UNCLASSIFIED

CT-2618

M-FRANES

Contract W-7412-eng-24
and
N. B. S.

CLASSIFICATION CANCELLED
DATE FEB 19 1957 *Alb*
For The Atomic Energy Commission
H. F. Canale
Chief, Declassification Branch

PROGRESS REPORT FOR DECEMBER 1944

by

A. G. Gray and J. G. Thompson

CLASSIFICATION CHANGED TO
CONFIDENTIAL
DATE 6/5/56
H. F. Canale
Chief, Declassification Branch *Ph*

This document is
PUBLICLY RELEASABLE
Hugh Kinser *N. Kinser*
Authorizing Official
Date 9/5/02

~~CONFIDENTIAL~~
This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

AEC RESEARCH AND DEVELOPMENT REPORT

Report received: February 2, 1945; Figures received: January 24, 1945
Issued: FEB 6 1945

This document is
PUBLICLY RELEASABLE
Hugh Kinser *N. Kinser*
Authorizing Official
Date 4/13/00

~~CONFIDENTIAL~~
This document contains information affecting the national defense of the United States within the meaning of the Espionage Act, U. S. C. 50; 51 and 32. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

UNCLASSIFIED

DISCLAIMER

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, 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 or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

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

[REDACTED]

ELECTROPLATING SECTION

SUMMARY:

The Manual of Commercial Operating Instructions for plating on tuballoy has been completed and is at the distribution center for circulation. A commercial type trichloroacetic acid pretreatment bath in operation for two months has shown consistently satisfactory results. The use of higher anodizing current densities for shorter periods of pretreatment has been shown to produce a uniform etch comparable with that obtained at lower current densities. Corrosion tests have been continued on various electroplates and combinations of electroplates for use as protective coatings in the Neutronic Reactor Loading Cartridge. Special heat treatment of relatively thin layer electroplates in silicone fluid at 300°C to form fused alloys has been found to improve corrosion resistance of coatings remarkably. Tests results have indicated that copper-tin, nickel-tin, nickel-copper-tin or nickel-zinc fused coatings within limits of thickness requirements will provide adequate protection during the cooling off period from the standpoint of protection of base metal and retaining of fission products within the slug. Recent work has been concentrated on the determination of minimum effective thicknesses of the fused electroplates for adequate corrosion protection. Copper-tin fused coatings of less than 0.001" thickness have shown good protection at 350°C for three months, and studies of adequate minimum thicknesses are now in progress.

Fundamental Study of Pretreatment of Tuballoy Prior to Plating

The Publications Office in Chicago in cooperation with Cleveland has edited, printed, and approved the Manual of Commercial Operating Instructions for plating on Tuballoy. The Manual is now at the distribution center awaiting circulation. Continued operation of the commercial type trichloroacetic acid pretreatment bath has shown that uniform removal of outer layers of tuballoy is possible under various anode current densities. By reducing the time of pretreatment, higher anode current densities may be used with same results obtained at lower current densities. After two months operation, the pretreatment bath is still giving consistently satisfactory results.

Evaluation of Coatings for Neutronic Reactor Cartridge

The development and evaluation of electroplated coatings for use in the Neutronic Reactor Loading Cartridge has been continued. Water corrosion tests on various electroplates and combinations of electroplates have revealed the superiority of relatively thin fused alloy coatings produced by heat treating layer electroplates such as copper and tin in a silicone fluid at 300°C for periods up to 3 hours. Of fundamental importance is the determination of the minimum effective thicknesses of these coatings necessary to provide adequate protection for the base metal tuballoy. Various thicknesses of several of the coatings have been prepared and are now in test. The various coatings being tested and the test results to date are recorded in Table I.

[REDACTED]

19

[REDACTED]

[REDACTED]

FIG. 2.-SOLUBILITY OF OXYGEN IN LIQUID TUBALLOY

CT-2618

TABLE I

Water Corrosion Test Results

<u>No. of Specimens</u>	<u>Description of Coating</u>	<u>Test Water Temp.</u>	<u>Days in Test</u>	<u>No. Failures</u>	<u>Days to Fail</u>
4	0.001" Cu-0.0001" Sn Treated in Silicone #700 3 Hrs; 300°C.	35°C	87	None	
6	0.0007" Cu-0.0001" Sn Treated in Silicone #700 3 Hrs; 300°C.	35°C	87	1	80
3	0.0007" Cu-0.0001" Sn Treated in Silicone #700 1-1/2 Hrs; 300°C.	35°C	87	None	
10	0.0001" Ni-0.003" Zn (Cyanide)	35°C	89	3 1 3 3	36 57 72 89
12	0.0001" Ni-0.0003" Zn (Acid)	35°C	78	2 7 1 2	37 59 64 78
6	0.0005" Ni-0.0001" Zn	50°C	75	All coatings pit corroded but giving pro- tection	
12	0.0005" Ni-0.0003" Zn Treated in Silicone #700 3 Hrs; 300°C.	35°C	67	None	
18	0.0003" Ni-0.0002" Cu- 0.00005" Sn treated in Silicone #700 2 Hrs; 300°C.	35°C	51	None (Some pit corrosion noted)	
11	0.0003" Ni-0.0005" Cu- 0.0001" Sn Treated in Silicone #700 3 Hrs; 300°C	35°C	37	None	
18	0.005" Cu-0.0001" Sn Treated in Silicone #700 2 Hrs; 300°C.	35°C	23	None	
12	0.0005" Ni-0.0002" Sn Treated in Silicone #700 2 Hrs; 300°C.	35°C	23	None	

Water Corrosion Test Results

No. of Specimens	Description of Coating	Test Water Temp	Days in Test	No. Failures	Days to Fail
12	0.0003" Ni-0.0001" Sn Treated in Silicone #700 2 Hrs; 300°C	35°C	18	none	
12	0.0007" Ni-0.0002" Sn Treated in Silicons #700 2 Hrs; 300°C	35°C	9	none	

The copper-tin heat treated coatings continue to evidence good protection after 87 days in test at 35°C. The one failure noted in these tests as contrasted with the 100% failure of 22 flash nickel-0.003" zinc plated slugs over approximately the same test period shows the superiority of these thin fused alloy coatings over a thicker straight electroplate. The nickel-zinc fused coatings (corroding process) still appear to be preventing corrosion of the base metal, but excessive corroding of the coating itself appears to be a disadvantage. Much less corrosion was noted in the specimens containing smaller percentages of zinc and a recommended ratio in thickness of nickel to zinc is 0.0005" Ni to 0.0001" Zn. Other coatings which are providing good protection but have been in test for shorter periods of time are the nickel-copper-tin and nickel-tin fused coatings. The tests on determination of minimum effective thickness have indicated that a minimum thickness for the copper-tin fused coating is 0.0007" Cu and 0.0001" Sn. Thinner coatings are evidencing a larger percentage of earlier failures.

On the basis of test results thus far, the copper-tin fused alloy coatings should provide adequate protection for tuballoy during the cooling off period. The nickel-zinc, nickel-tin, and nickel-copper-tin fused coatings although in test for shorter periods of time have evidenced good protection and work for the coming month will be concentrated on the continuation of these corrosion tests at 35°C in circulating water (composition supplied by Chicago). Work will also be started on the preparation of the Final Report covering all work done since beginning of contract. Specimens will be plated and treated according to recommended procedures to comply with requests to be received from Chicago for test coatings.

Molybdenum-Nickel Alloy Plating

The evaluation of the nickel-molybdenum pyrophosphate type bath for plating of nickel-molybdenum alloys was continued. A brief study of the cathode efficiency and composition of alloy deposit revealed that an alloy containing 50% molybdenum, 40% nickel, and 10% oxygen was deposited with an efficiency of approximately 10-15%. Further work on the deposition of the alloy on tuballoy was not started due to concentration of work on evaluation of coatings for use in the Neutronic Reactor Cartridge.

A. G. G.

4-
N. B. S.

REPORT FOR DECEMBER
on
METALLURGY OF TUBALLOY

J. G. Thompson, Supervisor

CONTENTS

	<u>Page</u>
Solubility of Oxygen in Liquid and Solid Tuballoy H. E. Cleaves, M. M. Cron, J. T. Sterling	5
Melting Point of Tuballoy H. E. Cleaves and A. I. Dahl	12

FIG. 1.-FURNACE FOR PREPARATION OF TUBALLOY INGOTS

Solubility of Oxygen in Liquid and Solid Tuballoy

The procedure followed in determining the solubility of oxygen in liquid and solid tuballoy included saturation of molten tuballoy with oxygen, chill casting the saturated metal to retain the oxygen dissolved in the liquid metal, analysis of the resulting ingots to determine the amount of oxygen dissolved in the tuballoy at the elevated temperatures and micro-examination of specimens of the ingots in the chill-cast and heat-treated condition to determine whether or not oxygen remained in solution in the solid metal.

