots move chaotically over the cathode surface. Two types of cathode spot are generally distinguished. During the initial stage of discharge operation, spots of the first type appear on electrodes made of variety of metals. They are characterized by fast moving over the surface with velocities of 10^3 to $4 \cdot 10^3$ cm/s and cause slight damage to the cathode. For instance, for copper the amount of material removed from the cathode upon passage of a unit charge through the cathode spot is $5 \cdot 10^{-7}$ g/C. The first-type spots may exist for a long time at low arc currents or on a rough, poorly degassed cathode surface.

As the cathode surface is further heated and degassed under the action of an arc discharge, spots of the second type appear. They have a substantially lower velocity, from 10 to 100 cm/s, and are characterized by a high rate of cathode erosion, $(5 \text{ to } 10) \cdot 10^{-5}$

g/C. It is generally believed that the current density in second type spots is lower than that in first-type spots. This belief is based on the fact that second-type spots leave on the cathode surface molten regions around 100 μm in size, while typical of first-type spots is the presence of numerous microcraters with dimensions of less than 10 μm . Moreover, the transverse dimension of the plasma blob appearing near the cathode surface for second-type spots is generally larger than that for first-type spots. In some cases, the so-called current onto an individual cathode spot is larger for almost immovable spot.

The term "current onto an individual cathode spot" is widely met in the literature. Let us treat this term in more detail. A high current vacuum arc behaves as a group of independent arc, as if connected in parallel, i.e. several spots operate on the cathode simultaneously. It was noted in numerous experiments that increasing the total arc current increases the number of cathode spots. Just this observation provided reason to introduce the notion of current onto an individual spot in early works. The values of this current for various cathode materials are listed in Table 1 (the data are taken from an article by L.P. Harris, see the book [1]).

Table 1

Cathode material	Liquid mercury	Zinc	Copper	Titanium	Tungsten
Spot current, A	2–7	9–20	75–100	70	250–300

However, if we consider the processes in a so-called single cathode spot in more detail, we may see that they are essentially nonstationary, and the cathode region under the plasma blob is not a molten metal bath being in a quiescent state. This is why the theoretical model described above, as well as other models, should be applied with care and aware of the processes actually occurring in the spot.

Even in his early works, Kesaev developed an approach according to which a cathode spot consists of individual cells whose number increases with increasing the current onto the spot. These cells may detach from the spot and they thus serve as centers of kind where new cathode spots appear, i.e. the process of spot division occurs. Within each spot, the cells disappear and appear again, so that, owing to the dynamic equilibrium between the processes of their appearance and disappearance, the current onto an individual spot is sustained. In the context of the above-said, an arc may extinguish in fact at any value of current. For this to happen, it is necessary that all cells stop operating at the same time. It is clear, that at a large current onto the spot, i.e. a large number of cells,

1. Introduction

the probability of arc extinguishing is very low, while decreasing the current sharply shortens the arc lifetime.

In later investigations, the notion of cathode spot fragments or cathode surface regions that provide the most intense electron emission (emission centers) were introduced. These terms are in fact alternative names for the so-called cells. In general, the up-to-date approach to a description of the cathode spot is based on the fact that at a large current several spot fragments or emission centers may operate simultaneously under one and the same plasma blob. Of course, the idea that these centers are independent molten metal baths situated alongside each other is too straightforward. This seems to be so in some cases; otherwise the fragments coalesce to form a large-area emission region. The pattern is dynamical as a whole, i.e. the sites of enhanced emission transfer even within a single spot. The outcome of these sites outside the edges of the molten metal zone is just perceived as the motion of the cathode spot over the surface. It is clear that decreasing the spot current decreases the number of fragments, and a fragment may be called a truly single cathode spot. Therefore, the authors of up-to-date investigations report for single cathode spots the current values substantially lower than those given in Table 1. For instance, Rakhovsky believes that for a copper cathode, the current onto a single spot is 15 to 20 A.

The ideas about the mechanism of initiation of a cathode spot fragment or, what is the same — about the mechanism of initiation of a truly single cathode spot, have been developed by Mesyats and co-workers. The essence of this approach is as follows. If a molten metal layer is present on the cathode surface and the current density is high enough, this state cannot be stable. The matter is that at a high current density the electric field at the cathode may reach values exceeding 10^6 V/cm. In this case field emission current is emitted from some microareas of the cathode surface. These microareas may appear both inside the molten metal bath due to a rough structure of the surface and at the bath edges. The cathode region appears to be unstable with respect to fluctuations in emission current, since increasing the emission current increases the ion flux onto the cathode. Under the action of the emission current and ion bombardment a microexplosion occurs on the cathode surface, i.e. there takes place the transition of field emission to explosive electron emission or, in other words, an explosive emission center is initiated.

So, we would like to stress once more that the process of formation of a new fragment is in essence the process of initiation of a new emission center. The characteristic time scale for the explosion is in the nanosecond range. As a result of explosion, a crater having a size of about $1\text{ }\mu\text{m}$ is formed on the cathode surface. If the cathode surface is contaminated or the current onto the spot is small, the crater will not grow in size, but a

new crater will appear at the edge of the microbath. In this case, the first-type spot mode is realized.

It seems that typical of the second-type spots is expansion of the molten metal zone in the place where an explosive emission center has appeared. Therefore, the traces left by such spots are large and the spots move over the surface more slowly. Thus, a cathode spot fragment in the stage of its initiation is called “an emission center” or sometimes “an explosive center”. Mesyats has suggested to use a unified term “ecton” including the first letters of both formerly used terms [5]. It is clear that the notion of ecton may thus be applied in a description of not only the mechanism of operation of a cathode spot in the nonstationary phase, but a variety of other types of discharge where microexplosions may occur at the cathode surface under the action of emission current, ion bombardment, and other factors.

As a conclusion let us discuss some results on examination of cathode erosion traces in view of the above described concept. This may be helpful in going to the discussion of the notion of a current density in an individual cathode spot. Harris in his review [1] presents a set of photographs taken from cathode surfaces in various modes of arc operation, including those from a copper cathode at an arc current of about 200 A and discharge duration of a few millisecond. The erosion trace left by the arc on the cathode has a width of 150 μm . The cathode spot current density is then estimated as $j = 10^6 \text{ A/cm}^2$. Nevertheless, it can be seen that the track bears little resemblance to a bath of undisturbed molten metal which was slowly solidifying as the current ceased. On the cathode, inside the wide track, deep melting regions and microcraters about 1 μm in size are seen. Similar microcraters are present at the edge of the wide track. Based on the above discussion, it is clear that at every instant a large number of cathode spot fragments were operating on the cathode; so the arc with such a current, strictly speaking, was not an arc with a single cathode spot. For instance, if we imagine that at some instant the whole current passed through a crater 1 μm in size, we shall obtain a fantastically high current density, $j = 2 \cdot 10^{10} \text{ A/cm}^2$.

This observation was taken into account by Daalder who performed measurements at lower arc currents. Supposing that the whole current could pass through a single crater, he obtained current densities of the order of 10^8 A/cm^2 .

Finally, the limiting case of decreasing the current and shortening the pulse was realized experimentally by Mesyats and co-workers. They used a tungsten point cathode. The arc current pulse duration could be varied from 50 ns to 1.3 μs , typical currents were from 2.6 to 50 A, and the arc operating voltage was about 50 V. Most illustrative are photographs taken for the current 2.6 A. For the pulse duration 50 to 100 ns, one or two

craters 5 to 7 μm in size were observed on the surface. As the pulse duration was increased, the number of craters increased, each new crater appearing at the edge of the preceding one, i.e. the cathode spot moved over the cathode. Based on the known pulse duration and length of the track left microcraters, the velocity of motion of the spot was estimated to be $6 \cdot 10^3$ cm/s. The current density through an individual microcrater was about 10^7 A/cm². It may be said regarding this experiment that the investigators evidently dealt with measuring the parameters of a cathode spot fragments or a single cathode spot whose current was a few amperes. We thus may see how great is the difference between the current onto a truly single cathode spot and the current onto a spot consisting of simultaneously operating fragments (e.g. for tungsten $i = 250$ to 300 A, as seen from Table 1).

With the above-said taken into consideration, we may raise the question as to whether the idealized cathode spot model described above is applicable for nonstationary spots. This model implies that the molten metal is at rest and evaporates in the form of an atom flux. These notions may be considered as a first approximation in estimating the condition of the cathode surface under the plasma, the parameters of the cathode layer, and the parameters of the plasma as such. In the process of discharge operation, explosive emission events occur under the plasma, which causes local deformation of the quasistationary cathode spot both inside the molten metal bath and at its edges. In the latter case, the spot covers new and new regions of the cathode surface. It should also be noted that in an explosive emission event not only atoms and ions are generated, but also metal microdrops are formed, that are generally indicated in experiments.

For the first-type spots that are usually characteristic of arc in an initial stage of development the cathode material enters the gap mainly due to microexplosive processes. In this case it is difficult to imagine a bath with melted metal that supplies a flux of evaporated atoms in the gap. The processes under a plasma blob are essentially non-steady-state and emission centers less than 10 μm in size come into existence on the cathode surface and move over it.

As the cathode in the local area of the first-type spot attachment is warmed-up, the second-type spot with emission region of about 100 μm forms. The microexplosions can also occur in this stage, however a considerable fraction of cathode material enters the gap in the form of atomic flux. Thus, for the spot of second type the model more closely resembles the actual situation.

1.3. Discharge features in the arc furnace

Proceeding from the above-described notions we can qualitatively predict the arcing in the furnace and formulate the objectives of the investigation more definitely. As it was noted, from 20 to 30 spots operate simultaneously on the cathode as the total steady-state arc current is about 2 kA. These spots are slowly moving over the surface; some of them may die and new cathode spots can originate. In particular, the new spots may be initiated at the side surface of the cathode.

It is apparent that in the course of arc operation the most of the total current flows onto the cathode spots. However, some fraction of the current provides for a glow-type semi-self-sustained discharge that closes onto the entire cathode surface. The reasons for this discharge appearance are a rather high heavy particle density and an availability of various kinds of secondary emission from the cathode. Hence, at any instant of time a glow-to-arc transition process may be responsible for a new cathode spot initiation. Besides that, a cathode spot may be provoked by the other mechanisms, for instance, due to impact a microdrop with the cathode surface.

Immediately after the cathode spot appearance we deal with the first-type cathode spot. As a result of microexplosion the microcrater about $10\text{ }\mu\text{m}$ in size arises on the cathode. On the one hand, it is the center of enhanced electron emission and, on the other hand, it supplies the cathode material into the cathode flare. A characteristic lifetime for such a single emission center is several tens of nanoseconds and current onto it constitutes several amperes. The new emission centers usually arise at the edge of the preceding center resulting in a motion of the cathode spot over the surface with a velocity of the order of 10^3 cm/s . However, when the total current in external circuit substantially exceeds the single emission center current the several emission centers can simultaneously operate on the cathode in immediate vicinity of each other. As a result the cathode locally heats up and a bath of melted metal $100\text{--}200\text{ }\mu\text{m}$ in size forms on the surface. In this case the cathode material enters the flare not only due to microexplosions but also due to evaporation and we can say that the fast-moving first-type spots transform into the slowly moving second-type spot. A characteristic time of the above transformation can be estimated proceeding from the size of the melted area ($l \approx 100\text{ }\mu\text{m}$) and the velocity of fast cathode spot motion ($v \approx 10^3\text{ cm/s}$). Then we have $t \approx l/v \approx 10\text{ }\mu\text{s}$.

Thus, after about $10\text{ }\mu\text{s}$ the arc discharge with the second-type spot is established. This stage is often referred to as quasi-steady-state arc. The parameters of the cathode flare and positive column is not subjected, in the average, to substantial variations although the local spatial fluctuations in plasma density on the time scale less than $10\text{ }\mu\text{s}$

are possible. The rather small size of the melted area prevents the large drops being separated from the surface. At this stage of discharge operation a microdrop flux is usually observed in experiments.

At the last stage a slow expansion of the melted area takes place. The process can be related to operation of a so-called group-type spot, i.e. to the situation in which several second-type spots operate under the same plasma flare. A characteristic time for such a regime to establish estimate exceeds 100 μ s.

Thus, the goal of this work in a general sense is to study the arc at the stages of second-type spot operation and large size drop formation.

1.4. Detailization of the goals for present work

Based on the above-described features of the arc in furnace, we can formulate the goals of this work as follows.

- a) Design the facility to model the arc discharge with the second-type cathode spot in the conditions close to that in arc furnace and found the plasma diagnostic techniques.
- b) Carry out the measurements of electron density and temperature for the discharge with the second-type cathode spot on solid electrodes.
- c) Estimate the thermal and directed velocities of ions in cathode flare.
- d) Investigate the peculiarities related to enhancing the neutral particle density, in particular, related to the presence of the liquid anode.
- e) Carry out the measurements in conditions where the liquid metal drop separates from the cathode.
- f) Develop the theoretical models for vacuum arc.

2. Development the electrical circuit and the discharge chamber design

2.1. General requirements for electrode system and electrical circuit.

As noted above, the feature of the arc furnace is that a number of cathode spots operate simultaneously on the surface and each of them may be at different stages of time development. In these conditions any measurements of plasma parameters will give some average values so that the interpretation of measurement data will be extremely hampered. It is clear that the electrode system and circuit design have to provide a cathode spot initiation and succeeding current attachment to this spot. Then after approximately 10 μ s we can say about establishment of the second-type spot and carry out the necessary measurements. In doing so, we must ensure the case in which the cathode spot is localized

on a predetermined place of the surface and the new spots, hampered the diagnostics, are not initiated.

The mechanisms of cathode spot initiation and discharge sustaining may depend on gas pressure. Therefore we intend to vary gas pressure in the experiments by filling the discharge chamber with Ar, He, N₂ and other species. Besides that the pressure in the actual furnace may be determined by the presence of liquid anode. Hence, the discharge chamber design must offer a possibility to carry out the experiments as a liquid anode is available.

It is significant that the neutral particle density and gap spacing in the furnace correspond to the left branch of Paschen's curve. In these conditions the discharge current may flow across not the shortest way but through the long paths. In particular, the hollow anode effect can play an important part in current sustaining. Therefore the discharge chamber design has to exclude the occurrence of the discharge current through long paths.

The current value of 100 A is sufficient to initiate an anode spot on solid anode. The presence of the anode spot may hamper the interpretation of experimental data. On the other hand, such a spot is an integral part of the vacuum discharge for some modes of its operation. Thus, we must provide for a possibility to initiate the discharge in both modes with and without the anode spot.