Preparation of Tuballoy-Oxygen Ingots

Saturation of liquid metal with oxygen was effected by melting a charge of tuballoy in a beryllia crucible lined with tuballoy-dioxide and maintaining at a definite temperature for a period of time, usually 30 minutes. A split steel mold was then raised from the furnace bottom to pouring position, the power was cut off and the stopper rod lifted from the opening in the crucible bottom, permitting the molten metal to flow into the mold. The furnace used in preparing the ingots is shown in Figure 1.

The temperature of the molten metal was determined by sighting into a black-body sight tube immersed in the melt. The portion of the sight tube in the crucible was closed end beryllia tube which was filled with beryllia powder up to the center of the melt. The outside of the beryllia tube was coated with oxide by alternately dipping into concentrated tuballoy nitrate solution and heating to decompose the nitrate. The upper portion of the sight tube was a porcelain tube cemented to the beryllia tube by means of a beryllia sleeve and cement consisting of beryllia moistened with beryllium chloride solution. The sight tube assembly was fired at about 1400°C to set the cement. The beryllia tube served both as a sight tube and as a stopper to close the hole in the crucible bottom. The accuracy of the temperature measurements was checked in preliminary melts by means of a thermocouple inserted in the sight tube and removed intermittently to permit observation with the optical pyrometer.

The beryllia crucible was lined by tamping tuballoy dioxide, moistened with a dilute solution of tuballoy chloride, around a mandrel suspended in the crucible. After removal of the mandrel the crucible and lining were dried at 200°C and then fired in an Arsen furnace at about 1700°C. The dioxide formed a fairly hard lining which served for several melts before relining was necessary. The higher oxide (X308) was also tried as a crucible lining, because of the possibility that this oxide might supply oxygen to the melt more readily. This lining was so soft and fragile that it was crushed by the weight of the charge, the resulting oxide particles being carried down into the mold when the melt was cast. Lining the bottom of the crucible with the dioxide, to support the charge, and the crucible wall with the higher oxide eliminated this difficulty. However, the oxygen content of metal held in contact with the higher oxide was similar to that of metal cast at the same temperature from crucibles lined entirely with the dioxide indicating that saturation was obtained as readily with the dioxide as with the higher oxide and that use of the higher oxide as lining was not advantageous. In preliminary tests the same oxygen content resulted from maintaining the melts at 1400°C for 15, 30 and 60 minutes, indicating that saturation was effected by contact with the oxide for 15 minutes. However, as a precaution most of the melts were held at a definite temperature for longer periods than 15 minutes.

The temperature of the split steel mold just before casting was about 500°C. The slight increase above room temperature resulted from inductive heating although the top of the mold was about 6 inches below the furnace coil until just before the casting was made. This mold formed a wedge-shaped ingot, one inch wide, $\frac{1}{4}$ inch thick at the bottom, about $\frac{5}{8}$ inch thick at the top and up to 4 inches in length. The mold surface was protected by smoking over burning light oil. Brushing the mold with cotton, followed by swabbing with ether removed the non-adherent soot and condensed oil. The mold surface so protected did not react with metal cast at temperatures up to 1635°C but was attacked by metal cast at temperatures above 1700°C. Contamination by iron in ingots cast at temperatures above 1700°C interfered with metallographic identification of oxide inclusions but did not appear to appreciably affect the oxygen solubility, such ingots having about the same oxygen content as metal solidified in the melting crucible from the same temperature.

The furnace atmosphere used in preparing most of the ingots was helium purified by passing through activated charcoal at liquid air temperature. The use of tank helium caused an increase in the nitrogen content of the metal.

Modifications in the melting procedure were made in attempts to increase the oxygen content of the metal. Addition to the charge of finely ground oxide, which had not been ignited and therefore might be expected to be more reactive than the crucible lining, did not result in increase in the oxygen content of the metal. The use of an atmosphere of mixed helium and oxygen also failed to increase the oxygen content of the metal over that resulting from use of a purified helium atmosphere. The effect of more drastic oxidation was investigated by impinging oxygen gas upon the surface of the melt through a porcelain tube projecting into the crucible. The maximum quantity of oxygen used was sufficient, theoretically, to oxidize about 30 percent of the metal charged but the weight of metal oxidized was about half that amount. Part of the oxygen was consumed in oxidizing XO_2 to X_3O_8 and some oxygen probably escaped with the helium, because the layer of oxide on the melt hindered oxidation of the metal.

The temperature observed at the center of the melt while oxygen was being added was about 300°C above that observed with application of the same furnace power without the addition of oxygen, a result of the heat liberated by the oxidation. The presence of columnar crystals in the crust of oxide on the surface of the furnace-cooled ingot indicated that the temperature at the surface of the ingot had been, at least temporarily, above the melting point of the oxide, stated by Ruff and Goecke (Zeit. angew. Chem. Vol. 24, 1911, p. 1489) to be 2196°C, although the observed temperature in the center of the melt was only 1720°C.

Despite the ample opportunity for oxygen absorption the oxygen content of ingots prepared with addition of oxygen gas was not materially different from the oxygen content of ingots held in contact with tuballoy oxide at the same temperatures in helium, additional evidence that the latter procedure effected saturation with oxygen.

The carbon content of most of the tuballoy available for melting stock was of the order of 0.05 percent. Under the microscope the carbon appeared as inclusions scattered profusely throughout the metal, interfering with the metallographic identification of oxide inclusions. It was thought that gradual elimination of carbon might accompany the saturation of the molten metal with oxygen, but holding tuballoy molten in vacuum in an oxide lined crucible at 1600°C for one hour did not produce a sub-

prepared from metal melted in helium or in helium plus oxygen showed that the variation in carbon content between the metal charged and the resulting ingot generally was within experimental error of the analytical procedure. Apparently selective oxidation of carbon, by reaction with oxygen or tuballoy oxide, is not a practical way of reducing the carbon content of molten tuballoy. Small amounts of low carbon metal, with 0.015 and 0.005 percent carbon respectively, became available for melting stock for one or two runs near the close of the investigation. While decrease in carbide inclusions was noticeable, particularly in the metal with 0.005 percent carbon, the quantity of inclusions present was still sufficient to interfere with identification of the oxide. The presence of carbon did not appear to affect the solubility of oxygen in the liquid tuballoy, the values for solubility in low and high carbon metal being similar.

Twenty two ingots, with oxygen contents from 0.003 to 0.033 percent, were prepared either by casting or by solidification in the crucible. The results obtained on a number of other runs were rejected for various reasons, principally because failure of refractories made contamination probable or prevented satisfactory determination of temperature. Results on all ingots prepared at temperatures above 2000°C were rejected for such reasons.

Solubility of Oxygen in Liquid Tuballoy

The values for oxygen obtained by vacuum fusion analyses of the 22 ingots are shown in Table I and graphically in Figure 2. It will be seen that there is considerable scattering of values particularly in ingots prepared at the higher temperatures. This scattering may result from such factors as segregation of oxide or from contamination by particles of crucible linings. Segregation was a characteristic of the furnace-cooled ingots 11, 13, 20 and 22, the oxygen content of the sample from the top invariably being higher than that of the bottom section.

FIG. 8.- SOLUBILITY OF OXYGEN IN TUBALLOY

Table I
Oxygen Content of Tuballoy Ingots

Ingot No.	Satura- tion Time Minutes	Final Tem- perature of Saturation Period, °C	Weight Percent of Oxygen Top	Bottom	Remarks
1	30	1205	0.004	0.003	Cast
2	60	1400	.006	.005	Cast
3	30	1405	.003	.003	Cast
4	30	1405	.004	.003	Oxide added to charge. Cast
5	30	1415	.005	.004	Oxide added to charge. Cast
6	30	1500	.008	.008	Oxide added to charge. Cast
7	30	1545	.009	.006	Cast
8	15	1550	.010	.008	Cast
9	60	1590	.006	.008	Oxygen-helium atmosphere, cast
10	60	1600	.009*		Cooled in furnace
11	60	1600	.020	.012	Vacuum melt, cooled in furnace
12	30	1615	.008	.010	Cast
13	30	1615	.019	.005	Vacuum melt, cooled in furnace
14	30	1630	.010	.010	Cast
15	60	1635	.011	.010	Oxygen injected, cast
16	30	1635	.011	.011	Cast
17	30	1715	.014	.015	Cast
18	15	1720	.019	.019	Oxygen injected, cast
19	60	1810	.016	.013	Cast
20	15	1900	.027	.021	Oxygen injected, cooled in furnace
21	15	1900	.033*		Oxygen injected, cooled in furnace
22	30	2000	.030	.023	Cooled in furnace

*These values were obtained on the center sections of short furnace cooled ingots.

Values for the solubility at 100°C intervals, from the curve drawn through points representing mean solubility values, and the solubility at the melting point from the extrapolated curve are given in Table II. The solubility increases from 0.0031 weight percent (0.046 atomic percent) at the melting point (1131°C) to 0.029 weight percent (0.432 atomic percent) at 2000°C.

Table II

Selected Values for the Solubility of Oxygen in Liquid Tuballoy

Temperature °C	Percent Oxygen	Atomic Percent
1131 (m.p.)	0.0031	0.046
1200	.0035	.052
1300	.0042	.063
1400	.0053	.079
1500	.0072	.107
1600	.0105	.156
1700	.0140	.208
1800	.0188	.280
1900	.0235	.350
2000	.029	.432

Ingots with still higher oxygen contents were prepared by holding the metal at temperatures above 2000°C but refractory failures prevented satisfactory temperature measurements. Also metallographic examination of such ingots disclosed the presence of globular inclusions of oxide which appeared to be the result of entrapment of molten oxide in the metal. Hence the oxygen values by vacuum fusion may have included mechanically entrapped inclusions as well as oxygen in solution in the liquid metal.

Solubility of Oxygen in Solid Tuballoy

The solubility in the solid metal was investigated by metallographic examination of specimens from the ingots. These specimens, either as cut from the ingots or after heat treatment, were mounted in bakelite, polished mechanically, finishing on 000 emery paper, then polished electrolytically in an electrolyte composed of equal parts of 85 percent orthophosphoric acid and glycerine, using an applied potential of 6 volts. The current varied with the area of the specimen but usually was about 0.1 ampere. Specimens were swabbed intermittently during polishing. With this procedure inclusions were retained and pitting was negligible.

Inclusions other than carbides, were not observed in chill cast metal with oxygen contents less than 0.008 percent. Occasional minute inclusions were present in chill cast metal with about 0.008 percent oxygen, illustrated in Figure 3A. In metal with slightly higher oxygen content such as ingot 15 with 0.011 percent oxygen (Figure 3B) the inclusions were coarser and more prevalent. In some areas these inclusions were definitely aligned, as is seen near the left edge of Figure 3B, in other areas they appear scattered at random.

The inclusions in ingot 17 (Figure 4A) with 0.014 percent oxygen were finer than in ingot 15 (Figure 3B) but were more prevalent. The tendency of the inclusions to form lines is apparent in Figure 4A. With increase in oxygen content the lines became heavier with occasional eutectiferous areas. Figure 4B, showing a line of oxide inclusions between carbide dendrites, is typical of metal with oxygen content greater than

0.020 percent.

Large globular inclusions were present near the top of ingots which had been held molten under an atmosphere of oxygen and then cooled in the crucible. These inclusions appeared to be the result of the entrapment of molten oxide in the melt. The top edge of the ingot shown in Figure 5 shows penetration of the melt by the oxide crust. These oxide globules were observed only in metal near the top of the furnace cooled ingots, usually within 0.1 inch of the top surface.

The absence of visible oxide particles in chill cast metal of 0.008 percent oxygen and less indicates either that oxygen is soluble to that extent or that the precipitated oxide particles are of sub-microscopic dimensions. If the latter condition obtains, annealing the metal at a suitable temperature for sufficient period should result in agglomeration of the sub-microscopic particles.

Sections from several of the ingots were annealed in vacuum for four hours at 625°, 725°, and 925°C, then cooled in the furnace, the time required to cool to room temperature being about 2 hours. Annealing at 625° and 725°C did not cause any perceptible alteration in the quantity or appearance of the inclusions, probably because diffusion at these temperatures is so slow that no detectable agglomeration of inclusions results in four hours. Annealing at 925°C for four hours was effective in causing the appearance of inclusions in the ingots with higher oxygen contents. In metal with 0.003 percent oxygen the inclusions produced were minute at 500 diameters (Figure 6A) and were seen more clearly by visual examination under the microscope than in the photomicrograph, presumably because of the superior resolving power of the eye as compared with the photographic emulsion.

With increasing oxygen content the inclusions produced by annealing at 925°C were more readily discerned. The inclusions resulting from annealing a specimen of ingot 12 (0.008 percent oxygen) at 925°C appeared to outline grain boundaries (Figure 6B). The appearance of the same metal in the chill cast condition was shown in Figure 3A. The effect of annealing in the gamma temperature range on inclusions previously visible was to coarsen them as is shown by comparison of photomicrographs of ingot 15 in the chill cast (Figure 3B) and annealed conditions (Figure 6C).

Metallographic examination of specimens of the ingots etched electrolytically in oxalic acid showed that the lines of inclusions which appeared to outline, in part, grain boundaries did not coincide with the alpha grain boundaries. The appearance of a specimen of ingot 20 annealed at 925°C and etched is shown in Figure 7. The alpha grains in the annealed metal are gross in contrast to the smaller grains outlined by the inclusions. The fact that agglomeration of oxide inclusions resulted from annealing in the gamma range but not from annealing in the beta range would seem to indicate that the grains outlined by the inclusions are those of the gamma phase.

Summarizing these results for the solubility in the solid metal, the oxides in chill cast metal with less than about 0.01 percent oxygen probably are present in the form of submicroscopic inclusions. Annealing in the gamma range for four hours or longer results in diffusion and agglomeration of the oxide to form inclusions visible at 500 diameters.

magnification. When the concentration of oxygen in the tuballoy is more than about 0.01 percent sufficient agglomeration occurs during solidification and in cooling to room temperature to produce visible inclusions. Subsequent annealing in the gamma range results in the coarsening of these inclusions.

The appearance of inclusions as a result of annealing tuballoy with as little as 0.003 percent oxygen in the gamma range indicates that the solubility of oxide in solid tuballoy is less than 0.003 percent.

Determination of the variation with temperature of oxygen solubility in the solid metal was not feasible because of the limits of precision of the analytical methods.

Summary

Graphic presentation of the data obtained in this investigation is shown in Figure 8. The solubility of oxygen in the liquid phase increases with rising temperature from 0.0031 at the melting point to 0.029 percent at 2000°C. The preparation of metal with oxygen contents apparently greater than 0.029 percent, by holding the molten metal in contact with oxide at unknown temperatures above the melting point of the oxide, indicates that increase in the solubility continues with increasing temperature above 2000°C.

From the solubility relations observed in other metals it would be expected that the solubility of oxygen in solid tuballoy would be less than in the liquid metal, and that the solid solubility would vary with temperature, particularly at the two transformation temperatures. The appearance of oxide inclusions in specimens with an oxygen content of only 0.003 percent, after annealing at 925°C, confirms the conclusion that the solubility of oxygen in solid gamma metal is less than in the liquid metal but the actual solubility in the solid phases at various temperatures has not been determined. Variations in an oxygen content of less than 0.003 percent are not determinable by available analytical procedures and microscopic methods are inapplicable because of the difficulty of identifying minute oxide inclusions in the presence of far greater quantities of the other inclusions, especially carbides, that exist in all available specimens of tuballoy. For these reasons the solubility of oxygen in solid tuballoy is shown as a dotted line, to indicate that the solid solubility at all temperatures is less than the value, 0.0031 percent, for the solubility of oxygen in liquid metal at the melting point.

For similar reasons the effect of dissolved oxygen on the melting point and transformation temperatures cannot be depicted but it would be expected that the effect of oxygen in concentrations less than 0.003 percent would be less than the precision of the methods used in determining these temperatures.

FIGURE 1. APPARATUS FOR DETERMINING MELTING POINTS

National Bureau of Standards in 1941, one of the first problems to be investigated was the melting of the metal. Available information was limited and incomplete. Melting point values of 1600 to 1800°C and 1850°C for the

- (1) J. W. Mellor, Comprehensive Chemistry of Inorganic and Theoretical Chemistry, 12, 15 (1939).

melting point of uranium, according to different investigators. A value of about, or less than, 1850°C, sometimes ascribed to Moissan, was given in several references and handbooks (2). The value of 1690°C reported by Driggs and Lilliendahl (3) is quoted in Metals Handbook (4). Computations based on

- (2) Ford's Mechanical Engineer's Handbook 596 (1928)
Van Nostrand's Chemical Annual 294 (1928)
International Critical Tables 1, 103 (1928)
Smithsonian Physical Tables 198 (1937)
General Engineering Handbook (C'Rourke) 126 (1930)
Handbook of Chemistry and Physics 1712 (1943)
Machinery's Handbook 1579 (1943)

- (3) F. H. Driggs and W. C. Lilliendahl, Ind. Eng. Chem., 22, 516 (1930).

- (4) Metals Handbook 80 (1939)

the position of uranium in the periodic table of the elements indicated a melting point of about 3600°C (5).

- (5) Miscellaneous Publications of the National Bureau of Standards, M126 (1937).

A small button of tuballoy, prepared by C. J. Rodden in June 1941, was observed to be molten in a beryllia crucible at temperatures estimated visually to be less than 1300°C. When larger masses of metal from other sources became available, two ingots were prepared, each one about 360 grams in weight, one from selected pieces of an ingot received from Metal Hydrides, Inc. and the other from a portion of a cup-shaped cake which was reported to be metal of electrolytic origin produced by Westinghouse. The selected pieces of each metal were melted in beryllia crucibles in vacuum to form ingots of the desired shape for the determination of the freezing points. The results of these determinations as reported by W. F. Roeser in Report A-215, indicated freezing points of 1075°C for the Metal Hydrides metal and 1100°C for the Westinghouse sample. The evolution of fumes and the distillation of impurities from the metal during some of the determinations created uncertainty as to the exact numerical values, but there was no question that the freezing point was about 1100°C and not the higher values indicated in the literature. These determinations and others made elsewhere furnished a basis for the value 1100 ± 25°C given in the Project Handbook issued in 1943. Subsequent observations, made in connection with

the production of high-purity metal in quantity, indicated that the best values probably were above the middle of this range. It would be expected that the progressive improvement in quality of the metal with improvements in production technique would be accompanied by a gradual change in the observed melting points. It appeared to be desirable, therefore, to correct the earlier determinations made at this Bureau by means of redeterminations of the melting point or freezing point of modern high-purity metal.