2.2. Electrical circuits

When analyzing techniques for arc discharge initiation we gave the preference to trigatron-type electrode system. The discharge chamber that has been used in experiments is shown schematically in Fig. 4. The electrodes 1, 3, and 4 are placed in the plexiglas chamber 5 whose internal diameter is 80 mm. The gap distance between the electrodes 3 and 4 varies from 0.5 to 2 cm and typical gas pressure is $p = 10^{-2}$ Torr.

The trigger unit consists of the electrodes 1, 3 and ceramic tube 2 of internal diameter 0.8 mm and external one 2 mm. As a pulsed voltage is applied between the electrodes 1 and 3, the auxiliary flashover occurs; depending on the voltage polarity the cathode spot can be initiated on both electrode 1 and electrode 3. As a result of tests the electrical circuits that meet the requirements of the present work have been chosen. Their descriptions are presented below.

Figure 5 shows the simplest and rather reliable circuit. Here, the cathode spot is initiated on the face of the wire electrode 1 and the main discharge current flows between the cathode 1 and grounded anode 4. The shunt ($R_s = 0.1 \Omega$) is used for current monitoring and the resistance divider ($R_1 = 10 \text{ k}\Omega$, $R_2 = 50 \Omega$) is used to record the potential applied to the electrode 1.

2. Development the electrical circuit and the discharge chamber design

The circuit operates in the following way. In starting position the capacitor bank C_0 is charged up to voltage $V_0 = 2$ to 5 kV. After triggering the thyatron T the negative pulse voltage V_0 is applied to the electrode 1 resulting in a flashover and initiation of the cathode spot on the electrode 1 . Then the auxiliary flashover current flows through the ballast resistor $R_b = 50 \Omega$ and the auxiliary resistor $R_3 = 2 \Omega$. Since the auxiliary resistor is present in the discharge circuit the potential of electrode 1 turns out to be negative with respect to grounded anode 4 so that the main arc current starts flowing between electrodes 1 and 4 . The pulse duration in the main circuit is controlled by capacitor C_0 and resistor R_b .

Voltage and current waveforms for the circuit under discussion are shown in Fig. 6. The frame 6a corresponds to the smallest charging voltage $V_0 = 1.5$ kV. Here, at the instant of thyatron trigger the voltage $-V_0$ is applied to electrode 1 . After a delay time t_d , which for the case under consideration is $t_d = 500$ ns, the flashover occurs and the voltage at the electrode 1 falls to a value of approximately equal to $V_0 R_3 / (R_b + R_3)$. At this moment the cathode spot is initiated on the electrode 1 , however the current in the anode circuit, i.e. the current through the shunt R_s , is equal to zero. Thereafter the current flowing between the electrodes 1 and 3 is intercepted to the electrode 4 and we can see the current rise through the shunt R_s . This current reaches a value of $i \approx V_0 / R_b$ in approximately $2 \mu s$.

When we increase the voltage V_0 the above-described pattern of discharge development remains unchanged (Fig. 6b and c). The delay time to flashover t_d decreases to be established at the level of less than 100 ns (see frame 6c). At voltage $V_0 = 3$ kV the main discharge current reaches the value of $i = 50$ A $\approx V_0 / R_b$ within two microseconds and the discharge operating voltage can be estimated as 25 V. Thus we can say that within $2 \mu s$ a steady-state arc discharge with the second-type spot, or with the several spots located closely to each other, appears in the electrode system 1 and 4 .

The latter statement is supported by the photograph of the gap (Fig. 7) corresponding to the waveforms in Fig. 6c. We can identify the cathode flare, approximately 0.5 cm in size, and the region of the cathode spot as such, i.e. the bright plasma blob immediately adjacent to the cathode. Note, that unlike Fig. 3 corresponding to a low-current density arc, here we call our attention not only to the cathode flare but also to the kern of the cathode flare, i.e. the cathode spot as such. Our preliminary spectral measurements show that the integral spectrum for the kern differs from that for the rest part of cathode flare.

Let us discuss now the discharge features related to an increase in current duration which is achieved by an increase in capacitance C_0 . The waveforms and the gap

photograph for capacitor $C_0 = 4\mu\text{F}$ and voltage $V_0 = 5\text{ kV}$ are presented in Fig. 8. The time scale is increased up to $50\text{ }\mu\text{s}/\text{div}$ with the voltage scale of $40\text{ V}/\text{div}$. Therefore, we fail to observe the delay stage of the discharge development in which the voltage $V_0 = 5\text{ kV}$ is applied to electrode 1 since the trace goes off the oscillograph screen. The oscillograph records a sum of discharge operating voltage and voltage drop across the resistor R_s . One can see that the discharge operating voltage depends only weakly on arc current.

The arc current amounts to 100 A at a maximum with a half-width of $150\text{ }\mu\text{s}$. In these conditions for some shots we can observe the microparticles ejected from the cathode. The trace of such a particle is visible in Fig. 8.

The arc discharge initiation circuit presented in Fig. 5 has a drawback related to the fact that the most fraction of the total energy $C_0 V_0^2 / 2$ is dissipated to ballast resistor R_b . Therefore we have tested a two-stage circuit design that is shown in Fig. 9. The circuit uses the capacitor $C_0 = 10\text{ nF}$ only to initiate the auxiliary arc discharge and the cathode spot on the electrode 1. In order to sustain the main discharge current the capacitor C_1 , that can be several tens of microfarads, is used. The circuit operates by the following way. In the starting position the capacitors C_1 and C_0 are correspondingly charged by the negative voltage $V_1 \leq 500\text{ V}$ and positive voltage V_0 up to 5 kV . Since the voltage V_1 is rather low the flashover can not develop. Once the thyatron is triggered a negative pulse voltage forms at the primary coil of the pulse transformer Tr . This pulse is inverted by the transformer and applied to electrode 3. As a result of flashover the cathode spot appears on the electrode 1 and auxiliary flashover current flows through the resistor R_b , resistor R_3 and capacitor C_1 to ground. After completing this pulse the main discharge current between the electrodes 1 and 4 is initiated under the action of voltage V_1 . The main pulse duration is controlled by resistor R_3 and capacitor C_1 .

Note one of the peculiarities for the circuit described. The capacitor C_0 is rather small and it is intended to initiate the cathode spot. The divider $R_1 R_2$ shows the potential of the electrode 3 with respect to ground and allows us to indicate the onset of flashover. On the other hand, after completing the discharge in the auxiliary circuit the electrode 3 represents virtually some sort of a probe under floating potential. The voltage measured at this probe offers an opportunity to obtain an additional information concerning the cathode flare plasma. Note once more, that for the above circuit the main discharge develops between the electrodes 1 and 4.

Another modification of the circuit design is presented in Fig. 10. It is seen that the circuit is intended to initiate the cathode spot on the electrode 3. Actually, after triggering the thyatron the auxiliary discharge current flows through the resistors R_b , R_3 and

2. Development the electrical circuit and the discharge chamber design

capacitor C_1 . As a result, the cathode spot appears on the electrode 1 and current may flow between the electrode 1 and 4. However the presence of capacitor C_1 provides for the main arc current between the electrodes 3 and 4. The corresponding waveforms for various voltages V_1 are shown in Fig. 11a and b.

The first current peak in Fig. 11a is caused by the discharge between electrodes 1 and 4 whose pulse duration is controlled by the capacitor C_0 and resistor R_b . Thereafter the arc current arises between the electrodes 3 and 4. This current tends to a steady-state value of about 100 A. For the example presented in Fig. 11a the voltage waveform does not indicate the early stages of discharge development since the voltage sensitivity (40 V/div) is extremely high and the voltage trace goes off the oscillograph screen. The trace indicates the potential of the electrode 1 for the subsequent stages as the capacitor C_0 is rather discharged.

Figure 11b shows the waveforms in the case of the higher voltage $V_1 = 280$ V as compared to Fig. 11a. It is seen that the main discharge current in the electrode system 3 and 4 develops faster. The discharge duration for the circuit under discussion can vary by varying the voltage V_1 and resistor R_3 .

Figure 11c shows the gap photograph with the voltage $V_1 = 500$ V, i.e. with the arc current close to 250 A. It is noteworthy that several cathode spots arise on the surface. The brightest of them is attached to the edge of the axial hole on the electrode 3. The spots on the flat part of the cathode appear in the later stage of arc discharge development. Besides that, with the current of 250 A we can observe the anode spots.

As noted above, such a mode of discharge operation is not desirable for plasma diagnostic, i.e. for the problem under solving the present work. However, this circuit design might be profitably employed if we deal with the another problem, namely, investigation of the new cathode spots initiation in the course of arcing. The design enables us to initiate the spot of the bulk electrode and investigate how this spot develops and how the new spots originate.

The circuit presented in Fig. 11 can readily be modified by inserting a pulse transformer that changes the voltage V_0 polarity from negative to positive one. Then the auxiliary arc discharge initiates the cathode spot on the electrode 3. The observations support that in this case the cathode spot on electrode 1 is absent and several spots are located on the surface of electrode 3.

Thus, the above-described preliminary obtained data have given us an opportunity to develop the discharge chamber design whose description is presented below.

2.3. Discharge chamber

A schematic of a discharge chamber is shown in Fig. 12. This drawing does not show the design in detail and only illustrates the main ideas on which this design is based. An electrode system and a heating unit for the experiments with a liquid anode are placed in the water-cooling chamber 1 130 mm in internal diameter made from stainless steel. The chamber envelop has four windows; three of them are intended for diagnostics and one of them serves as a vacuum pumping port. The diagnostic windows are protected by the mechanical gates 2 to prevent the glass from an excessive metal vapor deposition, especially in the course of experiments with a liquid anode.

The discharge trigger unit 3 is similar in design to that presented in Fig. 4. This unit is mounted on the upper flange of the chamber.

The heating unit provides for a liquid metal in the hard-melted crucible 4. The unit is mounted on the lower flange 5 of the chamber. The crucible is made of graphite. Its internal surface will be covered with titanium carbide if the need to protect the graphite from chemical reaction with liquid nickel arises. The graphite crucible is electrically isolated from current-passing leg 7 and connected with another current-passing grounded leg 8. The heater and crucible is thermally protected from the chamber envelop by means of molybdenum screens 9.

We are going to carry out the experiments by the following way. In the first stage a welding transformer is connected to the legs 7 and 8 so that a solid nickel starts being melted down. In this position the switch S is closed and the heater current flows through the leg 7, heater 6 and grounded leg 8. Once the process of melting is completed we disconnect the transformer from the leg 7 and open the switch S . Then the arc current can be initiated in the main gap and the current will flow through the liquid anode, the leg 8 and the shunt R_g . Thus, we shall record the current waveforms, as it has been demonstrated in Figs. 6, 8 and 11.

In conclusion it may be said that the unit to obtain a liquid anode is the most complicated one in the chamber design. We have carried out the preliminary tests and obtained a liquid nickel in a graphite crucible. However, the integration of the heater unit with the chamber envelop may run into unforeseen obstacles. In such a situation it will be necessary to modify the chamber design. Besides that, we have no enough experience to investigate the arc discharge with a liquid anode. Therefore we intend to carry out the experiments with the liquid anode at the final stage of this work with the purpose to analyze the discharge features related to the presence of the liquid anode in the chamber.

Currently the discharge chamber shown in Fig. 12 is in the manufacture stage.

3. Shadow method for electron density measurements

3.1. Principle of the method

One of the techniques to study the transparent plasma inhomogeneities in vacuum and gas discharges is a shadow Toepler method. When using this method we may obtain an illustrative qualitative information concerning a size of inhomogeneities (for instance, plasma blobs, shock waves and the like) and also the temporal and spatial patterns of inhomogeneities development. In individual cases the shadow method offers a possibility to obtain a quantitative information. Let us consider the principle of the shadow method.

Optical train for the method is illustrated in Fig. 13. Here, the light with uniform-phase wave-front is incident on the object of diameter L , for instance, a discharge channel. Since the object refractive index differs from that for environment, the wave front will deform. The distorted wave transits through the lens in the focus of which, strictly on the optical axis, the knife edge is placed. Due to the presence of the knife an amplitude modulation of the light wave occurs, i.e. a visualization of the object takes place. Obtained by this means a shadow image is indicated by the screen or photographic film.

A quantitative method of plasma diagnostic implies that an inverse problem must be solved, i.e. it is necessary to reproduce the object refractive index on the basis of shadow photograph and thereafter to calculate the plasma parameters from the index. Generally, the above problem is practically intractable. However, there exist the special cases that allow a quantitative treatment. One of these cases has been studied in our papers [6, 7] and the method developed has been used in investigations of high-pressure pulse discharges [7–9].

The theory advanced is true for the following simplified assumptions.

It is suggested that the object is absolutely transparent and cylindrically symmetrical, i.e. the refractive index depends only on a distance r from axis. The axis of symmetry is normal to the direction of incident wave propagation. The object refractive index does not substantially differ from environment, so that

$$n(r) = 1 + \kappa(r), \quad |\kappa| \ll 1. \quad (3.1)$$

A characteristic size of the object L assumes to be small as compared to other dimensions of the optical system so that the Fraunhofer approximation would be applied in calculation of diffraction. When passing through the object the light rays are considered to be rectilinear, i.e. the geometrical optics treatment is applicable

$$\lambda \ll L. \quad (3.2)$$

Deformation of the wave front is due to a phase shift and the shift is considered to be small

$$\varphi = \kappa k L \ll 1, \quad k = 2\pi/\lambda. \quad (3.3)$$

Note, that two last conditions show that the value of κ has to be extremely small

$$\kappa \ll L/\lambda \ll 1. \quad (3.4)$$

Thus, the method under consideration is applicable to the objects in which the diffractive deformation of the wave front exceeds the refractive deformation. This condition indicates the main distinction of the method discussed from classical Toepler method which is applied to the objects with the predominance of refraction.

The final expression that has been derived in papers [6, 7] for reproduction of the refractive index has the form

$$\kappa(r) = -\frac{\lambda}{4\pi^2} \int_0^r \frac{\varepsilon'(y) dy}{\sqrt{r^2 - y^2}}, \quad (3.5)$$

where λ is the wave length for incident light, $\varepsilon(y) = [I(y) - I_0]/I_0$ is the relative intensity of the light on the screen, I_0 is the intensity of the light background on the screen in absence of the object, $\varepsilon'(y)$ is the derivative of relative intensity.