Material from two sources was available for the new determinations, extruded rod RU 557 and biscuit metal B 871. Analytical data for the two metals, from determinations by chemical, spectrochemical, and vacuum fusion methods, indicated that the principal difference between the two metals was in the carbon and zinc contents, as is shown in the first two columns of Table I. Ingots of the desired shape for the melting point determination were prepared by forging. A hole for the sight tube was drilled longitudinally through each ingot, using carbide tipped drills.

Table I

Analyses of Ingots before and after the
Freezing Temperature Determinations

RU	Original material		After Freezing Temperature Determinations	
	557	B 871	Ru 557 in BeO	B 871 in ThO ₂
	ppm	ppm	ppm	ppm
Ag	L* 0.2	L* 0.2	L* 0.2	L* 0.2
Al	L 10.	L 10.	L 10.	L 10.
B	L 2.	L .2	.3	.2
Ca	L 5.			
Cd		L 3.		
Cu	1 to 5	L 1.	5 to 10	L 5.
Fe	50	45.	64	58.
K	L 5.	L 5.		
Li		L .3		
Mg	L 5.	5 to 10	L 5.	L 5.
Mn	5.	L 5.	5.	6.
Na	1 to 5	L 5.	L 5.	L 5.
Ni		L 5.		L 5.
Pb		L 1.		
Zn		40 to 80		
C	350 to 500	150.	5.	7.
O ₂	30.	20.	20.	20.
N ₂	20.	30.	6.	6.
H ₂	1.	5.	L 1.	L 5.

*L : "less than".

Determinations of the melting (or freezing) point were made in the apparatus shown in Figure 1. The metal in the crucible was heated inductively to a temperature about 50°C above its melting point, held molten to insure uniformity of temperature throughout the melt, and then allowed to cool slowly until the arrest in the cooling curve was reached, denoting the freezing point. The crucible was completely enclosed in thermal insulation material, now shown in the sketch. Temperature observations were made by sighting an optical pyrometer on the surface of the powdered refractory in the lower end of the sight tube. All runs were made in an atmosphere of helium which had been deoxidized by passing over heated copper turnings.

The first determination was made with an ingot of RU 557 metal in a beryllia crucible, duplicating the arrangements used in the earlier determinations. The arrest in the first cooling curve occurred at 1125°C. When the metal was remelted and a second cooling curve was run, the arrest occurred at a slightly higher temperature. This increase in the freezing point in successive cooling curves continued until the total time that the metal had been held in the molten state amounted to 15 hours and the freezing point had risen to 1131.5°C. This value was not changed by holding the metal molten for an additional 5 hours. The observed values for the freezing point are recorded in the first column of Table II.

Table II

Freezing Temperatures of Three Specimens of Tuballoy

Time held in the molten state hours	Sample RU 557 in BeO °C	Sample B 871 in ThO ₂ °C	Sample RU 557 in Graphite °C
0.	1125	1128	1128
.5	1127	1128.5	
1.	1128	1129	
2.	1129	1130	
5.	1130	1131.5	1129.5
7.			1131.
10.	1131	1133	
15.	1131.5	1133.5	1131.5
20.	1131.5	1133.5	

The next determination was made on B 871 metal in a thoria crucible, with thoria sight tube and granular thoria for thermal insulation. The results were similar to, but 2 or 3°C higher than those obtained in the first determination. The freezing temperature, 1128°C in the initial cooling curve, increased in successive determinations and finally leveled off at 1133.5°C, after the metal had been in the molten state for 15 hours (see Table II).

These results indicate that the freezing temperature of modern metal is higher than the values obtained in earlier determinations with less pure metal. The small differences in composition of the two metals, and the change from beryllia to thoria crucibles did not appreciably

affect the results. The gradual rise in the freezing temperature might be the result of either an increase in impurities which raised the freezing temperature or an elimination of impurities which had lowered the freezing temperature.

After the determinations were completed, both ingots were covered with a heavy crust, grayish in color, and of approximately uniform thickness on all surfaces of contact between the metal and the crucible or sight tube. This crust apparently was formed by reaction of the metal with BeO and ThO₂, and contained essentially the same impurities as the original metal, and in approximately the same proportions. In addition to the impurities originally present in the metal, the crust in contact with BeO contained about 50 parts per million of beryllium. On the other hand, thorium was not detected in the spectroscopic analysis of the crust on the ingot which had been melted in thoria. Whatever the reaction was, its effects were confined to the production of the crust on the outer surfaces of the ingots. The underlying metal had the same oxygen content, 20 to 40 ppm, as it had originally, and there were no microstructural features to indicate a pickup of oxygen, beryllium, or thorium.

Additional evidence that the gradual increase in the freezing temperature was not due to an increase in oxygen content, from reaction with BeO or ThO₂, was obtained by determining the freezing temperature of RU 557 metal in a graphite crucible equipped with a graphite sight tube, thereby eliminating contact of the molten metal with any oxide refractory. The results obtained were practically identical with those previously obtained with RU 557 metal in a BeO crucible. As recorded in Table II, the initial freezing temperature in the graphite crucible was 1128°C; the freezing temperature increased with successive observations and finally leveled off at 1131.5°C, after the metal had been held molten for about 15 hours. The uniformity of results from all three of the determinations indicate that the nature of the crucible did not affect the results, because the same impurities could not be picked up, in the same amounts and at the same rate, from BeO, ThO₂, and graphite.

Analyses of the ingots after the freezing temperature determinations showed practically no change for many of the impurities. The iron content of each ingot increased about 15 ppm as a result of the repeated melting and freezing. The small potassium content of both original metals was eliminated as were the small contents of zinc, lead, and lithium originally present in the B 871 metal. The nitrogen content of each metal also was reduced, but all of these changes were of the order of a few parts per million and would not be expected to have much of an effect on the freezing temperature. The outstanding change in composition was the reduction in carbon contents, as shown in Table I. The carbon content of B 871 metal, melted in thoria, was reduced from 150 to 7 ppm; carbon in RU 557 metal, 350 to 500 ppm, was reduced to 5 ppm when a beryllia crucible was used. Even when a graphite crucible was used, the melting and freezing procedure reduced the carbon appreciably, to 110 ppm. for a sample representing the full cross section of the ingot.

These unusually low carbon contents were confirmed qualitatively by the results of microscopic examination. The RU 557 metal melted in beryllia was practically free from carbide inclusions. The B 871 ingot, melted in thoria, was equally free from carbides except for the extreme top of the ingot and an occasional area on the side wall, where large

carbide crystals occurred in clusters. In the RU 557 ingot melted in graphite, there was a definite concentration of small carbide particles near the sides and top of the ingot, and the analytical sample included some of the carbide-rich skin. Most of this ingot, like the other two, was essentially free from carbides, indicating that the carbon content of much of the ingot was appreciably lower than the mean value for a full cross section. Both the microscopic appearance and the analytical data indicate that these specimens are lower in carbon content than any other specimens of tuballoy examined in this laboratory.

The reduction in carbon content in the freezing temperature determinations was unexpected in view of the repeated observation, in previous work on the solubility of oxygen in molten metal, that remelting under mildly or definitely oxidizing conditions did not appreciably affect the carbon content of tuballoy. However, in these earlier experiments the metal was heated rapidly and to higher temperatures and the resulting vigorous stirring kept the carbides dispersed throughout the metal. In the freezing point determinations the metal was held quietly molten, with little or no stirring, at temperatures only slightly above the melting point. Under these conditions the carbides were free to agglomerate and migrate to the top or to the solid skin of the side walls. For example the center of the B 871 ingot contained 7 ppm of carbon, a sample near the top of the ingot contained 16 ppm, and the crust attached to the top contained 1100 ppm of carbon.

These results indicate that the solubility of carbon in tuballoy, at temperatures near the melting point is low, probably not over 5 ppm, and that carbon contents of 300 to 500 ppm, normally found in tuballoy, are the result of heating the metal to temperatures appreciably above the melting point, in contact with carbon. Holding the metal quietly molten for extended periods of time, preferably in a beryllia or thoria container, should result in the production of metal with lower carbon contents than have been obtained previously, even in biscuit metal.

Summary

1. Holding the metal barely molten for several hours resulted in a decrease in the content of several impurities, either by volatilization or by migration to the top and side walls. The most pronounced change in composition during the freezing point determinations was the virtual elimination of carbide inclusions. ✓
2. While the metal was held molten the freezing temperature increased slowly to a final constant value, 5 or 6°C above the initial freezing temperature.
3. These results were not affected by the crucibles used, i.e., the same results were obtained in beryllia, thoria, and graphite crucibles. ✓
4. The best results for the freezing temperature of tuballoy were obtained at 150°C, for metal which contains about 5 ppm of carbon. At 150°C, 20 ppm of carbon, and higher amounts of other impurities, as measured in this work. ✓

Wensel

DISTRIBUTION LIST FOR REPORT NO. CT-2618 M

Copy 2 OF 7 Copies

Series A

NO. NAME

1. Eckhart Library
2. Argonne Library
3. New Chemistry Library
4. New Chemistry Library
5. Site B Library
6. Site B Library
7. A/E, Chicago
8. A. H. Compton
9. Norman Hilberry
10. H. E. Metcalf
11. H. E. Metcalf
12. R. S. Mulliken
13. J. C. Varner
14. T. R. Hogness
15. G. T. Seaborg
16. V. P. Jesse
17. J. C. Stearns
18. E. P. Wigner
19. Wigner Center
20. W. H. Zachariasen
21. J. J. Nickson
22. E. W. Brugmann
23. J. H. Chapin
24. F. G. Foote
25. A. B. Greninger
26. Clinton Lab.
27. Clinton Lab.
28. Clinton Lab.
29. Clinton Lab.
30. Clinton Lab.
31. Clinton Lab. (R. L. Doan)
32. Clinton Lab. (M. D. Whitaker)

NO. NAME

33. K. D. Nichols
34. H. T. Wensel
35. H. T. Wensel
36. H. T. Wensel
37. J. B. Conant
38. R. A. Lavender
39. du Pont-WIL
40. du Pont-HEW
41. du Pont-HEW
42. Norman Hilberry-HEW
43. Los Alamos
44. Los Alamos
45. Los Alamos
46. Los Alamos
47. Los Alamos
48. H. D. Smyth
49. F. H. Spedding
50. C. A. Thomas
51. E. D. Eastman
52. W. M. Latimer
53. J. C. Chipman
54. J. C. Chipman
55. H. E. Cleaves
56. Zay Jeffries
57. H. W. Russell
58. A/E, Mad. Sq. Area
59. Information Office File
60. Information Office File
61. Information Office File
62. Information Office File
63. Information Office File

REPORT NOT SENT TO;

A/E, WIL

This document contains information affecting the national defense of the United States within the meaning of the Espionage Act, U. S. C. 50-32 and 32. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

C7-2618

17

8

34

63

SERIES

ISSUED TO:

1. THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN MEANING OF THE ESPIONAGE ACT, U.S.C. 50; 32 AND 32. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.
2. BEFORE THIS DOCUMENT CAN BE READ BY A PERSON OTHER THAN THE ONE TO WHOM IT WAS ASSIGNED, HIS NAME MUST BE ON THE LIBRARY LIST OF THOSE AUTHORIZED TO READ MATERIAL ON THIS SUBJECT, OR PERMISSION MUST BE OBTAINED FROM THE ASSISTANT DIRECTOR OR THE DIRECTOR OF THE INFORMATION DEPARTMENT, OR THROUGH AN APPROPRIATE SECTION CHIEF OR HIGHER OFFICER WHO MUST BE CONVINCED THAT THE PERSON NEEDS TO READ THE DOCUMENT FOR THE SUCCESS OF HIS WORK.
3. THIS IS A CLASSIFIED DOCUMENT AND IS TO BE KEPT ONLY IN A GUARDED AREA. SECRET MATERIAL MUST BE KEPT IN A LOCKED SAFE OR A LOCKED FILING CASE WITH TUMBLER LOCK. CONFIDENTIAL MATERIAL MUST BE KEPT IN AT LEAST A LOCKED FILING CABINET.
4. A SECRET OR CONFIDENTIAL DOCUMENT IS NOT TO BE COPIED OR OTHERWISE DUPLICATED WITHOUT PERMISSION OF THE ORIGINATING OFFICE. EXTENSIVE NOTES ON THE CONTENTS OF A SECRET REPORT MAY BE TAKEN ONLY IN A BOUND NOTEBOOK WITH NUMBERED PAGES, HAVING THE DESIGNATION SECRET. THIS MUST BE SAFEGUARDED IN THE SAME WAY AS A SECRET REPORT. OTHER NOTES MUST BE AVOIDED, BUT IF MADE MUST BE DONE IN A FORM MEANINGLESS TO ANYONE BUT THE WRITER AND LATER DESTROYED.
5. THE PERSON OR OFFICE TO WHOM A SECRET OR CONFIDENTIAL DOCUMENT IS ISSUED IS ACCOUNTABLE FOR THE DOCUMENT AT ALL TIMES. A SYSTEM OF ACCOUNTABILITY BY SIGNED RECEIPTS OR A SIGNED RECORD BOOK MUST ALWAYS BE USED. PERMISSION FOR TRANSMISSION TO ANOTHER OFFICE OTHER THAN THAT OF THE ASSIGNEE MUST BE OBTAINED THROUGH THE INFORMATION OFFICE AND RECORDED THERE.
6. AS SOON AS THE DOCUMENT IS NO LONGER NEEDED, IT IS TO BE RETURNED TO THE INFORMATION OFFICE WHEREUPON THE INDIVIDUAL WILL BE RELIEVED OF THE RESPONSIBILITY FOR ITS SAFEKEEPING.
7. THE FORM BELOW IS USED IN ROUTING THIS REPORT AND MUST BE SIGNED BY EACH PERSON WHO READS IT.

[illegible]

UNCLASSIFIED

CT-2618
M-F&NBS

Contract W-7412-eng-24
and
N. B. S.

CLASSIFICATION CANCELLED
DATE FEB 19 1957 *OK*
For The Atomic Energy Commission
H. F. Canale
Chief, Declassification Branch

PROGRESS REPORT FOR DECEMBER 1944

by

A. G. Gray and J. G. Thompson

This document is
PUBLICLY RELEASABLE
Exempt *N. Kinser*
Authorizing Official
Date *9/5/02*

~~CONFIDENTIAL~~
This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

AEC RESEARCH AND DEVELOPMENT REPORT

Report received: February 2, 1945; Figures received: January 24, 1945
Issued: FEB 6 1945

This document is
PUBLICLY RELEASABLE
Hugh Kinser *H. Kinser*
Authorizing Official
Date *4/3/00*

~~CONFIDENTIAL~~
This document contains information affecting the national defense of the United States within the meaning of the Espionage Act, U.S.C. 5043 and 32. Its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

UNCLASSIFIED

SUMMARY:

ELECTROPLATING SECTION

The Manual of Commercial Operating Instructions for plating on tuballoy has been completed and is at the distribution center for circulation. A commercial type trichloroacetic acid pretreatment bath in operation for two months has shown consistently satisfactory results. The use of higher anodizing current densities for shorter periods of pretreatment has been shown to produce a uniform etch comparable with that obtained at lower current densities. Corrosion tests have been continued on various electroplates and combinations of electroplates for use as protective coatings in the Neutronic Reactor Loading Cartridge. Special heat treatment of relatively thin layer electroplates in silicone fluid at 300°C to form fused alloys has been found to improve corrosion resistance of coatings remarkably. Tests results have indicated that copper-tin, nickel-tin, nickel-copper-tin or nickel-zinc fused coatings within limits of thickness requirements will provide adequate protection during the cooling off period from the standpoint of protection of base metal and retaining of fission products within the slug. Recent work has been concentrated on the determination of minimum effective thicknesses of the fused electroplates for adequate corrosion protection. Copper-tin fused coatings of less than 0.001" thickness have shown good protection at ~~300°C~~ for three months, and studies of adequate minimum thicknesses are now in progress.

dist. in low T. only

Fundamental Study of Pretreatment of Tuballoy Prior to Plating

The Publications Office in Chicago in cooperation with Cleveland has edited, printed, and approved the Manual of Commercial Operating Instructions for plating on Tuballoy. The Manual is now at the distribution center awaiting circulation. Continued operation of the commercial type trichloroacetic acid pretreatment bath has shown that uniform removal of outer layers of tuballoy is possible under various anode current densities. By reducing the time of pretreatment, higher anode current densities may be used with same results obtained at lower current densities. After two months operation, the pretreatment bath is still giving consistently satisfactory results.

Evaluation of Coatings for Neutronic Reactor Cartridge

The development and evaluation of electroplated coatings for use in the Neutronic Reactor Loading Cartridge has been continued. Water corrosion tests on various electroplates and combinations of electroplates have revealed the superiority of relatively thin fused alloy coatings produced by heat treating layer electroplates such as copper and tin in a silicone fluid at 300°C for periods up to 3 hours. Of fundamental importance is the determination of the minimum effective thicknesses of these coatings necessary to provide adequate protection for the base metal tuballoy. Various thicknesses of several of the coatings have been prepared and are now in test. The various coatings being tested and the test results to date are recorded in Table I.