Figure 14 illustrates the above-discussed technique of shadow photographs processing. For instance, if the object has a refractive index $\kappa(r)$ depending on r as shown in Fig. 14a, then the relative light intensity on the screen will correspond to curve 2. At the upper part of the screen, i.e. for the right half of the curve 2, we observe an excess of the intensity over background and at the lower part of the screen the light intensity decreases as compared to background. Thus, having experimentally obtained curve 2 we can process this curve, using Eq. (3.5), and reproduce curve 1. It can be readily seen that the accuracy of the method is determined by the precision of the $\varepsilon'(y)$ measurements. The most accuracy corresponds to the point $y = 0$, since in the vicinity of this point the function $\kappa(y)$ is linear as a rule. Then proceeding from Eq. (3.5) we obtain

$$\kappa(0) = -\lambda \varepsilon'(0)/8\pi. \quad (3.6)$$

3. Shadow method for electron density measurements

The method is the most illustrative as the object is a discharge channel in the absence of the shock waves and the light wave front deformation is determined by electron density. It is known that in this case the refractive index can be represented as

$$n = 1 - \frac{r_e \lambda^2}{2\pi} n_e, \quad (3.7)$$

where $r_e = 2.82 \cdot 10^{-13}$ cm is the classical electron radius, n_e is the electron density.

Thus, the shadow image enables us to derive the curve I for any channel cross-section and thereafter to calculate the electron density distribution over the channel radius.

The estimates show that the technique is applicable for measuring the electron density falling within the broad range

$$Ln_e = 5 \cdot 10^{14} \text{ to } 5 \cdot 10^{16} \text{ cm}^2. \quad (3.8)$$

Previously we used this technique for a breakdown in overvolted gaps [7, 8]. A ruby laser with a pulse duration of 5 ns has been employed as a source of light radiation. One can gain an impression of a spatial resolution of the technique directed to Fig. 15 [9], where the shadow photographs and the data on their processing are presented. Since the copies of the photographs do not illustrate the fine details we have presented here an original photograph for the instant of 200 ns. The discharge was initiated in argon with a point (cathode)-plane gap, pressure of 300 Torr, gap spacing of 0.3 cm and discharge current of 250 A. The electron densities are shown in the units of 10^{17} cm^{-3} . We can distinct at the photographs the cathode flare and the discharge column. The method allows us to identify a microstructure of the column. For instance, photograph at the moment $t = 200$ ns shows the filaments 60–100 μm in diameter.

The above account suggests that the vacuum arc cathode flare is a quite suitable object for the shadow diagnostics. The flare cross dimension seems to be of 0.5 cm. Then we can expect to measure the electron density ranging from 10^{15} to 10^{17} cm^{-3} . We are going to use the shadow method in the present work.

It is clear that the experimental arrangement has to be substantially reconstructed as compared to the previous experiments. In particular, we intend to use He-Ne laser with a pulse duration of $t \geq 10 \mu\text{s}$ as the source of radiation. This arrangement is currently in the stage of adjustments and tests. The setup description is presented below.

3.2. Experimental setup

The setup skeleton diagram is shown in Fig. 16. As the source of probe radiation the steady-state He-Ne laser is used. Its output radiation is transformed into the light pulses by means of the electromechanical gate and optical gate depended on Pockels cell. The final pulse duration may be varied from 10 to 100 μ s. The mechanical gate is used to prevent a spurious irradiation of the screen from the steady-state laser. The open time for this gate is about 1 ms, so that the final pulse duration is controlled by optical gate.

To trigger the setup units at given instants on the time scale the six-channel delay pulse generator is employed. It forms the clock triggering pulses with a jitter of no more than 100 ns. The arrangement operates in the following sequence. At first, the clock pulse is fed to channel *I* in order to trigger the pulse generator for electromechanical gate. Thereafter the channel 2 functions to trigger the main discharge circuit (to trigger the thyatron for one of the designs in Figs. 5, 9, and 10). Then the delay time between the channels *II* and *III* offers a possibility to control the instant in which the diagnostic radiation enters the discharge chamber. The diagnostic pulse duration is controlled by generator for optical gate.

Figure 17 shows a diagram of the unit forming the optical pulse. The crystal Pockels cell forms the preliminary light pulse that enters the telescope system in order to obtain the light beam 2.5 cm in diameter. In the focus of lens l_1 the diaphragm with an aperture 10 μ m in diameter is placed. It serves to filter out the light waves that may arise due to diffraction at an airborne dust and at other inhomogeneities of optical system. As a result, the quality of the output light wave is improved.

The light beam with the uniform-phase wave-front travels to the discharge chamber and visualization system (see Fig. 13). The windows of discharge chamber are installed at Brewster angle to diminish a spurious scattered radiation.

The arrangement described is currently in the test stage. The preliminary results that are expected to be obtained will allow us to gain a better understanding with respect to using the shadow method in arc plasma diagnostics.

4. Measurements of electron temperature and electron density by spectroscopic methods

4.1. Principle of electron temperature measurements

Determination of the electron temperature in a plasma is usually connected with the measurements of light intensity for the separate spectral lines with the aim to calculate the temperature from measurement data. However, these calculations demand a preliminary information concerning the elementary processes in plasma, i.e. the processes that sustain an excitation level population. In general case the problem of such calculations is extremely complicated. A resolution seems to be possible only for limiting range of the plasma parameters as a treatment of the plasma processes can be reduced to the simple models. The processes in arc discharge plasma are often treated in the context of the local thermodynamic equilibrium model (LTE) or the partial local thermodynamic equilibrium model.

The former model supposes that the detailed balancing principle holds true for certain plasma volume. Then the following conditions are fulfilled.

- Heavy particles have Maxwell velocity distribution function with temperature T_a .
- Electrons also have Maxwell function with temperature T_e , that in general case differs from T_a .
- Distribution of the excited level population obeys the Boltzmann's statistics.
- Population of excited levels is connected with electron density by Saha equation.

It is clear that the conditions in plasma will closer correspond to LTE-model as electron density increases. Therefore, number of papers put forward the estimates to determine a minimal value of the electron density starting from which it is possible to use LTE-model. For instance, a validity criterion of LTE-model for optically thin plasma has the form [11]

$$n_e \geq 10^{14} T_e^{1/2} (E_k - E_i)^3, \quad (4.1)$$

where $(E_k - E_i)$ is the energy difference between the energy levels k and i ; the values of T_e and E are taken in electronvolts.

Let us apply the latter formula for the arc discharge that has to be investigated in present work. The maximum difference in energy is the ionization potential, i.e. for Mg $(E_k - E_i)_{\max} = 7.65$ eV. Then for T_e we obtain $n_e \geq 8 \cdot 10^{16} \text{ cm}^{-3}$.

One of the gases that is suitable for spectroscopic measurements is argon. In accordance with the conditions of the present work we may fill the discharge chamber

with certain fraction of argon. However the criterion (4.1) for argon plasma is fulfilled only starting from $n_e \approx 7 \cdot 10^{17} \text{ cm}^{-3}$ since the ionization potential is equal to 15.76 eV.

It is clear that a high electron density may be characteristic of the cathode spot region. However the electron density in the cathode flare, according to our estimates, must be substantially lower.

Criterion (4.1) may be moderated if we assume that do not all levels are in equilibrium with continuum but only the levels lying higher than ground state. This is the essence of partial LTE-model. Then we have for Mg ($E_k - E_i$) = 3.3 eV, for Ar ($E_k - E_i$) = 2.5 eV and the threshold electron densities are correspondingly $n_e = 6 \cdot 10^{15} \text{ cm}^{-3}$ and $2.7 \cdot 10^{15} \text{ cm}^{-3}$. These values of electron density seem to be reasonable for vacuum arc cathode flare. Therefore we are planning to measure the relative light intensity for various spectral lines and apply the partial LTE-model to calculate the electron temperature.

In context of the model the level populations n_m and n_n obey the Boltzmann's law

$$\frac{n_m}{n_n} = \frac{g_m}{g_n} \exp\left[-\frac{E_m - E_n}{kT_e}\right], \quad (4.2)$$

where g_m and g_n are the statistical weights of the levels, E_m and E_n are the excitation energies.

The intensities of radiation from m -level and n -level are determined as

$$I_m = n_m A_m h\nu_m, \quad I_n = n_n A_n h\nu_n, \quad (4.3)$$

where A_m and A_n are the probabilities of radiative transitions, $h\nu_m$ and $h\nu_n$ are the quantum energies.

Taking into account Eqs. (4.2) and (4.3) we readily obtain

$$\frac{I_m}{I_n} = \frac{\nu_m}{\nu_n} \frac{A_m}{A_n} \frac{g_m}{g_n} \exp\left[-\frac{E_m - E_n}{kT_e}\right]. \quad (4.4)$$

The latter relation links the relative intensity of radiation and electron temperature, since all other parameters are the spectroscopic constants whose values are known from literature.

Note, that criterion (4.1) is only a necessary but not sufficient condition in order that the partial LTE-model hold true. Therefore, a particular attention must be paid to selection of the upper levels E_m , E_n and the radiative transitions that will be used in measurements. It is typically that the measurement procedure involves a preliminary stage.

At this stage the intensities and their time dependence for a number of spectral lines are investigated. The results obtained serve as a basis for selection of the radiative transitions that seems to be suitable in temperature measurement. As the transitions are selected correctly then the measurement data with using the different pairs of spectral lines must give the same values of temperature.

We carried out the electron temperature measurement in our previous investigations [13] for gas discharge in argon and this experience will be profitably used in the measurements planned.

4.2. Experimental setup and procedure

Experimental arrangement for spectroscopic investigations of arc discharge is shown in Fig. 18. The image of the discharge gap is projected on the planes of the spectrograph entrance slit and monochromator slit by quartz lenses. Experimental arrangement allows to photograph the discharge spectrums in the designs where the slit is located normally to the gap axis as well as parallel to axis. Typical entrance slit width is of 0.01 mm. In order to photograph the integral spectrums spectrograph ISP-30 with linear dispersion of 60 Å/mm and spectrograph STE-1 with linear dispersion of 3.8 Å/mm are employed.

The time dependencies of spectral lines intensity are recorded by means of monochromator MDR-3, photomultiplier tube FEU-38 and oscillograph. The monochromator linear dispersion for one of the diffraction gratings is 12 Å/mm and for another diffraction grating is 24 Å/mm. The spectral measurements can be carried out in the range of wavelengths from 3000 Å to 8300 Å.

When measuring the total spectral line intensity the monochromator exit slit is matched in such a way that the overall line width could be fallen within the slit. Typically, we take three readings from photomultiplier: one of them Φ_0 is at the center of line and two another, Φ_1 and Φ_2 , are at the spectral line wings. Then the total line intensity is calculated as

$$I(\lambda) = \mu(\lambda) \left[\Phi_0 - \frac{\Phi_1 + \Phi_2}{2} \right], \quad (4.5)$$

where $\mu(\lambda)$ is the transmission coefficient for optical system.

This procedure enables us to subtract the continuum radiation from the line intensity and to obtain both the relative intensity of two spectral lines and the ratio of spectral line intensity to continuum intensity. The estimates of the spectral line profiles are carried out in the conditions where the width of the entrance slit is equal to that of exit slit ($\Delta l = 0.01$ mm).

4.3. Electron density measurements

The most simple technique to measure a high electron density is based on the studies of hydrogen lines H_α and H_β whose profile may be broadened due to Stark effect. The method does not require the thermodynamic equilibrium in plasma. For the diagnostic purpose there is no need to measure the whole line profile; it is quite enough to obtain only the line half-width. We are going to use the hydrogen lines H_α and H_β in diagnostics.

Figure 19 [12] shows the calculated half-width of H_α and H_β -lines versus the electron density for various electron temperatures. It is seen that the temperature dependence is very weak, which allows to define the electron density as the temperature is known only estimate. Taking into account the spatial resolution of the photoelectrical method we expect that it will be possible to measure the electron density values $n_e \geq 10^{14} \text{ cm}^{-3}$.

Stark effect can be harnessed with not only using the hydrogen lines but also the lines of other elements. The broadening mechanism is usually characterized by parameters ω and α that depend on electron density and electron temperature in plasma. These parameters for variety of elements are presented in literature. The half-width is expressed through these values as follows

$$\Delta\lambda = 2\omega n_e 10^{-16} \left[1 + 1.75\alpha n_e^{1/4} \cdot 10^{-4} (1 - 0.75r_D) \right], \quad (4.6)$$

where $\Delta\lambda$ is taken in Å, n_e is the electron density in cm^{-3} , r_D is the ratio of average distance between ions in plasma to Debye screening distance:

$$r_D = 6^{1/3} \pi^{1/6} \left(\frac{e^2}{kT_e} \right)^{1/2} n_e^{1/6}, \quad (4.7)$$

where e is the elementary charge in CGSE-units, k is Boltzmann's constant in CGSE-units, T_e is the electron temperature in absolute degrees.

The literature data analysis shows that some of the MgI and ArI lines are characteristic of the high values of Stark broadening parameters ω and α . This offers an opportunity to use such lines for electron density measurements.

On the other hand, there exist the lines of MgI and MgII that have very low values of ω and α . Then the line profile is governed by Doppler broadening. Since the vacuum arc near-cathode region forms the directed flux of fast ions we are planning to estimate the ion velocities based on Doppler effect. Principle of the method and some estimates are presented below.

5. Measurements of fast ion velocities

5.1. Introduction

One of the characteristic of vacuum arc phenomenon is a so-called abnormal ions that travel toward the anode, i.e. opposite in direction to external electric field. There are number of studies where the experimental data and their interpretation are presented [14–16]. Most of the measurements have been carried out for the arcs with the second-type cathode spots. The abnormal ion current constitutes typically from 8 to 10 per cent of the total discharge current in external circuit. The measurements show that a spatial distribution of ion flux is peaked in anode direction. The flux contains both the single-charged and the multi-charged ions. The ion kinetic energy can be in excess of potential difference across the electrodes during arcing. As it had been founded, the ion flux is generated in a near cathode region. Therefore, it was assumed that an ability to generate the ion flux is a distinctive feature of vacuum arc cathode spot. However, the mechanism of such a generation is not currently elucidated. There exist a variety of the contradictory models that fail to interpret the experimental data.

Notice, that the fast ions play an important part in arc current sustaining. First, a positive space charge, that builds-up in the gap due to the ion flux, ensures an extremely effective neutralization for electron space charge in the arc positive column. Thus, a column has a high conductivity and low potential drop.

Second, the ion flux is one of the main sources for anode heating. As applied to the arc furnace this means that the ions give a substantial contribution to maintain the anode in liquid state. One of the goals of this work is the measurements of ion velocities and elucidation of the reasons resulting in their generation.

The data presented in Sec. 2 show that at the arc current of 100 A and gap distance of 1 to 2 cm three characteristic regions can be discerned in the gap: the cathode spot including a small bright plasma blob adjacent to cathode, the cathode flare 0.5 cm in size and the positive column. In accordance with our concept the ion acceleration occurs in the cathode flare region since the potential is non-monotonically distributed along the gap (see Fig. 3); the falling portion of the potential distribution curve is responsible for acceleration process. The experiments planned are directed to validate the above concept.

It is necessary to stress the following circumstance. In this consideration we are dealing with the ions that originate in a near cathode region. Some of the models predict that the fast ions are generated immediately in the cathode spot plasma as a result of microexplosive processes on the cathode. Our approach states that the origination of ions

and their acceleration occur along the whole distance of the cathode flare. However, for both of the cases we imply that the ions arise in the near cathode plasma, the cathode flare including.

On the other hand, it is known that the arc discharge for some modes of its operation is characterized by a negative anode voltage drop. Then the ion flux onto the anode can be formed in a near anode sheath where the potential decreases. Most typical example of such a discharge is low-pressure arc discharge with hollow anode that is widely used in electron and ion plasma sources. Here, a low-density plasma builds-up in the anode cavity and the negative voltage drop region is adjacent to the anode. Another example of similar type discharge seems to be possible as the anode comes into direct contact with the cathode flare plasma. Then a narrow sheath with the negative voltage drop may be formed near the anode:

In our experiments we intend to reproduce the conditions in which ion flux originated only in the near cathode plasma will be under study. It is possible if the gap distance is in substantial excess of the cathode flare size. In this case the spectral measurements offer an opportunity to study Doppler shift and Doppler broadening for the spectral lines in the flare and obtain an information on ion velocities.

5.2. Experimental setup and procedure

An experimental arrangement for studying the Doppler effect is presented in Fig. 20. The figure shows the cathode flare that, as it is expected, generates the ion flux. The ions propagate over the whole directions, however the flux is peaked toward the anode. The optical observations and the records of the flare spectrums are carried out along the discharge axis, as shown in Fig. 20. Then, for the short lifetime of the excited ions we may assume that the light intensity is directly proportional to the number of ions in the observed region. At a low gas density and with a small values of parameters ω and α the spectral line profile is governed by Doppler effect. As a transactional ion velocity exceeds or comparable with a chaotic velocity we may observe not only a broadening but also a shift of ion spectral lines relatively a zero position λ_0 . Let us make the simple estimates.

When a source of radiation moves with a velocity v and a receiver is immovable the observed wavelength is connected with the velocity v by relation

$$\lambda = \lambda_0 \left(1 + \frac{v}{c} \cos \theta \right) / \sqrt{1 - \frac{v^2}{c^2}}, \quad (5.1)$$

where c is the light speed, θ is the angle between the line of observation and the direction of the source motion. In our case $v \ll c$ and for the estimates we may assume that the ions mainly travel toward the spectrograph ($\theta = \pi$). Then the wavelength shift is determined as

$$\Delta\lambda = (\lambda_0 - \lambda) = \lambda_0 \frac{v}{c}. \quad (5.2)$$

Taking into account that the energy of a single-charged ion is connected with velocity as $v = (2eV/M)^{1/2}$ we obtain

$$\Delta\lambda = \frac{\lambda_0}{c} \left(\frac{2eV}{M} \right)^{1/2}, \quad (5.3)$$

where M is the ion mass.

To enhance the sensitivity of the technique it is desirable to experiment with the small-mass ions. Then for MgII ion at $\lambda_0 = 2790.8 \text{ \AA}$ and energy $eV = 50 \text{ eV}$ we obtain $v = 2 \cdot 10^6 \text{ cm/s}$ and shift $\Delta\lambda = 0.19 \text{ \AA}$. Such a shift can be recorded if we use the spectrograph with linear dispersion of $3.8 \text{ \AA/mm}$ that is in available. Thus, this set of experiments must include the investigation of Doppler effect for MgI and MgII spectral lines and interpretation of measurement data.

6. Conclusion

The present report contains the results of the preliminary experiments on modeling the discharge in arc furnace, the design of the discharge chamber developed on the basis of the preliminary results and the description of the procedures that we are going to use in experiments. The final objective to be pursued by this research is to develop the arc models that could be applicable to the discharge in arc furnace. The experiments planned have to give a contribution to development of these models.

At the moment it is not absolutely clear which of the above-described experimental techniques will be the most informative and ensure the most contribution to the problem. We intend to obtain some experimental results with using the all set of the techniques. However, we believe that the program of experiment can be corrected during this work.

References

1. J.M. Lafferty, Ed., *Vacuum Arcs. Theory and Application*, John Wiley & Sons, New York, Chichester, Brisbane, Toronto.
2. G.A. Mesyats and D.I. Proskurovsky, *Pulsed Electrical Discharge in Vacuum*, Springer-Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo.
3. A.V. Bolotov, A.V. Kozyrev, and Yu.D. Korolev. "Physical model for a cathode layer of a vacuum arc with non-monotonic potential distribution in near-cathode plasma," *Fizika plazmy*, Vol. 19, No 5, pp. 709–719, 1993 (in Russian).
4. A.V. Bolotov, A.V. Kozyrev, and Yu.D. Korolev, "Physical model of low current density vacuum arc," *XVI Intern. Symp. on Discharge and Electrical Insulation in Vacuum*, 23-30 May, 1994, Proceedings of SPIE, Vol. 2259, pp. 82-85.
5. G.A. Mesyats, *Ectons*, Part 1, Ekaterinburg, Nauka, 1993 (in Russian).
6. A.V. Kozyrev and K.A. Tinchurin, "Reproduction of a refractive index for weak-refracting transparent inhomogeneities," *Optika i spektroskopiya*, Vol. 59, No 2, pp. 377–380, 1985 (in Russian).
7. S.A. Genkin, A.V. Kozyrev, Yu.D. Korolev, and K.A. Tinchurin, "Measurements of electron density in a stage of channel propagation for a nanosecond space discharge with using the Toepler method," *Zhurnal tekhnicheskoi fiziki*, Vol. 55, No 6, pp. 1216–1218, 1985 (in Russian).
8. A.V. Kozyrev, Yu.D. Korolev, and K.A. Tinchurin, "Spark channel formation in nitrogen for a breakdown in overvolted gaps," *Fizika plazmy*, Vol. 14, No 14, pp. 1003–1007, 1988 (in Russian).
9. Yu.I. Bichkov, A.U. Suslov, K.A. Tinchurin, and A.G. Yastremskii, "Microstructure of high-current discharge in argon," *Fizika plazmy*, Vol. 17, No 2, pp. 196–204, 1991 (in Russian).
10. R.H. Huddlestyone and S.L. Leonard, Eds., *Plasma diagnostic techniques*, Academic Press, New York–London, 1965.
11. W. Lochte-Holtgreven, Ed., *Plasma diagnostics*, North-Holland Publishing Company, Amsterdam, 1968.
12. H.R. Griem, *Plasma Spectroscopy*, New York, 1964.
13. Yu.D. Korolev, O.V. Korshunov, A.P. Khuzeev, V.F. Chinnov, and I.A. Shemyakin, "Investigation of a high-current-diffuse discharge in argon," *Teplofizika vysokikh temperatur*, Vol. 23, No 5, pp. 853–857, 1985 (in Russian).

14. C.W. Kimblin, "Erosion and ionization in the cathode spot region of vacuum arc," *J. Appl. Phys.*, Vol. 44, No 7, pp. 3074–3081, 1973.
15. H.C. Miller, "Constraints imposed upon theories of the vacuum arc cathode region by specific ion energy measurements," *J. Appl. Phys.*, Vol. 52, No 7, pp. 4523–4530, 1981.
16. D.T. Tuma, C.L. Chen, and D.K. Davies, "Erosion products from the cathode spot region of a copper vacuum arc," *J. Appl. Phys.*, Vol. 49, No 7, pp. 3821–3831, 1978.

Fig. 1. Principle of operation of an electric arc furnace.

Fig. 2. Schematic representation of a vacuum arc cathode spot.

Fig. 3. Illustration for a model of vacuum arc with diffuse cathode spot attachment.

Fig. 4. Schematic of the discharge chamber and electrode system.

1 - wire electrode ϕ 0.6 mm; 2 - ceramic insertion;
 3 - auxiliary electrode; 4 - anode; 5 - chamber envelope; 6 - flang for vacuum pump.

Fig. 6. Voltage waveforms at the electrode 1 (V_1) and current waveforms onto the electrode 4 (i_4) corresponding to the design shown in Fig. 5.

a. - $V_0 = 1.5$ kV, b. - 1.8 kV, c. - 3 kV.

Fig. 7. Glow photograph corresponding to Fig. 6c.

$$C_o = 1 \mu\text{F}, V_o = 3 \text{ kV}, p = 10^{-2} \text{ Torr}, d = 2 \text{ cm}.$$

Fig. 8. Voltage waveform at the electrode 1, current waveform onto the electrode 4, and glow photograph.

$$C_0 = 4 \mu F, V_0 = 5 \text{ kV}, p = 10^{-2} \text{ Torr}, d = 2 \text{ cm}.$$

Fig. 2. Two-stage circuit for initiation of an arc discharge between the electrodes 1 and 4.

$$C_0 = 10 \text{ nF}, V_0 = 2-5 \text{ kV}, C_1 = (10-100) \mu\text{F}, \\ V_1 = (200-500) \text{ V}.$$

Fig. 10. Two-stage circuit for initiation of an arc discharge between the electrodes 3 and 4.

a.

b.

c.

Fig. 11. Voltage waveform at the electrode 1 and current waveform through the shunt R_s for the circuit design shown in Fig. 10.

$C_0 = 10 \text{ nF}$, $V_0 = 5 \text{ kV}$, $C_1 = 10 \text{ } \mu\text{F}$, $R_3 = 2 \text{ } \Omega$.

a. - $V_1 = 250 \text{ V}$, b. - $V_1 = 280 \text{ V}$.

c - glow photograph for $V_1 = 500 \text{ V}$, $C_1 = 20 \text{ } \mu\text{F}$.

Fig. 12. Schematic of discharge chamber with a hard-melted crucible.

Fig. 13. Visualization of an object by Toepler method.

Fig. 14. Illustration for a light intensity on a screen with using the shadow method of visualization.

Fig. 15. Shadow photographs of a high-current-diffuse discharge in argon ($p = 300$ Torr) at different instants and electron densities on discharge axis in units of 10^{17} cm^{-3} .

Fig. 16. Skeleton diagram of the arrangement to realize the shadowgraph method.

Fig. 17. Skeleton diagram of the unit to form optical diagnostic pulse.

Fig. 18. Experimental setup for spectroscopic measurements.

Fig. 19. Half-width of the Stark-broadening spectral lines as the functions of electron density and electron temperature.

Fig. 20. Experimental setup for the measurements of Doppler shift in the spectral lines.

Russian Academy of Sciences
Siberian Division
High Current Electronics Institute

Scientific Report

**Characterization of a Metal Vapor Burning
on Nickel-Magnesium Cathode**

(Report No 2, Contract AM-7666)

Principal Investigator:
Prof. Yuri Korolev

A handwritten signature in black ink, consisting of several fluid, overlapping strokes that form a stylized representation of the name Yuri Korolev.

Tomsk, April 1995

Context

1. Introduction	2
1.1. General requirements for experimental arrangement	2
1.2. The features of a high-current vacuum arc on cold cathode	2
1.3. Discharge features in the arc furnace	12
1.4. Detailization of the goals for present work	13
2. Development the electrical circuit and the discharge chamber design	13
2.1. General requirements for electrode system and electrical circuit.	13
2.2. Electrical circuits	14
2.3. Discharge chamber	18
3. Shadow method for electron density measurements	19
3.1. Principle of the method	19
3.2. Experimental setup	22
4. Measurements of electron temperature and electron density by spectroscopic methods	23
4.1. Principle of electron temperature measurements	23
4.2. Experimental setup and procedure	25
4.3. Electron density measurements	26
5. Measurements of fast ion velocities	27
5.1. Introduction	27
5.2. Experimental setup and procedure	28
6. Conclusion	29
References	30
Figures	32

Fig. 20. Experimental setup for the measurements of Doppler shift in the spectral lines.

Russian Academy of Sciences
Siberian Division
High Current Electronics Institute

Scientific Report

**Characterization of a Metal Vapor Burning
on Nickel-Magnesium Cathode**

(Report No 2, Contract AM-7666)

Principal Investigator:
Prof. Yuri Korolev

A handwritten signature in black ink, consisting of several fluid, overlapping strokes that form a stylized representation of the name Yuri Korolev.

Tomsk, April 1995

Context

1. Introduction	2
1.1. General requirements for experimental arrangement	2
1.2. The features of a high-current vacuum arc on cold cathode	2
1.3. Discharge features in the arc furnace	12
1.4. Detailization of the goals for present work	13
2. Development the electrical circuit and the discharge chamber design	13
2.1. General requirements for electrode system and electrical circuit.	13
2.2. Electrical circuits	14
2.3. Discharge chamber	18
3. Shadow method for electron density measurements	19
3.1. Principle of the method	19
3.2. Experimental setup	22
4. Measurements of electron temperature and electron density by spectroscopic methods	23
4.1. Principle of electron temperature measurements	23
4.2. Experimental setup and procedure	25
4.3. Electron density measurements	26
5. Measurements of fast ion velocities	27
5.1. Introduction	27
5.2. Experimental setup and procedure	28
6. Conclusion	29
References	30
Figures	32

1. Introduction

In the preceding report [1] the subject of the work has been founded, the experimental methods which are intended to be applied have been described and the first results on an arc discharge modeling have been presented. This report contains the further results according to the statement of work.

The investigation is mainly related to spectroscopic measurements in arc discharges on Ni and Mg cathodes and comparison the measurement data with theoretical model. Correspondingly, the report addresses the following issues:

- Selection of discharge chamber designs offering a possibility to model the different discharge modes.
- Integral spectrum investigations for different arc discharge regions.
- Spectral line shift and broadening measurements with the aim to obtain an information on heavy particle velocities and electron density.
- Creation of a theoretical model and its comparison with the experimental data obtained.

2. Experimental setups and general features of arc discharge

2.1. Discharge features for different constructions of electrode system

The aim of this work is to investigate a model arc discharge in such modes of the operation that are close to the actual arc discharge in arc furnace. Recall, that the vacuum furnace gap comprises a parallel-plane electrode system 20 cm in diameter with a current of 2 kA. In these conditions about 20 spots operate on the cathode simultaneously and an average current density to the anode is about 6 A/cm^2 .

In order that measurement data could be adequately interpreted we have to model the furnace in the form of an experimental arrangement that provides an arc discharge with single cathode spot and total current of about 100 A. In other words, the discharge in experimental setup should operate as if this is a fraction of high-current discharge operating in the furnace. The problem is rather intricate since, unlike the classical glow discharge, the arc discharge does not obey similarity laws.