12

B

CT-2618

TABLE I

Water Corrosion Test Results

<u>No. of Specimens</u>	<u>Description of Coating</u>	<u>Test Water Temp.</u>	<u>Days in Test</u>	<u>No.</u>	<u>Failures</u>	<u>Days to Fail</u>
4	0.001" Cu-0.0001" Sn Treated in Silicone #700 3 Hrs; 300°C.	35°C	87		None	
6	0.0007" Cu-0.0001" Sn Treated in Silicone #700 3 Hrs; 300°C.	35°C	87	1		80
3	0.0007" Cu-0.0001" Sn Treated in Silicone #700 1-1/2 Hrs; 300°C.	35°C	87		None	
10	0.0001" Ni-0.003" Zn (Cyanide)	35°C	89	3 1 3 3		36 57 72 89
12	0.0001" Ni-0.0003" Zn (Acid)	35°C	78	2 7 1 2		37 59 64 78
6	0.0005" Ni-0.0001" Zn	50°C	75		All coatings pit corroded but giving pro- tection	
12	0.0005" Ni-0.0003" Zn Treated in Silicone #700 3 Hrs; 300°C.	35°C	67		None	
18	0.0003" Ni-0.0002" Cu- 0.00005" Sn treated in Silicone #700 2 Hrs; 300°C.	35°C	51		None (Some pit corrosion noted)	
11	0.0003" Ni-0.0005" Cu- 0.0001" Sn Treated in Silicone #700 3 Hrs; 300°C	35°C	37		None	
18	0.005" Cu-0.0001" Sn Treated in Silicone #700 2 Hrs; 300°C.	35°C	23		None	
12	0.0005" Ni-0.0002" Sn Treated in Silicone #700 2 Hrs; 300°C.	35°C	23		None	

Water Corrosion Test Results

<u>No. of Specimens</u>	<u>Description of Coating</u>	<u>Test Water Temp</u>	<u>Days in Test</u>	<u>No. Failures</u>	<u>Days to Fail</u>
12	0.0003" Ni-0.0001" Sn Treated in Silicone #700 2 Hrs; 300°C	35°C	18	none	
12	0.0007" Ni-0.0002" Sn Treated in Silicons #700 2 Hrs; 300°C	35°C	9	none	

The copper-tin heat treated coatings continue to evidence good protection after 87 days in test at 35°C. The one failure noted in these tests as contrasted with the 100% failure of 22 flash nickel-0.003" zinc plated slugs over approximately the same test period shows the superiority of these thin fused alloy coatings over a thicker straight electroplate. The nickel-zinc fused coatings (corroding process) still appear to be preventing corrosion of the base metal, but excessive corroding of the coating itself appears to be a disadvantage. Much less corrosion was noted in the specimens containing smaller percentages of zinc and a recommended ratio in thickness of nickel to zinc is 0.0005" Ni to 0.0001" Zn. Other coatings which are providing good protection but have been in test for shorter periods of time are the nickel-copper-tin and nickel-tin fused coatings. The tests on determination of minimum effective thickness have indicated that a minimum thickness for the copper-tin fused coating is 0.0007" Cu and 0.0001" Sn. Thinner coatings are evidencing a larger percentage of earlier failures.

On the basis of test results thus far, the copper-tin fused alloy coatings should provide adequate protection for tuballoy during the cooling off period. The nickel-zinc, nickel-tin, and nickel-copper-tin fused coatings although in test for shorter periods of time have evidenced good protection and work for the coming month will be concentrated on the continuation of these corrosion tests at 35°C in circulating water (composition supplied by Chicago). Work will also be started on the preparation of the Final Report covering all work done since beginning of contract. Specimens will be plated and treated according to recommended procedures to comply with requests to be received from Chicago for test coatings.

Molybdenum-Nickel Alloy Plating

The evaluation of the nickel-molybdenum pyrophosphate type bath for plating of nickel-molybdenum alloys was continued. A brief study of the cathode efficiency and composition of alloy deposit revealed that an alloy containing 50% molybdenum, 40% nickel, and 10% oxygen was deposited with an efficiency of approximately 10-15%. Further work on the deposition of the alloy on tuballoy was not started due to concentration of work on evaluation of coatings for use in the Neutronic Reactor Cartridge.

A.G.G.

DECLASSIFIED

~~SECRET~~

W. B. S.

REPORT FOR DECEMBER

on

METALLURGY OF TUBALLOY

J. G. Thompson, Supervisor

CONTENTS

	<u>Page</u>
Solubility of Oxygen in Liquid and Solid Tuballoy H. E. Cleaves, M. M. Cron, J. T. Sterling	5
Melting Point of Tuballoy H. E. Cleaves and A. I. Dahl	12

~~SECRET~~

RECEIVED

48

FIG. 1.-FURNACE FOR PREPARATION OF TUBALLOY INGOTS

DECLASSIFIED

Solubility of Oxygen in Liquid and Solid Tuballoy

The procedure followed in determining the solubility of oxygen in liquid and solid tuballoy included saturation of molten tuballoy with oxygen, chill casting the saturated metal to retain the oxygen dissolved in the liquid metal, analysis of the resulting ingots to determine the amount of oxygen dissolved in the tuballoy at the elevated temperatures and micro-examination of specimens of the ingots in the chill-cast and heat-treated condition to determine whether or not oxygen remained in solution in the solid metal.

Preparation of Tuballoy-Oxygen Ingots

Saturation of liquid metal with oxygen was effected by melting a charge of tuballoy in a beryllia crucible lined with tuballoy-dioxide and maintaining at a definite temperature for a period of time, usually 30 minutes. A split steel mold was then raised from the furnace bottom to pouring position, the power was cut off and the stopper rod lifted from the opening in the crucible bottom, permitting the molten metal to flow into the mold. The furnace used in preparing the ingots is shown in Figure 1.

The temperature of the molten metal was determined by sighting into a black-body sight tube immersed in the melt. The portion of the sight tube in the crucible was closed end beryllia tube which was filled with beryllia powder up to the center of the melt. The outside of the beryllia tube was coated with oxide by alternately dipping into concentrated tuballoy nitrate solution and heating to decompose the nitrate. The upper portion of the sight tube was a porcelain tube cemented to the beryllia tube by means of a beryllia sleeve and cement consisting of beryllia moistened with beryllium chloride solution. The sight tube assembly was fired at about 1400°C to set the cement. The beryllia tube served both as a sight tube and as a stopper to close the hole in the crucible bottom. The accuracy of the temperature measurements was checked in preliminary melts by means of a thermocouple inserted in the sight tube and removed intermittently to permit observation with the optical pyrometer.

The beryllia crucible was lined by tamping tuballoy dioxide, moistened with a dilute solution of tuballoy chloride, around a mandrel suspended in the crucible. After removal of the mandrel the crucible and lining were dried at 200°C and then fired in an Arsen furnace at about 1700°C. The dioxide formed a fairly hard lining which served for several melts before relining was necessary. The higher oxide (X308) was also tried as a crucible lining, because of the possibility that this oxide might supply oxygen to the melt more readily. This lining was so soft and fragile that it was crushed by the weight of the charge, the resulting oxide particles being carried down into the mold when the melt was cast. Lining the bottom of the crucible with the dioxide, to support the charge, and the crucible wall with the higher oxide eliminated this difficulty. However, the oxygen content of metal held in contact with the higher oxide was similar to that of metal cast at the same temperature from crucibles lined entirely with the dioxide indicating that saturation was obtained as readily with the dioxide as with the higher oxide and that use of the higher oxide as lining was not advantageous. In preliminary tests the same oxygen content resulted from maintaining the melts at 1400°C for 15, 30 and 60 minutes, indicating that saturation was effected by contact with the oxide for 15 minutes. However, as a precaution most of the melts were held at a definite temperature for longer periods than 15 minutes.

DECLASSIFIED

The temperature of the split steel mold just before casting was about 50°C. The slight increase above room temperature resulted from inductive heating although the top of the mold was about 6 inches below the furnace coil until just before the casting was made. This mold formed a wedge-shaped ingot, one inch wide, $\frac{1}{4}$ inch thick at the bottom, about $\frac{5}{8}$ inch thick at the top and up to 4 inches in length. The mold surface was protected by smoking over burning light oil. Brushing the mold with cotton, followed by swabbing with ether removed the non-adherent soot and condensed oil. The mold surface so protected did not react with metal cast at temperatures up to 1635°C but was attacked by metal cast at temperatures above 1700°C. Contamination by iron in ingots cast at temperatures above 1700°C interfered with metallographic identification of oxide inclusions but did not appear to appreciably affect the oxygen solubility, such ingots having about the same oxygen content as metal solidified in the melting crucible from the same temperature.

The furnace atmosphere used in preparing most of the ingots was helium purified by passing through activated charcoal at liquid air temperature. The use of tank helium caused an increase in the nitrogen content of the metal.

Modifications in the melting procedure were made in attempts to increase the oxygen content of the metal. Addition to the charge of finely ground oxide, which had not been ignited and therefore might be expected to be more reactive than the crucible lining, did not result in increase in the oxygen content of the metal. The use of an atmosphere of mixed helium and oxygen also failed to increase the oxygen content of the metal over that resulting from use of a purified helium atmosphere. The effect of more drastic oxidation was investigated by impinging oxygen gas upon the surface of the melt through a porcelain tube projecting into the crucible. The maximum quantity of oxygen used was sufficient, theoretically, to oxidize about 30 percent of the metal charged but the weight of metal oxidized was about half that amount. Part of the oxygen was consumed in oxidizing XO_2 to X_3O_8 and some oxygen probably escaped with the helium, because the layer of oxide on the melt hindered oxidation of the metal.