In the preceding report we suggested the technique to initiate an arc discharge at a small cathode area with the total current of about 100 A. Then the near cathode regions comprise a cathode spot and a cathode flare region approximately 0.5 cm in size. It is known that the processes in the near cathode plasma are as a rule responsible for sustaining the cathode spot and discharge characteristics as a whole. However, as applied to dis-

charge in the furnace the near anode processes may play an important part as well, since the anode current provides for the melted state of anode surface. Thus for some experiments we have to model the conditions in which the arrived at the anode energy corresponds to that in arc furnace.

In our experiments we use the different designs of electrode system. In each specific case the choice of the design is dictated by the task that is intended to be solved in experiment. The typical designs, their advantages and disadvantages are discussed in this section.

In general case in the course of arcing we can distinguish within the gap the cathode spot, cathode flare region, positive column and near anode region. The arc in the presence of well-defined positive column can be readily obtained when using the design shown in Fig. 2.1. The distinctive feature of the discharge mode lies in the fact that the positive column plasma forms due to hollow anode effect. Anode potential drop is negative, so that an oscillatory motion of electrons in the cavity results in effective plasma generation even with low gas pressure. Total anode current is determined by the electrons whose energy is rather high to overcome a near-anode potential barrier and by ion flux. Because the current closes to internal wall of the anode cavity uniformly and the current density is low, the anode spots do not arise. A plasma forming medium for the cathode flare is the cathode material vapor whereas the positive column plasma mainly forms in ambient gas. The conditions under discussion are the most favorable to investigate the near cathode processes since the interpretation of the experimental data is simplified due to the absence of the anode vapor in the gap.

Another limiting case for the discharge operating conditions was realized in our preceding experiments [1]. The parallel-plane electrode system and dielectric discharge chamber were used here (see Fig. 4 in the report [1]). The discharge current closes to the plane anode so that controlling the anode current density we have a chance to obtain discharge both with the anode spots and without that. Although the total current onto the chamber is equal to zero it does not mean that the charged particle fluxes onto the dielectric wall are absent. The wall is charged by a negative potential with respect to the grounded anode in such a way that electron flux is equal to ion flux and the total current is virtually zero. The design under consideration offers a possibility to model the conditions in which the energy delivery to the anode is close to actual arc furnace. However, it is questionable whether any design with a dielectric chamber could be combined with a liquid anode unit. Therefore, we have performed the experiments for a design with metal discharge chamber. The corresponding results are presented below.

2. Experimental setups and general features of arc discharge

A typical discharge chamber and electrical circuit are shown schematically in Fig. 2.2. Here, the anode is electrically isolated from chamber envelope. In the course of experiments the chamber can be grounded, connected with the anode as well as be at floating potential. The design where the discharge chamber is connected with the anode is best suited to perform experiments. However, we are to keep in mind that the discharge conditions correspond to the left branch of Paschen's curve. Therefore, the current may close to not only the plane anode but the chamber envelope as well. The cavities that are inevitably present on the envelope (the ports for optical observations, pumping port and the like) can play a part of a hollow anode so encouraging the current to flow to the chamber. Hence, in order to prevent the hollow anode effect and provide for the case where the main fraction of the current flows to anode we must correctly choose the anode diameter, chamber diameter, size of the entrance ports, *etc.* Let us consider the experimental results in more detail.

We tested the different internal diameters of discharge chamber. Presented below are the results for chamber with envelope diameter of 100 mm, distance from cathode to discharge chamber end of 50 mm and anode diameter of 30 mm. The gas pressure was varied from $5 \cdot 10^{-2}$ to 10^{-2} Torr and typical gap spacing was 15 mm.

Figure 2.3 corresponds to the case that the discharge chamber is under floating potential and, hence, the total current flows to anode disk (switch *S* in Fig. 2.2 is in position *I*). For the presented sample the oscillograph deflection sensitivity is rather high. Then we do not observe an initial stage of the voltage oscillogram, since the trace goes off the screen and we virtually record the steady state discharge operating voltage. This voltage is slightly increases with decreasing the current.

A comparison between the described conditions and the case where the total current closes only to the discharge chamber is shown in Fig. 2.4. Here, the anode is under floating potential that is the arc discharge with the hollow anode operates in chamber. The discharge operating voltage for the latter case is somewhat higher than that for the former conditions. Thus, it can be concluded that the discharge current may flow both to the chamber envelope and disk anode.

The most simple way to eliminate the current onto the envelope is to keep it under floating potential. However, such a design can be inconvenient in certain experiments. Therefore we have measured the fraction of total current flowing to the chamber in the conditions where the chamber is grounded. The results are presented in Fig. 2.5. We can see that in initial stage some fraction of total current flows to the grounded chamber (the trace *b* goes lower than the trace *a*). However, after 4 μ s the traces *a* and *b* are superimposed, *i.e.* the current is intercepted by the disk anode. Hence, it follows that for the de-

scribed design the hollow anode effect does not play an essential part in the steady-state stage of discharge operation. Note, that proceeding from these experiments we have chosen the chamber and anode sizes for the experimental setup with melted anode.

2.2. Integral spectrums of the different discharge regions

In this section the integral spectrums of vacuum arc on Ni cathode are presented. Experiments were carried out with the discharge chamber shown in Fig. 2.2. The discharge initiation circuit corresponded to Fig. 5 from preceding report [1]; the main circuit elements were as follows: capacitor $C_0 = 4 \mu\text{F}$, voltage $V_0 = 4 \text{ kV}$, ballast resistor $R_b = 50 \Omega$. Residual gas pressure was $p = 2 \cdot 10^{-2} \text{ Torr}$, gas gap distance $d = 15 \text{ mm}$.

The gap image was projected onto the plane of spectrograph entrance slit with an enlargement of 1.5. The entrance slit width was 0.04 mm. The spectrograph slit plane was perpendicular to cathode plane and the slit itself was perpendicular to discharge axis. Thus, we had an opportunity to record spectrums from different regions along gap axis. In particular, as the distance between the cathode and direction of observation $l = 0$, then the cathode spot spectrum is recorded. As a gap region in the vicinity of point $l = 2 \text{ mm}$ is projected onto the slit the cathode spectrum is absent, *i.e.* we record a radiation from cathode flare. At last, the condition $l = 7 \text{ mm}$ supposedly corresponds to positive column radiation.

It should be stressed the following circumstance. In order to obtain the spectrums on a photofilm it is necessary to provide an exposition of several thousand pulses. The total charge that is carried by the arc is several tens of coulombs with a typical erosion rate of 10^{-4} g/C . Then in the course of experiment a noticeable cathode erosion take place, *i.e.* the cathode length decreases and on completion of the expose procedure the cathode plane turns out to be inside the ceramic insert 2 (see Fig. 2.2). In order to prevent this effect we used the cathode of a rather "large" diameter ($D = 1.5 \text{ mm}$). However, the results showed that at $l = 0$ we did not obtain the cathode spot spectrum in "clear sense" but recorded the combined radiation from cathode spot and cathode flare region.

The data on identification of spectra are listed in Table 2.1. Presented here are the nickel spectral lines that have reliably identified (note, that we used a nickel 9.93 per cent pure). In addition, the spectrum contains the weak lines of other elements (Mg and Mo) and also the band of second positive system of nitrogen supposingly. These impurity lines are marked in Fig. 2.6. The figure demonstrates some fragments of total spectrum and allows to judge the spectral line intensities and qualitative features of the spectrums for different discharge regions.

2. Experimental setups and general features of arc discharge

Table 2.1. Spectral lines for Ni atoms and single-charged Ni ions from the regions located at different distances from cathode.

N	atom /ion	λ , Å [2]	Upper energy level, eV [2]	energy levels, cm ⁻¹ [3]	distance from cathode, mm		
					0	2	7
1	II	2375.42	7.08	—	+	+	—
2	II	2405.17	—	—	+	+	—
3	II	2413.05	—	—	+	+	—
4	II	2416.13	6.99	14995–56371	+	+	+
5	II	2437.89	6.76	13550–54557	+	+	+
6	II	2473.15	—	—	+	+	—
7	II	2510.87	6.62	—	+	+	+
8	II	2525.30	11.57	—	+	+	—
9	II	2545.90	6.73	—	+	+	—
10	II	2554.99	11.58	—	+	+	—
11	II	2560.30	—	—	+	+	—
12	II	2565.92	11.57	—	+	+	—
13	II	2584.00	8.46	—	+	+	—
14	II	2606.26	11.74	—	+	+	—
15	II	2609.94	11.38	—	+	+	—
16	II	2615.06	11.59	—	+	+	—
17	II	2665.25	—	—	+	+	—
18	II	2679.11	11.58	—	+	+	—
19	II	2684.28	11.38	—	+	+	—
20	II	2708.63	11.44	—	+	+	—
21	II	2742.83	11.59	—	+	+	—
22	II	2759.02	—	—	+	+	—
23	II	2768.79	—	—	+	+	—
24	II	2775.33	—	—	+	+	—
25	I	2798.65	4.54	880–36601	+	+	—
26	I	2803.14	—	—	+	+	+
27	II	2805.67	—	—	+	+	—
28	II	2864.02	11.44	—	+	+	+
29	I	2914.01	4.42	1332–35639	+	+	—
30	I	2943.91	4.23	205–34163	+	+	—

Characterization of a Metal Vapor Burning on Nickel-Magnesium Cathode (Contract AM-7666)

N	atom /ion	λ , Å [2]	Upper energy level, eV [2]	energy levels, cm ⁻¹ [3]	distance from cathode, mm		
					0	2	7
31	II	2947.45	—	—	+	+	—
32	I	2994.46	4.17	205–33590	+	+	+
33	I	3003.63	4.24	880–34163	+	+	+
34	I	3012.00	4.54	3410–36601	+	+	+
35	I	3029.29	—	—	+	+	—
36	I	3037.94	4.11	205–33112	+	+	+
37	I	3050.82	4.09	205–32973	+	+	+
38	I	3054.32	4.17	880–33611	+	+	+
39	I	3057.64	4.27	1713–34409	+	+	+
40	II	3087.08	—	—	+	+	—
41	I	3101.88	4.42	3410–35639	+	+	+
42	I	3134.11	4.17	1713–33611	+	+	+
43	I	3232.96	3.84	0–30923	+	+	+
44	I	3243.06	3.85	205–31031	+	+	—
45	II	3274.90	—	—	+	+	—
46	II	3289.98	15.97	—	+	+	—
47	I	3315.66	3.85	880–31031	+	+	—
48	I	3320.26	3.90	1332–31442	+	+	—
49	I	3320.77	—	—	+	+	—
50	II	3350.42	—	—	+	+	—
51	I	3369.57	3.67	0–29669	+	+	+
52	I	3380.57	4.09	3410–32982	+	+	+
53	I	3392.99	3.67	205–29669	+	+	+
54	II	3407.30	—	—	+	+	—
55	I	3414.77	3.65	205–29481	+	+	+
56	I	3423.71	3.84	1713–30913	+	+	+
57	I	3433.56	3.63	205–29321	+	+	+
58	I	3437.28	3.60	0–29084	+	+	+
59	I	3452.89	3.69	880–29833	+	+	+
60	I	3458.47	3.80	1713–30619	+	+	+
61	I	3472.55	3.67	880–29669	+	+	+
62	I	3485.89	3.77	1713–30392	+	+	—

2. Experimental setups and general features of arc discharge

N	atom /ion	λ , Å [2]	Upper energy level, eV [2]	energy levels, cm ⁻¹ [3]	distance from cathode, mm		
					0	2	7
63	I	3492.96	3.65	880–29501	+	+	+
64	I	3500.85	3.70	1352–29888	+	+	–
65	I	3515.05	3.63	880–29321	+	+	+
66	I	3524.54	3.54	205–28569	+	+	+
67	I	3548.19	3.71	2217–30392	+	+	–
68	I	3566.37	3.90	3410–31442	+	+	+
69	I	3571.87	3.63	1332–29321	+	+	–
70	I	3597.71	3.65	1713–29501	+	+	–
71	I	3619.39	3.85	3410–31031	+	+	+
72	I	3674.15	3.40	205–27415	+	+	–
73	I	3688.42	3.63	2217–29321	+	+	–
74	I	3722.48	3.54	1713–28569	+	+	–
75	I	3736.81	3.73	3410–30163	+	+	–
76	II	3769.46	6.39	—	+	+	–
77	I	3775.57	3.71	3410–29888	+	+	–
78	I	3783.53	3.70	3410–29833	+	+	–
79	I	3832.87	3.39	—	+	+	–
80	I	3858.30	3.63	3410–29321	+	+	–
81	II	4067.05	—	—	+	+	–
82	II	4279.21	9.51	—	+	+	–
83	I	4401.55	6.00	25754–48467	+	+	–
84	I	4459.04	6.08	26666–49086	+	+	–
85	I	4606.23	6.29	29013–50717	+	+	–
86	I	4648.66	6.08	27580–49086	+	+	–
87	II	4679.16	9.64	—	+	+	–
88	I	4715.78	6.17	28578–49778	+	+	–
89	I	4937.34	6.11	—	+	+	–
90	I	5142.77	6.11	29888–49328	+	+	–
91	I	5462.49	6.11	—	+	+	–

In particular, the distinctive feature of the cathode spot spectrum is a continuum in the wave length range from 3300 to 4000 Å. It points to high heavy particles density in the cathode spot. For the example under discussion the cathode spots arose uniformly over

the surface from one pulse to another. Therefore, as it is seen in Fig. 2.6, the height of continuum region at the photograph corresponds to cathode diameter.

Figure 2.7 shows a fragment of spectrum for the case that the spots did not attach over the cathode surface uniformly but were localized on the separate microareas. Here, the intensity of continuum spectrum is not uniform throughout the height; it consists of the separate strips corresponding to the places where the spots are localized. Evidently that the height of the separate strip offers an opportunity to estimate the cathode spot transverse size. Such an estimate gives the cathode spot diameter from 130 to 150 μm which is in agreement with literature data on the second-type cathode spot erosion region.

The discharge column intensity is substantially lower than that for cathode flare. Besides, some lines are not registered in the column as seen from Table 2.1 and Fig. 2.6. Note, that this effect apparently is not due to a simple decrease in the column spectral line intensities. It could be related to the different excitation mechanisms in the cathode flare region and column.

Thus, the data on nickel cathode can be considered as a foundation for succeeding analysis. In this report we are not ready to give their detail interpretation and to determine the electron temperature and physical mechanisms of level excitation.

Another set of experiments is related to the use of Mg cathode. As compared to nickel the magnesium erosion rate and, correspondingly the spectral line intensities are substantially larger. Besides, the lines quantum parameters and the level structure are well known which offers a good opportunity to interpret the experimental data. The experimental results on arc with magnesium cathode and discussion are presented in Sect. 3.

2.3. Qualitative model of the near cathode regions for a vacuum arc with constricted cathode spot

Before discussing the measurement data in more detail and offering their interpretation let us coin the main notions and present a qualitative model that we have suggested for vacuum arc with constricted cathode spot. The model is based on a variety of results on vacuum arcs including that presented in Section 3 of this report. However, we consider that it is appropriate to describe the model in this section in order to treat the subsequent experimental data referring to this model.

Let us discuss the features of the region that we previously called a cathode spot. The size of this region is less than 1 mm lengthwise. In this work we did not perform the detail investigations of the cathode spot. However, we can use the results of the other researchers and review the commonly accepted approaches for description of this region. Then, taking into account the non-monotonic potential distribution concept [4, 5], we

2. Experimental setups and general features of arc discharge

shall make the changes both in terminology and in treatment of some experimental results. This analysis will allow us to suggest the model to interpret the processes in the intermediate region between the cathode spot and cathode flare as well as in the cathode flare as such.

One additional comment is necessary to do before the succeeding discussion. The experiments of G.A. Mesyats with co-workers [6, 7] show that the cathode spot operation is accompanied by microexplosions of the cathode surface. This mode is especially characteristic of the first-type cathode spots that chaotically move over the cathode surface with velocity of 10^3 to $4 \cdot 10^3$ cm/s. In the course of the second-type spot operation the microexplosions can also take place. It is evidently that the microexplosion is essentially non-steady-state process and its development may result in deformation both a spatial structure of the near cathode regions and potential distribution along discharge axis. However it is usually agreed that the second-type spots can exist in steady-state mode (without the microexplosions) during a certain short time interval. The presented below is a consideration for such a steady-state mode.

The most-used treatment of a cathode spot is illustrated in Fig. 2.8. Shown here are the cathode surface with the micro-bath of melted metal about $100 \mu\text{m}$ in size and three cathode regions. As well as in the classical glow discharge, there exists the cathode voltage drop region of length l_c immediately adjacent to the cathode. The narrow region *II* is often referred to as ionization zone, since it is implied that electrons leave the cathode voltage drop region with the energy of eV_c and produce the most intensive ionization in the region *II*. The direct measurements for the length of regions *I* and *II* are practically impossible. However, some attempts of such measurements have been performed. In particular, in Ref. 8 it is pointed out that the cathode voltage drop region have the length of the order of 10^{-3} cm and the length of the region *II* is about 10^{-2} cm. It should be stressed that the above values are rather approximate. As a whole, the described regions *I* and *II* together with the melted metal bath are usually united by the term: cathode spot.

Then the plasma region *III* in Fig. 2.8 is usually referred to as the space of low-voltage arc. This term implies that the voltage drop across the region *III* is low as compared to V_c .

Thus, if we adopt the potential distribution as it is shown in Fig. 2.8, we are to base on the quite definite suppositions when constructing a model of cathode spot. At present time these suppositions have already assumed the significance of postulates, although non of them have been confirmed by direct measurements. These postulates are as follows:

- Potential increases monotonically in the direction from cathode to anode and the cathode voltage drop does not exceed the arc operating voltage. Therefore if we place the

anode in the region *III*, *i.e.* ignite an arc in the short gap, then the arc operating voltage has to be $V_p \approx V_c$.

- The length of the cathode layer (cathode voltage drop region) is substantially less than electron free path; hence the ionization does not occur in the cathode layer and this layer constitutes a specific vacuum diode with ion neutralization.
- The ions enter the cathode layer from the boundary of region *II* and the ion current can not exceed the classical Bohm current from plasma. On the other hand, the cathode emissivity is very large. Consequently, the ion current at the cathode, as distinct from glow discharge, constitutes a negligibly small fraction of the total current and the total arc current is close to emission current.

Emphasize once more that the above presented suppositions have no direct experimental evidences. For instance, as an evidence that the potential of region *III* varies rather weakly the results on probe measurements are usually invoked. However, the probe under floating potential in plasma shows a voltage approximately kT_e/e less than the actual plasma potential. Thus, if an electron beam with energy of eV_c penetrates in the region *III* from the cathode layer the probe measurements have no sense, since the probe is charged by fast electrons and its potential will be substantially lower than the actual plasma potential.

As an another evidence in support of the above suppositions the arc operating voltage measurements in the short gaps are often brought. However, there are no reasons to believe that the arc operating voltage is the same as V_p , since the presence of anode will inevitably result in potential distortion, in particular, due to appearance of anode voltage drop region.

Analysis of great body of data compels us to reconsider the main prerequisites of cathode spot model. Our suppositions are based on the concept of non-monotonic potential distribution along the gap. The model and comparison of the calculated data with experiment for the arc with diffuse cathode spot attachment are described in detail in Ref. 4. Then in Ref. 5 we presented the first results on constricted cathode spot. We shall not repeat the mathematical treatment here but outline the general idea of the model. The idea can be readily understood by a comparison between Fig. 2.8 and Fig. 2.9.

The potential distribution along the discharge gap is not monotonic. The potential reaches its maximum value V_c at the boundary of the cathode layer and descends in a near cathode plasma. At the plasma boundary the value of potential is $V_{\min}$ (Fig. 2.9). Since the region of "potential hump" makes up a potential trap for electrons, then the electrons execute an oscillatory motion inside this region so that the efficient ionization of the cath-

2. Experimental setups and general features of arc discharge

ode material vapor is provided. Such conditions are similar to some extent to those in a low pressure glow discharge with hollow cathode.

It can readily be seen that the ions from plasma (the region to the right from point l_c) have no possibility to penetrate into the cathode layer. Thus, the ion current to the cathode is provided by the ions that are originated in Ol_c region. It is important to stress that cathode vapor ionization is performed not by the electrons that start from the cathode but the energetic thermal electrons from plasma that may overcome the potential barrier and fly into Ol_c layer. Clearly, the probability of ionization is the higher, the higher plasma temperature and the longer the time during which starting from cathode atom crosses the cathode layer. Some preliminary calculation results for an arc with constricted cathode spot are listed in Table 2.2.

Table 2.2. Calculated parameters of a constricted steady-state cathode spot on a bulk cold cathode. Total arc current value is $i = 5$ A.

Metal	j , A/cm ²	T_e , eV	V_c , V	V_{min} , V	j_{ic}/j , %	G , g/C	n_{e0} , cm ⁻³
Mg	$8 \cdot 10^5$	0.8	9	2	81	$4 \cdot 10^{-3}$	$2 \cdot 10^{20}$
Cu	$2 \cdot 10^5$	4.5	32	9	66	$7 \cdot 10^{-5}$	$5 \cdot 10^{18}$
Ni	$1 \cdot 10^5$	1.8	16	4	60	$4 \cdot 10^{-4}$	$2 \cdot 10^{19}$
Ti	$6 \cdot 10^3$	2.5	20	9	26	$6 \cdot 10^{-5}$	$7 \cdot 10^{17}$

The table uses the following notation: j — the arc current density at the cathode; T_e — the electron temperature in near cathode plasma; V_c and V_{min} correspond to Fig. 2.9; j_{ic}/j — the fraction of ion current at the cathode in total arc current; G — the erosion rate of the cathode material; n_{e0} — the plasma density in the vicinity of point l_c .

Note, that the results presented have to be considered as estimative; we do not aim here to discuss the phenomena in the cathode spot in detail. However the parameters of the cathode spot are well within the scatter in measurement data of different authors [8].

Now let once more refine the terminology. Earlier we spoke repeatedly of a cathode spot and a cathode flare. It is clear that when basing of non-monotonic potential distribution concept we imply that the cathode spot incorporates not only the melted metal bath and the near cathode regions *I* and *II* in Fig. 2.8, but also the region *III*. In other words, the cathode spot involves the near cathode plasma blob as such (see Fig. 2.9), and we shall refer to this blob as the cathode spot plasma.

On the other hand, the experiments show that for the gap distances more than 1 cm the gap contains a high density cathode spot plasma (substantially less than 1 mm length-wise) and a low density plasma of the cathode flare (the size of the flare is about 5 mm).

Evidently that in a transition region between these two kinds of plasmas a potential drop layer (a so-called sheath of excess space charge) have to be presented [9]. The existence of such a sheath is a characteristic of transition region between two plasmas that have different densities and different temperatures. As we believe, this sheath plays conceptually a part of a cathode voltage drop region for some specific gap in which the surface of the cathode spot plasma can be considered as a fictitious cathode surface. Thus, harnessing the idea of non-monotonic potential distribution, we shall arrive at the pattern of potential distribution for the long gap shown in Fig. 2.10. This is precisely the approach which will allow us to treat the experimental results of Section 3.

Now let us describe Fig. 2.10 in more detail. As noted above, the value of $V_{\min}$, *i.e.* the potential at the boundary of the cathode spot, is not large. Therefore, for the sake of simplicity let us assume that $V_{\min} = 0$, *i.e.* the potential of the cathode spot plasma boundary is equal to cathode potential. In addition, we shall use the term "cathode voltage drop region" when characterizing the layer Ol_c in Fig. 2.10, although in reality this is a transition sheath between the cathode spot plasma and cathode flare plasma. It is clear that the cathode spot supplies electrons and neutral particles to the cathode flare. The ions can not be injected from the spot to flare since they fail to overcome the potential barrier eV_c . This is one of the reasons why the cathode spot plasma boundary is spatially restricted. The neutral particles are generated as a result of cathode material evaporation and due to microexplosions of the cathode surface. In the strict sense the microexplosions may be responsible for deformation of the cathode spot plasma boundary. However, the experiments show that the size of the cathode spot is substantially less than that for the cathode flare. Thus, we shall assume that the spot boundary is spatially stabilized and supplies an atom flux and electron flux to cathode flare region.

After assumptions made it can readily be seen that the description of the cathode flare and the Ol_c sheath is virtually reduced to non-monotonic potential distribution model that we developed previously for low current density arc with diffuse cathode spot. Let us modify the description as applied to conditions under consideration.

At a large gap spacing we may distinct in the gap the cathode flare and a positive column region. As the experiments show, for vacuum arc with a current of about 100 A the positive column is readily observed for the gap distances more than 5 cm. The outer boundary of the cathode flare in Fig. 2.10 corresponds to coordinate x_m . The relation between the cathode vapor density and the distance x_m is such that the electron free path for ionization either compares with x_m or exceeds it. Therefore, the presence of the potential hump region $0x_m$ is important for keeping the ionization degree in the cathode flare high. This region is a potential trap for the electrons having started from the cathode spot and

2. Experimental setups and general features of arc discharge

lost in collisions an energy greater than eV_m . They remain inside the potential well and owing to their oscillating motion provide for efficient plasma generation inside the cathode flare.

The cathode sheath length $0l_c$ is far smaller as compared to all free paths, nevertheless, ionization of atoms may occur in this region. The ionization is produced not by the electrons that start from cathode spot boundary (point $x = 0$), but by the energetic thermal electrons from the cathode flare plasma, which may fly into the potential barrier region $0l_c$ (corresponding calculations are presented in Ref. 4). If an atom has been ionized within the length $0l_c$ it returns back in the cathode spot in the form of an ion. This ion flux is one of the sources of heating both the cathode spot plasma and the cathode.

Figure 2.10 shows that if the ionization of atoms occurs between the points l_c and x_1 , the ions produced are accelerated in the region where the characteristic $V(x)$ has a negative slope, thereby constituting an ion flux onto the anode. Since the distance $l_c x_1$ is rather large, the single and multi-charged ions can be originated here. The total discharge current through the section x_m includes in itself the "abnormal" ion flux and flux of electrons whose energy is high enough to overcome the potential barrier $e(V_c - V_m)$.

At the boundary between the cathode flare and positive column there exists a transition region $x_m x_{col}$ with potential drop $(V_1 - V_m)$. This is a so-called double sheath of excess space charge which is usually available at the boundary of plasmas having different densities and temperatures. As an example we may point to classical glow discharge where such a sheath (Faraday dark space) is present between negative glow and positive column. Note, that this analogy is not artificial. In fact, the cathode flare region resembles the negative glow in many respects. As measurements show, the potential in the negative glow region is actually descending [8, 9] although the most of researches do not take this fact into account or do not mention about it at all.

It can readily be seen that the region $x_1 x_{col}$ is a potential trap for ions that originate in this region. Accumulation of ions inside the trap and a space ion charge created by "abnormal" ion flux onto the anode offer prerequisites to the high-efficiency neutralization of electron space charge in region $x_m d$. As a result, the positive column and region $x_m x_{col}$ can pass a high current at moderate voltage drop. Note, that the ions can not be accumulate in the vicinity of point x_m in infinite quantities. Their death must be due to recombination process. Besides, it is possible that there exists a small potential hump with an energy of kT_i as shown in Fig. 2.10 by dashed line. The role of this hump is to cut out the ions that may enter the region $x_1 x_{col}$ from positive column.

At large gap distance there is a negative voltage drop region near the anode (see Fig. 2.10). In the present work we concentrate our attention on the near cathode processes, therefore we shall not discuss the anode voltage drop region.

Thus, after the description of the model we can discuss the experimental results and compare them with the model.

3. Spectroscopic investigation of the cathode flare plasma

3.1. Introduction

One of the phenomena characteristic of vacuum arc is the availability of ion flux which moves toward the anode, *i.e.* in opposition to external electric field direction. There are a number of publications where the data on measurements on fast ion fluxes are presented [1–12]. However, a conventionally accepted mechanism to treat this phenomenon, even on qualitative level, is absent by now.

According to statement of work we are to investigate the process of fast ion generation. As can be concluded from Sec. 2.3, for the large gap distances ($d > 1$ cm) the acceleration of ions occurs in the cathode flare region. The preliminary estimates [1] showed that a registration of fast ions both inside and outside the cathode flare can be performed by measuring the spectral line Doppler shift. In so doing it is desirable to ensure the conditions in which the anode does not enter into direct contact with cathode flare plasma, *i.e.* the gap distance has to be rather large in order that a positive column be available in the gap. The results and discussion on spectral line shift and broadening are presented below.

3.2. Principle of method

The measurement principle is illustrated in Fig. 3.1. The spectral line observations are performed through the aperture in anode. If a particle has a velocity v the radiation wavelength is defined by the relation

$$\lambda = \lambda_0 \frac{1 - v/c \cos \theta}{\sqrt{1 - v^2/c^2}}, \quad (3.1)$$

where c is the velocity of light, θ is the angle between direction of observation and particle velocity vector, λ_0 is the wavelength for immovable particle.