The temperature observed at the center of the melt while oxygen was being added was about 300°C above that observed with application of the same furnace power without the addition of oxygen, a result of the heat liberated by the oxidation. The presence of columnar crystals in the crust of oxide on the surface of the furnace-cooled ingot indicated that the temperature at the surface of the ingot had been, at least temporarily, above the melting point of the oxide, stated by Ruff and Goetze (Zeit. angew. Chem. Vol. 24, 1911, p. 1489) to be 2196°C, although the observed temperature in the center of the melt was only 1720°C.

Despite the ample opportunity for oxygen absorption the oxygen content of ingots prepared with addition of oxygen gas was not materially different from the oxygen content of ingots held in contact with tuballoy oxide at the same temperatures in helium, additional evidence that the latter procedure effected saturation with oxygen.

The carbon content of most of the tuballoy available for melting stock was of the order of 0.05 percent. Under the microscope the carbon appeared as inclusions scattered profusely throughout the metal, interfering with the metallographic identification of oxide inclusions. It was thought that gradual elimination of carbon might accompany the saturation of the molten metal with oxygen, but holding tuballoy molten in vacuum in an oxide lined crucible at 1600°C for one hour did not produce a substantial change in the carbon content. Furthermore, survival of the ingots

6a

CT-2618

A

B

Figure 3. - Oxide inclusions in chill cast tuballoy with 0.008 and 0.011 percent oxygen. Electrolytically polished. x 500.

A - 0.008 percent oxygen. Several minute oxide inclusions, in addition to carbide inclusions, are observed in ingot 12.

B - 0.011 percent oxygen. Oxide inclusions are more prevalent in ingot No. 15.

DECLASSIFIED

6b

A

B

Figure 4. - Oxide inclusions in chill cast ingot with 0.014 percent oxygen and furnace-cooled ingot with 0.021 percent oxygen. Electrolytically polished. x 500.

- A - 0.014 percent oxygen. Oxide is present as fine inclusions in ingot No. 17. Tendency to alinement is apparent.
- B - 0.021 percent oxygen. Line of oxide inclusions appears between carbide inclusions in ingot No. 20, cooled in crucible.

DECLASSIFIED

Figure 5. - Section through top of ingot No. 20 showing oxide layer extending into metal and entrapped globular oxide inclusions. Electrolytically polished. x 100.

Figure 7. - Grain boundaries in ingot No. 22, revealed by etching electrolytically in oxalic acid solution, do not coincide with lines of inclusions. x 100.

DECLASSIFIED

A

B

C

Figure 6. - Oxide inclusions in tuballoy annealed four hours at 900°C.
Electrolytically polished. x 500.

- A - 0.003 percent oxygen. A few scattered inclusions appear in ingot No. 1.
- B - 0.008 percent oxygen. Selected area in ingot No. 12 where inclusions are aligned.
- C - 0.011 percent oxygen. Oxide inclusions in ingot No. 15 are coarsened by annealing.

prepared from metal melted in helium or in helium plus oxygen showed that the variation in carbon content between the metal charged and the resulting ingot generally was within experimental error of the analytical procedure. Apparently selective oxidation of carbon, by reaction with oxygen or tuballoy oxide, is not a practical way of reducing the carbon content of molten tuballoy. Small amounts of low carbon metal, with 0.015 and 0.005 percent carbon respectively, became available for melting stock for one or two runs near the close of the investigation. While decrease in carbide inclusions was noticeable, particularly in the metal with 0.005 percent carbon, the quantity of inclusions present was still sufficient to interfere with identification of the oxide. The presence of carbon did not appear to affect the solubility of oxygen in the liquid tuballoy, the values for solubility in low and high carbon metal being similar.

Twenty two ingots, with oxygen contents from 0.003 to 0.033 percent, were prepared either by casting or by solidification in the crucible. The results obtained on a number of other runs were rejected for various reasons, principally because failure of refractories made contamination probable or prevented satisfactory determination of temperature. Results on all ingots prepared at temperatures above 2000°C were rejected for such reasons.

Solubility of Oxygen in Liquid Tuballoy

The values for oxygen obtained by vacuum fusion analyses of the 22 ingots are shown in Table I and graphically in Figure 2. It will be seen that there is considerable scattering of values particularly in ingots prepared at the higher temperatures. This scattering may result from such factors as segregation of oxide or from contamination by particles of crucible linings. Segregation was a characteristic of the furnace-cooled ingots 11, 13, 20 and 22, the oxygen content of the sample from the top invariably being higher than that of the bottom section.

FIG. 8.- SOLUBILITY OF OXYGEN IN TUBALLOY

DECLASSIFIED

Table I

Oxygen Content of Tuballoy Ingots

Ingot No.	Saturation Time Minutes	Final Temperature of Saturation Period, °C	Weight Percent of Oxygen		Remarks
			Top	Bottom	
1	30	1205	0.004	0.003	Cast
2	60	1400	.006	.005	Cast
3	30	1405	.003	.003	Cast
4	30	1405	.004	.003	Oxide added to charge. Cast
5	30	1415	.005	.004	Oxide added to charge. Cast
6	30	1500	.008	.008	Oxide added to charge. Cast
7	30	1545	.009	.006	Cast
8	15	1550	.010	.008	Cast
9	60	1590	.006	.008	Oxygen-helium atmosphere, cast
10	60	1600	.009*		Cooled in furnace
11	60	1600	.020	.012	Vacuum melt, cooled in furnace
12	30	1615	.008	.010	Cast
13	30	1615	.019	.005	Vacuum melt, cooled in furnace
14	30	1630	.010	.010	Cast
15	60	1635	.011	.010	Oxygen injected, cast
16	30	1635	.011	.011	Cast
17	30	1715	.014	.015	Cast
18	15	1720	.019	.019	Oxygen injected, cast
19	60	1810	.016	.013	Cast
20	15	1900	.027	.021	Oxygen injected, cooled in furnace
21	15	1900	.033*		Oxygen injected, cooled in furnace
22	30	2000	.030	.023	Cooled in furnace

*These values were obtained on the center sections of short furnace cooled ingots.

Values for the solubility at 100°C intervals, from the curve drawn through points representing mean solubility values, and the solubility at the melting point from the extrapolated curve are given in Table II. The solubility increases from 0.0031 weight percent (0.046 atomic percent) at the melting point (1131°C) to 0.029 weight percent (0.432 atomic percent) at 2000°C.

Table II

Selected Values for the Solubility of Oxygen in Liquid Tuballoy

Temperature °C	Percent Oxygen	Atomic Percent
1131 (m.p.)	0.0031	0.046
1200	.0035	.052
1300	.0042	.063
1400	.0053	.079
1500	.0072	.107
1600	.0105	.156
1700	.0140	.208
1800	.0188	.280
1900	.0235	.350
2000	.029	.432

Ingots with still higher oxygen contents were prepared by holding the metal at temperatures above 2000°C but refractory failures prevented satisfactory temperature measurements. Also metallographic examination of such ingots disclosed the presence of globular inclusions of oxide which appeared to be the result of entrapment of molten oxide in the metal. Hence the oxygen values by vacuum fusion may have included mechanically entrapped inclusions as well as oxygen in solution in the liquid metal.

Solubility of Oxygen in Solid Tuballoy

The solubility in the solid metal was investigated by metallographic examination of specimens from the ingots. These specimens, either as cut from the ingots or after heat treatment, were mounted in bakelite, polished mechanically, finishing on 000 emery paper, then polished electrolytically in an electrolyte composed of equal parts of 85 percent orthophosphoric acid and glycerine, using an applied potential of 6 volts. The current varied with the area of the specimen but usually was about 0.1 ampere. Specimens were swabbed intermittently during polishing. With this procedure inclusions were retained and pitting was negligible.

Inclusions other than carbides, were not observed in chill cast metal with oxygen contents less than 0.008 percent. Occasional minute inclusions were present in chill cast metal with about 0.008 percent oxygen, illustrated in Figure 3A. In metal with slightly higher oxygen content such as ingot 15 with 0.011 percent oxygen (Figure 3B) the inclusions were coarser and more prevalent. In some areas these inclusions were definitely aligned, as is seen near the left edge of Figure 3B, in other areas they appear scattered at random.

The inclusions in ingot 17 (Figure 4A) with 0.014 percent oxygen were finer than in ingot 15 (Figure 3B) but were more prevalent. The tendency of the inclusions to form lines is apparent in Figure 4A. With increase in oxygen content the lines became heavier with occasional eutectiferous areas. Figure 4B, showing a line of oxide inclusions between carbide dendrites, is typical of metal with oxygen content greater than

0.020 percent.