Since the particle velocity $v \ll c$, the Eq. (3.1) can be written as

$$\lambda = \lambda_0 \left(1 - \frac{v}{c} \cos \theta \right). \quad (3.2)$$

3. Spectroscopic investigation of the cathode flare plasma

Thus, if the particle moves in spectrograph direction, *i.e.* $\theta < \pi/2$, the wavelength observed decreases as compared to λ_0 ; for $\theta > \pi/2$ as the particle moves outward the spectrograph, the wavelength observed is more than λ_0 .

It can readily be seen that for isotropic particle velocity distribution Doppler effect results only in spectral line broadening; the line profile remains symmetrical and maximum in intensity corresponds to the wavelength λ_0 . However, if a translational motion is combined with chaotic motion, then a deformation of spectral line profile will occur and maximum in intensity will be shifted relative to position λ_0 . Hence, the spectral line profile contains an information on translational component of particle velocities.

For the case shown in Fig. 3.1 the results of measurements offer a possibility to conclude of velocity component $v_x = v \cos\theta$, since

$$v_x = c \frac{\lambda_0 - \lambda}{\lambda_0} . \quad (3.3)$$

We shall further estimate the atom and ion velocities using Eq. (3.3). Let specify in advance that for the particles moving toward the anode the velocity v_x will be considered with the "plus" sign and for the particles moving toward the cathode we shall consider the velocity v_x with the "minus" sign.

Also note, that proceeding from the velocity we can readily obtain the translational particle energy

$$u_x = \frac{Mc^2}{2} \left(\frac{\lambda_0 - \lambda}{\lambda_0} \right)^2 , \quad (3.4)$$

where M is the mass of atom or ion.

3.3. Experimental arrangement and procedure

The described above principle has been realized with different electrode system designs. One of the cathode unit designs is shown in Fig. 3.2. The method of discharge initiation corresponded to that described in report [1] and Sec. 2.1 of this report. The discharge operated typically at current of 100 A and half-pulse-width of 150 μ s.

The cathode flare image was projected onto the plane of spectrograph entrance slit with the scale 1:1 by the lens of 112 mm focus distance. To photograph spectrums the spectrograph STE-1 was used with linear dispersion of 3.8 $\text{\AA}/\text{mm}$, 4.7 $\text{\AA}/\text{mm}$ and 6.4 $\text{\AA}/\text{mm}$ for V, IV and III orders of diffractive grating, correspondingly.

The relative position of the electrode system and entrance slit can be understood from Fig. 3.2. The direction of observation is in line with discharge axis, and the entrance slit plane is parallel to cathode plane. Note, that our aim was to record the cathode flare radiation and prevent the cathode spot radiation from entering the entrance slit. Typically, a several thousands of pulses were necessary to obtain a spectrum photograph. In each separate pulse the cathode spot arises spontaneously in any point of cathode, so that the spot image may accidentally fall onto spectrograph slit. However, the probability of this event is not high and, as a consequence, the shown in Fig. 3.2 design enables us to obtain the cathode flare spectrums. Since the height of the slit is larger than cathode flare diameter, the upper and bottom sections of spectral lines contain information of positive column radiation.

Another cathode unit modification and experimental arrangement as a whole are shown in Fig. 3.3. Here, the aperture 2 mm in diameter is located at the cathode axis; diameter of the flat cathode part, where the cathode spot is initiated, measures 4 mm. The Fig. 3.3 shows that the arc discharge can operate between the cathode and anode *I* as well as between the cathode and anode *II*. In particular, as the switch *S* is in the position *I* and negative voltage pulse is applied to cathode *I* a flashover across the dielectric insert 2 occurs. Since the auxiliary flashover circuit includes the resistor R_3 , the arc current will be intercepted to the main anode *I*. In this case the experimental arrangement virtually corresponds to Fig. 3.2. The fast ions move toward the spectrograph and we should expect that a maximum in spectral line intensity will shift to the short wavelength range.

As the switch *S* is in position *II* the main discharge operates between the cathode and anode *II*. The electrode system is completely symmetrical so that the discharge parameters for the both cases will not differ. However, the fast ions move outward the spectrograph and the spectral line maximum should be shifted to the long wavelength range. This design offers an opportunity to define the position of unshifted spectral line λ_0 . Actually, because the shift occurs in opposite directions, the position λ_0 is located at the centre between two shifted lines.

3.4. Experimental results and comparison with the model

The experiments described below were carried out with the discharge chamber shown in Fig. 3.3. The internal chamber diameter was 270 mm; the distance from cathode to chamber end was 180 mm. As it is seen, the grounded chamber envelope serves as the discharge gap hollow anode. We used different cathode unit designs, in particular, those shown in Figs. 3.3 and 3.2. The cathode was made of magnesium and the auxiliary electrode 3 was made of stainless steel.

3. Spectroscopic investigation of the cathode flare plasma

The residual gas pressure was 10^{-5} to 10^{-4} Torr. At such a low pressure the electron free path exceeds the gap length. However, due to hollow anode effect, we have the case that positive column plasma forms inside the anode cavity. Between the cathode flare and positive column plasma there exists a potential drop region. Therefore, as distinct from the data in Fig. 2.5, the discharge operating voltage in this experiments constitutes 60 eV at the current of 100 A. Taking the above-said into account, let us dwell on the experimental data.

Fig. 3.4 shows the pattern of spectral lines for magnesium ion. The measurement method corresponds to Fig. 3.2. Since the projected onto the entrance slit plane is the image of cathode flare we record mainly the flare radiation and a radiation from positive column zone immediately adjacent to flare. These data allow to estimate the cathode flare transverse size (cathode flare diameter), because the flare radiation intensity is higher as compared to the column intensity and the flare spectral lines broaden in more extent than column lines. The marked in Fig. 3.4 cathode flare transverse size amounts to 4.5 mm. However, we must take into consideration that the spectrum has been obtained at large number of pulses and for each pulse the cathode spot arose in any point of cathode. As a result, with the cathode 1 mm in diameter the region that is marked in Fig. 3.4 is about 1 mm more than the actual size of cathode flare. Thus, we can estimate the cathode flare diameter from 3.5 to 4 mm.

Figure 3.4 also indicates a shift of ion spectral lines. In order to demonstrate the shift we superimposed the spectrum of atmospheric pressure arc, whose lines are collisionally broadened, on the spectrum under discussion. The lines $\lambda_0 = 2802.7 \text{ \AA}$ and $\lambda_0 = 2795.5 \text{ \AA}$ are resonance, therefore they are characteristic of extremely high self-absorption in atmospheric pressure arc. As a result, each separate line shows a sharp decrease in intensity in the vicinity of λ_0 , *i.e.* the dark region at the center of line. It can readily be seen from Fig. 3.4. that the low pressure arc lines $\lambda = 2802.7 \text{ \AA}$ and $\lambda = 2795.5 \text{ \AA}$ do not fall exactly at the center of dark region but they are shifted to the left. Thus, the ion spectral lines outside the flare are shifted to the short wavelength range, *i.e.* the ion flux has a velocity component directed to anode.

It turned out that the shift of lines is characteristic of not only the ions but the atoms as well. In particular, such a shift for resonance line $\lambda_0 = 2852.13 \text{ \AA}$ of Mg atom is shown in Fig. 3.5, where we can also see the broadened line of atmospheric pressure arc with the collapse at the center and low pressure arc line that shifts to the left.

One more illustration for the line shifts is demonstrated in Fig. 3.6. The experiments have been carried out with the cathode unit design shown in Fig. 3.3. In the case that the switch S is in position I the spectral lines are shifted to the short wavelength range and

when the switch S is in position II the lines shift to the long side. Thus, we can see the "double" lines at the photograph. Note, that in these experiments the cathode diameter was 4 mm. Since the cathode spots move over the surface, the cathode flare region in photograph of Fig. 3.6 is larger, than that for photograph of Fig. 3.4.

Using the discharge spectrums we have made the photometry of atom and ion lines in order to obtain their profiles. After that we expressed the wavelength in units of velocity v_x in accordance with Eq. 3.3. One of the patterns of such a treatment is presented in Fig. 3.7. Curve 1 is the profile of ion spectral line for the region inside the flare. Since the direction of observation is on line with discharge axis (see Fig. 3.3), both the ions from region inside the flare and from positive column give a contribution to spectral line luminosity. Curve 2 shows the spectral line profile outside the flare, *i.e.* the contribution to the line luminosity gives the ions from positive column region. At last, curve 3 is the profile of magnesium atom line inside the flare.

The spectral line shift and broadening are governed by Doppler effect so that the profiles carry an information on directed ion and atom velocities. Let us discuss this information based on the discharge model shown in Fig. 2.10.

First of all our attention is engaged to the fact that maximums in atom and ion light intensities are shifted to the right for the same distance $\Delta\lambda = 0.03 \text{ \AA}$ which corresponds to directed velocity $v_x = 0.32 \cdot 10^6 \text{ cm/s}$. According to the model the cathode flare plasma-forming medium, *i.e.* the medium that maintains the existence of the flare, is the cathode material vapor. This vapor enters the flare region from the cathode spot, and the directed atom velocity is determined by the energy of heavy particles in the cathode spot plasma. Then, proceeding from Eq. (3.4), we can estimate the average energy of atoms injected from the cathode spot as $u_x = 1.3 \text{ eV}$. The estimate is in a good agreement with cathode spot plasma temperature [6]. (It should be noted that we speak of a high density plasma of cathode spot where the electron and heavy particle energies are close to each other).

In Fig. 3.7 we can see the region of positive values of velocity v_x and the region of negative v_x , *i.e.* curve 1 broadening is determined to both the fast ions moving to the anode and ions moving to the cathode as well. Before discussing this curve let us pay attention to the curve 2 that represents the ion line profile outside the flare. It can readily be seen that the ions have only a component of velocity directed to anode. In accordance with the potential hump model the ions which originate in the section $l_c x_1$ and do not lose the directed energy in collisions escape from the flare and enter the positive column. Then the ions originated near l_c point should have a maximal energy of $e(V_c - V_1)$ at the boundary of the column, and the ion energy spectrum must range from zero to $e(V_c - V_1)$. Maximum in curve 2 should correspond to some average energy in ion spec-

3. Spectroscopic investigation of the cathode flare plasma

trum. Thus, proceeding from the shift of curve 2 relative to position λ_0 , we can estimate the potential hump height.

For instance, maximum in curve 2 corresponds to velocity $v_x = 1.34$ cm/s or similarly the ion energy $u_x = 22.5$ eV. Hence, it is reasonable to say that the potential hump height $e(V_c - V_1)$ is not less than 22.5 eV. However, it is more correct to find this height from maximal ion energy that we observe in positive column, but the precision of such a measurement will not be high. On the one hand, the width of curve 2 is comparable with instrumental profile for the spectrograph STE-1 which results in decreasing the measurement accuracy at the spectral line wings. On the other hand, the energy u_x is correlated to ion velocity by quadratic dependence which, in turn, decreases the measurement accuracy. Nevertheless, let assume that we reliably register the ions of velocity $v_x = 2 \cdot 10^6$ cm/c (see Fig. 3.2). Then the energy of these ions, *i.e.* the potential hump height, is equal to 50 eV.

Taking the above-mentioned into account we can offer the interpretation for curve 1. Recall, that the curve summarizes the ion line radiation both inside and outside the flare. Correspondingly, it can be readily understood that the second peak in curve 1 is due to radiation of ions leaving the flare, *i.e.* the ions that have crossed the point x_{col} . The broadening of the curve to the right from position $\lambda_0(v_x = 0)$ is determined by the ions which move toward anode. This broadening is provided by the ions originated at the section $l_c x_m$. Hence, the ion spectrum should range from zero to $e(V_c - V_m)$ and the right section of curve 1 indicates the total height of potential hump $e(V_c - V_m)$. Strictly speaking, the ions that arise at the section $0l_c$ just near the point l_c can overcome a low potential barrier and cross the point l_c , as far as the atoms have a directed velocity. Therefore, when we refer to Fig. 2.10 we point out the coordinates l_c and x_m approximately. It does not introduce alternations in our discussion, since the directed atom energy $u_x = 1.3$ eV is negligibly small.

On the other hand, the region $x_1 x_{col}$ constitutes a potential trap for ions originated here. Besides, the ions that arise at $l_c x_1$ section can also be trapped by the $x_1 x_{col}$ region on condition that they have lost their directed energy in collisions. Thus, we can see that the section $x_m x_{col}$ is responsible for ion acceleration toward cathode. The accelerated at this section ions form the left side of curve 1. Proceeding from these reasons we have an opportunity to estimate the potential drop between the cathode flare and positive column. It is seen from curve 1 that we reliably register the directed to cathode ions with velocity $v_x = (1 - 1.5) \cdot 10^6$ cm/s. Then, taking the velocity $v_x = 1.5 \cdot 10^6$ cm/s we obtain the energy $u_x = 30$ eV. Thus, the rough estimate of the potential drop yields $(V_1 - V_m) = 30$ V.

It is notable that the experimental data offer a possibility to estimate the value of V_m . Actually, when decreasing the gap spacing the arc discharge transits to the mode in

which the positive column and potential drop region $x_m x_{col}$ are absent. In this case the discharge operating voltage is approximately equal to V_m . (The situation looks like classical glow discharge where an anode is placed into Faraday dark space). As we mentioned earlier, at gap distance $d = 0.5-1$ cm and current $i = 100$ A the discharge operating voltage $V_a \approx V_m = 25$ V. Hence, we readily obtain the cathode potential drop voltage as follows:

$$V_c \approx V_m + (V_1 - V_m) + (V_c - V_1) \geq 100 \text{ V.}$$

Curve 3 in Fig. 3.7 is the magnesium atom spectral line profile. We have already noted that the shift of peak is determined by the energy of neutral atoms in cathode spot. The atom line is also broadened but not in such extent as ion line. Besides, the atom line is slightly non-symmetrical relative to position of maximum. The line profile is governed not only by the energy of atoms in cathode spot but the processes in the cathode flare as well. In particular, the reaction of resonant charge exchange may result in origination of fast atoms and, consequently, give a contribution into line broadening.

The above discussed experiments related to the case that the special precautions have been taken to prevent the cathode spot radiation from entering the spectrograph slit. It enables us to interpret the processes in the cathode flare and in the region $x_m x_{col}$. However, in accordance with the model some fraction of atoms is to be ionized in cathode layer Ol_c . We have made the experiments to observe these atoms.

The experiments have been carried out with the setup shown in Fig. 2.3 as the switch S was in position II . The cathode aperture diameter was 3 mm and external cathode diameter was 4 mm. Thus, the width of the cathode ring, where the spot arose, was decreased up to 0.5 mm. In such conditions, the cathode spot can be attached not only to external edge of cathode but also to internal edge as is shown in Fig. 3.8. Then some fraction of ion flux accelerated in the layer Ol_c can pass through the aperture and move towards spectrograph. A spectral line profile for such conditions is shown in Fig. 3.8. By and large the profile under discussion is similar to that shown in Fig. 3.7 (curve 1). However, we can see the additional peak in intensity shifted to the value $\Delta\lambda = -0.26 \text{ \AA}$. This peak is due to the ions accelerated in the cathode layer and moved toward spectrograph. Proceeding from the shift we estimate the cathode potential drop as $V_c > 100$ V. This value is in a good agreement with the previous estimates.

In conclusion of this section let us discuss the issue of charged particle balance in cathode flare. A neutral atom flux enters the flare where effective ionization occurs and atoms transform to ions. The main channel for ion disappearing is the flux toward anode. However, the ions whose energy is not high enough accumulate in the potential trap re-

3. Spectroscopic investigation of the cathode flare plasma

gion $x_1 x_{col}$. Then the natural way for their death seems to be recombination process. Consequently, we should expect that the spectral lines that accompany the recombination process are to be present in spectrum. One of the recombination channels is two-body recombination with forming the intermediate auto-ionization states. The auto-ionization energy levels for Mg as well as the spectral transitions from these levels are known. We observed these weak lines in cathode flare spectrum. The lines are listed in Table 3.1.

Table 3.1.

λ , Å	Upper level energy, eV	Lower level energy, eV
2809.80	10.36	5.95
2811.78	10.35	5.95
2811.11	10.35	5.95
3899.50	10.35	7.18
4409.90	10.00	7.19

It seems reasonable to say that the upper levels for these transitions are populated in the recombination process.

Thus, the presented measurement data fit in the potential hump model quite well. However, the non-monotonic potential distribution is characteristic of low pressure discharge plasma where electron free path exceeds the plasma dimension. In other words, the heavy particle concentration should not be high, since it is necessary to provide the directed motion of ions and electrons through the flare without collisions. The direct measurements of electron density in support of the fact that cathode flare plasma is actually collisionless are presented below.

3.5. Electron density measurements in cathode flare

The most-used method to measure the electron density is based on measurements of Stark broadening for spectral lines. The broadening is usually defined by parameters ω and α that are weakly dependent on electron temperature and electron density [13, 14]. The spectral line half-width is expressed in terms of these parameters as follows

$$\Delta\lambda = 2\omega n_e 10^{-16} \left[1 + 1.75\alpha n_e^{1/4} \cdot 10^{-4} (1 - 0.75r_D) \right], \quad (3.5)$$

where $\Delta\lambda$ is obtained in Å, n_e is the electron density taken in cm^{-3} , r_D is the ratio of average distance between ions to Debye radius:

$$r_D = 6^{1/3} \pi^{1/6} \left(\frac{e^2}{kT_e} \right)^{1/2} n_e^{1/6}, \quad (3.6)$$

where e is the elementary charge in CGSE units, T_e is the electron temperature in Kelvin degrees.

Earlier we discussed data for the spectral lines whose parameters ω and α are small and Stark broadening is negligible. However, magnesium spectrum incorporates the lines which are characterized by substantial Stark broadening. In particular, the line MgI ($\lambda_0 = 3092.984 \text{ \AA}$) has parameter $\omega = 0.347$ and $\alpha = 0.222$ for electron density $n_e = 10^{16} \text{ cm}^{-3}$ [13]. We have used this line for measuring electron density in cathode flare plasma.

Experiments have been carried out with the arrangement shown in Fig. 3.3. The cathode unit design corresponded to Fig. 3.2. The profile of spectral line $\lambda_0 = 3092.984 \text{ \AA}$ in conditions that direction of observation is parallel to discharge axis is shown in Fig. 3.9 (curve 1). Spectral line is shifted to the right due to Doppler mechanism. Nevertheless, the line profile broadenes both due to Doppler effect and Stark effect. It can readily be concluded when comparing the spectral line $\lambda_0 = 3829.35 \text{ \AA}$ in Fig. 3.7 and the line under discussion. In the former case the spectral line half-width is $\Delta\lambda \approx 0.095 \text{ \AA}$ whereas for Fig. 3.9 the half-width is equal to $0.3 \text{ \AA}$. Thus, the prevailing contribution into the latter line broadening mechanism gives Stark effect. If we assume that the line half-width due to only Stark broadening constitutes $0.2 \text{ \AA}$ then, in accordance with Eq. 3.5, we obtain electron density $n_e = 2.3 \cdot 10^{15} \text{ cm}^{-3}$. It is evidently that electron density decreases with distance from point l_c . Here we observe radiation along the discharge axis, *i.e.* along the whole depth of cathode flare. As a result, we measure the maximum electron density in the vicinity of point l_c .

Curve 2 in Fig. 3.9 has been obtained for another conditions. The direction of observation was perpendicular to discharge axis and spectrograph slit was placed at the distance of 1.5 mm from the cathode, *i.e.* virtually from the point l_c . Our attention is engaged to the fact that the line profile is symmetric and the line itself is not shifted relatively to position λ_0 . This is understandable, since at transverse observation we do not register Doppler shift. The electron density at the distance of 1.5 mm from cathode decreases as compared to the former case, hence the half-width line decreases as well. Apparently, Stark line profile and Doppler profile are comparable to each other, therefore, correct measurements of electron density at distance of 1.5 mm from cathode are made difficult.

Thus, we can conclude that the electron density in the cathode flare is of the order of 10^{15} cm^{-3} . Note, that residual gas density in these experiments is less than 10^{15} cm^{-3} , *i.e.* cathode flare plasma totally forms from cathode material vapor. The vapor ionization de-

3. Spectroscopic investigation of the cathode flare plasma

gree is very high. In particular, in calculations for arc with diffuse cathode spot [4] we assumed that the cathode flare plasma was completely ionized and achieved good agreement with experimental discharge characteristics.

4. Conclusion

The main experimental result of this report seems to be in the fact that the quantitative information on directed velocities of heavy particles and electron density in the cathode flare have been obtained. Proceeding from this information and basing on the analysis of the other results we have proposed the model for the arc with constricted cathode spot that allowed us to treat experimental regularities. The model proposed can be considered as a foundation to interpret the discharge features in arc furnace.

However, it should be noted that the phenomena which accompany the overmelting of metal in arc furnace are substantially complicated as compared to arc operating conditions in model experiments. For instance, the arc discharge in furnace differs from classical arc discharge on the cold cathode by a variety of distinctive features: an elevated metal vapor pressure in the gap, non-steady-state phenomena related to forming the large size metal drops, presence of liquid anode, *etc.*

We believe that the further investigations should be carried out by means of gradual introduction of the new factors in arc discharge under study. On the one hand, this approach will enable us to model the actual arc furnace more correct and, on the other hand, the gradual completion of arc discharge operating conditions offers a possibility to modify the model itself. In particular, we are planning to use the other experimental procedures described in report [1] and investigate the effect of residual gas on discharge characteristics. Besides, as it was considered we intend to produce experiments with Ni-Mg alloy cathode and with liquid anode.

References

1. "Characterization of a Metal Vapor Burning on Nickel-Magnesium Cathode", *Scientific Report No 1, Contract AM-7666*, Tomsk, January 1995.
2. A.N. Zaidel, V.K. Prokofev, C.M. Raiski, N.A. Slavny and E.Ya. Shreder, *Tables of spectral lines*, Moscow: Nauka, 1977 (in Russian).
3. C.H. Corliss and W.R. Bozman, *Experimental transition probabilities for spectral lines of seventy elements*, National Bureau of Standards Monograph 53, Issued July 20, 1962.
4. A.V. Bolotov, A.V. Kozyrev, and Yu.D. Korolev, "Physical model for a cathode layer of a vacuum arc with non-monotonic potential distribution in near-cathode plasma," *Fizika plazmy*, Vol. 19, No 5, pp. 709–719, 1993.
5. A.V. Bolotov, A.V. Kozyrev, and Yu.D. Korolev, "Physical model of low current density vacuum arc," in *XVI Intern. Symp. on Discharge and Electrical Insulation in Vacuum*, 23–30 May, 1994, Proceedings of SPIE, Vol. 2259, pp. 82–85.
6. G.A. Mesyats and D.I. Proskurovsky, *Pulsed Electrical Discharge in Vacuum*, Berlin, Heidelberg, New York, London, Paris, Tokyo: Springer-Verlag.
7. G.A. Mesyats, *Ectons*, Part I, Ekaterinburg, Nauka, 1993 (in Russian).
8. V.L. Granovski, *Electrical current in gas. Steady-state current*, Moscow: Nauka, 1972 (in Russian).
9. B. Chapman, *Glow Discharge Processes*, New York, Chichester, Brisbane, Toronto, Singapore: John Wiley & Sons.
10. H.C. Miller, "Constraints imposed upon theories of the vacuum arc cathode region by specific ion energy measurements," *J. Appl. Phys.*, Vol. 52, No 7, pp. 4523–4530, 1981.
11. D.T. Tuma, C.L. Chen, and D.K. Davies, "Erosion products from the cathode spot region of a copper vacuum arc," *J. Appl. Phys.*, Vol. 49, No 7, pp. 3821–3831, 1978.
12. A.A. Plyutto, V.N. Ryzhkov, and A.T. Kapin, *Sov. Phys. – JETP*, Vol. 20, p. 328, 1965.
13. W. Lochte-Holtgreven, Ed., *Plasma diagnostics*, Amsterdam: North-Holland Publishing Company, 1968.
14. H.R. Griem, *Spectral line broadening by plasmas*, New York and London: Academic Press, 1974.

Fig. 2.1. Electrical circuit and chamber design with a hollow anode.

1 - cathode, 2 - ceramic insertion,
 3 - auxiliary electrode, $R_1 R_2$ - voltage divider,
 R_S - current shunt.

Fig. 2.2. Electrical circuit and discharge chamber design
with metal chamber envelope $R_b = 50\Omega$, $R_3 = 2\Omega$,
 $R_s = 0.025\Omega$, $C_0 = 4\mu\text{F}$, $V_0 = 4\text{ kV}$.

Fig. 2.3. Voltage waveform at the electrode 1 and current waveform through the shunt R_s . Switch S is in position I, chamber envelope is under floating potential.

Fig. 2.4. Voltage waveforms at the electrode 1 and current waveforms through the shunt R_s .

a - switch S is in position I, chamber envelope is under floating potential;

b - switch S is in position II, anode is under floating potential.

Fig. 2.5. Voltage waveforms at the electrode 1 and current waveforms through the shunt R_s .

a - switch S is in position I, chamber envelope is under floating potential;

b - switch S is in position I, chamber envelope is grounded.

Fig. 2.6. Optical spectra for vacuum arc on Ni cathode taken at different distances from the cathode surface.

- $l = 0$ - cathode spot region
- $l = 2 \text{ mm}$ - cathode flare
- $l = 7 \text{ mm}$ - off the cathode flare

cathode

$l=0$

$l=2\text{mm}$

$l=7\text{mm}$

3000 3200 $\lambda, \text{\AA}$

Fig. 2.6. (Continuation)

Fig. 2.6. (Continuation)

Fig. 2.7. Fragment of cathode spot region spectrum for the case that the spot not uniformly initiates over the cathode surface.

Fig. 2.8. Illustration for a typical treatment of the near cathode regions in vacuum arc. I - cathode voltage drop region, II - ionization region, III - low voltage arc region.

Fig. 2.9. Near cathode regions with non-monotonic potential distribution. I - cathode voltage drop, II - cathode spot plasma blob.

Fig. 2.10. Qualitative illustration for potential, electric field and charged particle density distributions along a long-distance gap.

Fig. 3.1. Principle of the Doppler shift measurements.

Fig. 3.2. Method of registration of the spectral line shifts for cathode flare plasma.

Fig. 3.3. Experimental arrangement for observation of the ion motion toward the spectrograph (position I for the switch S) and outward the spectrograph (position II for the switch S). 1 - cathode, 2 - dielectric insert, 3 - auxiliary electrode.

Fig. 3.4. Pattern of the magnesium ion spectral lines for experimental arrangement shown in Fig. 3.2. Linear dispersion is 3.7 Å/mm.

Fig. 3.5. Illustration of the Doppler shift for the magnesium atom spectral line. (Method of corresponds to Fig. 3.2.4.)

Fig. 3.6. Magnesium ion spectral lines obtained with the ion motion toward the spectrograph (line shift to the left) and outward the spectrograph (line shift to the right). Linear dispersion is 4.7 Å/mm. Method of observation corresponds to Fig. 3.3.

Fig. 3.7. Spectral lines profiles with the wavelength expressed in terms of particle velocity (Eq. 3.3). Experimental arrangement corresponds to Fig. 3.3.

Fig. 3.8. Ion spectral line profile for the cathode flare with the experimental arrangement shown in Fig.3.3. Switch S is in position II.

Fig. 3.9. Stark broadening for the atom spectral line in the cathode flare with experimental arrangement shown in Fig. 3.2.

- 1 - observation along discharge axis;
- 2 - observation transverse discharge axis at a distance of 2 mm from cathode spot.

Contents

1. Introduction	2
2. Experimental setups and general features of arc discharge.....	2
2.1. Discharge features for different constructions of electrode system.....	2
2.2. Integral spectrums of the different discharge regions	5
2.3. Qualitative model of the near cathode regions for a vacuum arc with constricted cathode spot.....	9
3. Spectroscopic investigation of the cathode flare plasma	15
3.1. Introduction.....	15
3.2. Principle of method.....	15
3.3. Experimental arrangement and procedure.....	16
3.4. Experimental results and comparison with the model.....	17
3.5. Electron density measurements in cathode flare.....	22
4. Conclusion	24
References.....	25
Figures	26

DISTRIBUTION:

- 1 US Department of Energy
Attn: John Hnatio
NN-1, x66319
Forrestal Building, Rm. GA087
1000 Independence Ave., SW
Washington, DC 20585
- 54 USIC
Attn: Mike Deagan, President
1524 Victoria Farms
Vienna, VA 22182
- 1 MS 0360 A. R. C. Westwood, 1000
- 1 MS 0467 Dennis Croessman, 5091
- 1 MS 0609 William Moffatt, 1841
- 1 MS 0725 Thomas Hunter, 6900
- 1 MS 1409 Alton Romig, 1800
- 1 MS 1134 Brian Damkroger, 1833
- 30 MS 1134 Frank Zanner, 1833
- 1 MS 9018 Central Technical Files, 8523-2
- 5 MS 0899 Technical Library, 13414
- 1 MS 0619 Print Media, 12615
- 2 MS 0100 Document Processing, 7613-2