Large globular inclusions were present near the top of ingots which had been held molten under an atmosphere of oxygen and then cooled in the crucible. These inclusions appeared to be the result of the entrapment of molten oxide in the melt. The top edge of the ingot shown in Figure 5 shows penetration of the melt by the oxide crust. These oxide globules were observed only in metal near the top of the furnace cooled ingots, usually within 0.1 inch of the top surface.

The absence of visible oxide particles in chill cast metal of 0.008 percent oxygen and less indicates either that oxygen is soluble to that extent or that the precipitated oxide particles are of sub-microscopic dimensions. If the latter condition obtains, annealing the metal at a suitable temperature for sufficient period should result in agglomeration of the sub-microscopic particles.

Sections from several of the ingots were annealed in vacuum for four hours at 625°, 725°, and 925°C, then cooled in the furnace, the time required to cool to room temperature being about 2 hours. Annealing at 625° and 725°C did not cause any perceptible alteration in the quantity or appearance of the inclusions, probably because diffusion at these temperatures is so slow that no detectable agglomeration of inclusions results in four hours. Annealing at 925°C for four hours was effective in causing the appearance of inclusions in the ingots with higher oxygen contents. In metal with 0.003 percent oxygen the inclusions produced were minute at 500 diameters (Figure 6A) and were seen more clearly by visual examination under the microscope than in the photomicrograph, presumably because of the superior resolving power of the eye as compared with the photographic emulsion.

With increasing oxygen content the inclusions produced by annealing at 925°C were more readily discerned. The inclusions resulting from annealing a specimen of ingot 12 (0.008 percent oxygen) at 925°C appeared to outline grain boundaries (Figure 6B). The appearance of the same metal in the chill cast condition was shown in Figure 3A. The effect of annealing in the gamma temperature range on inclusions previously visible was to coarsen them as is shown by comparison of photomicrographs of ingot 15 in the chill cast (Figure 3B) and annealed conditions (Figure 6C).

Metallographic examination of specimens of the ingots etched electrolytically in oxalic acid showed that the lines of inclusions which appeared to outline, in part, grain boundaries did not coincide with the alpha grain boundaries. The appearance of a specimen of ingot 20 annealed at 925°C and etched is shown in Figure 7. The alpha grains in the annealed metal are gross in contrast to the smaller grains outlined by the inclusions. The fact that agglomeration of oxide inclusions resulted from annealing in the gamma range but not from annealing in the beta range would seem to indicate that the grains outlined by the inclusions are those of the gamma phase.

Summarizing these results for the solubility in the solid metal, the oxides in chill cast metal with less than about 0.01 percent oxygen probably are present in the form of submicroscopic inclusions. Annealing in the gamma range for four hours or longer results in diffusion and agglomeration of the oxide to form inclusions visible at 500 diameters.

DECLASSIFIED

magnification. When the concentration of oxygen in the tuballoy is more than about 0.01 percent sufficient agglomeration occurs during solidification and in cooling to room temperature to produce visible inclusions. Subsequent annealing in the gamma range results in the coarsening of these inclusions.

The appearance of inclusions as a result of annealing tuballoy with as little as 0.003 percent oxygen in the gamma range indicates that the solubility of oxide in solid tuballoy is less than 0.003 percent.

Determination of the variation with temperature of oxygen solubility in the solid metal was not feasible because of the limits of precision of the analytical methods.

Summary

Graphic presentation of the data obtained in this investigation is shown in Figure 8. The solubility of oxygen in the liquid phase increases with rising temperature from 0.0031 at the melting point to 0.029 percent at 2000°C. The preparation of metal with oxygen contents apparently greater than 0.029 percent, by holding the molten metal in contact with oxide at unknown temperatures above the melting point of the oxide, indicates that increase in the solubility continues with increasing temperature above 2000°C.

From the solubility relations observed in other metals it would be expected that the solubility of oxygen in solid tuballoy would be less than in the liquid metal, and that the solid solubility would vary with temperature, particularly at the two transformation temperatures. The appearance of oxide inclusions in specimens with an oxygen content of only 0.003 percent, after annealing at 925°C, confirms the conclusion that the solubility of oxygen in solid gamma metal is less than in the liquid metal but the actual solubility in the solid phases at various temperatures has not been determined. Variations in an oxygen content of less than 0.003 percent are not determinable by available analytical procedures and microscopic methods are inapplicable because of the difficulty of identifying minute oxide inclusions in the presence of far greater quantities of the other inclusions, especially carbides, that exist in all available specimens of tuballoy. For these reasons the solubility of oxygen in solid tuballoy is shown as a dotted line, to indicate that the solid solubility at all temperatures is less than the value, 0.0031 percent, for the solubility of oxygen in liquid metal at the melting point.

For similar reasons the effect of dissolved oxygen on the melting point and transformation temperatures cannot be depicted but it would be expected that the effect of oxygen in concentrations less than 0.003 percent would be less than the precision of the methods used in determining these temperatures.

FIGURE 1. APPARATUS FOR DETERMINING MELTING POINTS

DECLASSIFIED

When metallurgical studies of uranium were initiated at the National Bureau of Standards in 1941, one of the first problems to be investigated was the melting of the metal. Available information was limited and indefinite. Mellor⁽¹⁾ cited values of 1300 to 1400°C, 1600°, and 1850°C for the

-
(1) J. W. Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, 12, 15 (1932).
.....

melting point of uranium, according to different investigators. A value of about, or less than, 1850°C, sometimes ascribed to Moissan, was given in several references and handbooks⁽²⁾. The value of 1690°C reported by Driggs and Lillienahl⁽³⁾ is quoted in Metals Handbook⁽⁴⁾. Computations based on

-
(2) Kent's Mechanical Engineer's Handbook 596 (1923)
Van Nostrand's Chemical Annual 294 (1926)
International Critical Tables 1, 105 (1926)
Smithsonian Physical Tables 198 (1927)
General Engineering Handbook (O'Rourke) 126 (1940)
Handbook of Chemistry and Physics 1712 (1943)
Machinery's Handbook 1579 (1943)
.....

- (3) F. H. Driggs and W. C. Lilliendahl, Ind. Eng. Chem., 22, 516 (1930).

- (4) Metals Handbook 80 (1939)

.....
the position of uranium in the periodic table of the elements indicated a melting point of about 3600°C⁽⁵⁾.
.....

- (5) Miscellaneous Publications of the National Bureau of Standards, M126 (1937).
.....

A small button of tuballoy, prepared by C. J. Rodden in June 1941, was observed to be molten in a beryllia crucible at temperatures estimated visually to be less than 1300°C. When larger masses of metal from other sources became available, two ingots were prepared, each one about 360 grams in weight, one from selected pieces of an ingot received from Metal Hydrides, Inc. and the other from a portion of a cup-shaped cake which was reported to be metal of electrolytic origin produced by Westinghouse. The selected pieces of each metal were melted in beryllia crucibles in vacuum to form ingots of the desired shape for the determination of the freezing points. The results of these determinations as reported by W. F. Roeser in Report A-215, indicated freezing points of 1075°C for the Metal Hydrides metal and 1100°C for the Westinghouse sample. The evolution of fumes and the distillation of impurities from the metal during some of the determinations created uncertainty as to the exact numerical values, but there was no question that the freezing point was about 1100°C and not the higher values indicated in the literature. These determinations and others made elsewhere furnished a basis for the value 1100 ± 25°C given in the Project Handbook issued in 1943. Subsequent observations, made in connection with

the production of high-purity metal in quantity, indicated that the best values probably were above the middle of this range. It would be expected that the progressive improvement in quality of the metal with improvements in production technique would be accompanied by a gradual change in the observed melting points. It appeared to be desirable, therefore, to correct the earlier determinations made at this Bureau by means of redeterminations of the melting point or freezing point of modern high-purity metal.

Material from two sources was available for the new determinations, extruded rod RU 557 and biscuit metal B 871. Analytical data for the two metals, from determinations by chemical, spectrochemical, and vacuum fusion methods, indicated that the principal difference between the two metals was in the carbon and zinc contents, as is shown in the first two columns of Table I. Ingots of the desired shape for the melting point determination were prepared by forging. A hole for the sight tube was drilled longitudinally through each ingot, using carbide tipped drills.

Table I

Analyses of Ingots before and after the
Freezing Temperature Determinations

RU	Original material		After Freezing Temperature Determinations	
	557	B 871	Ru 557 in BeO	B 871 in ThO ₂
	ppm	ppm	ppm	ppm
Ag	L* 0.2	L* 0.2	L* 0.2	L* 0.2
Al	L 10.	L 10.	L 10.	L 10.
B	L 2.	L .2	.3	.2
Ca	L 5.			
Cd		L 3.		
Cu	1 to 5	L 1.	5 to 10	L 5.
Fe	50	45.	64	58.
K	L 5.	L 5.		
Li		L .3		
Mg	L 5.	5 to 10	L 5.	L 5.
Mn	5.	L 5.	5.	6.
Na	1 to 5	L 5.	L 5.	L 5.
Ni		L 5.		L 5.
Pb		L 1.		
Zn		40 to 80		
C	350 to 500	150.	5.	7.
O ₂	30.	20.	20.	20.
N ₂	20.	30.	6.	6.
H ₂	1.	5.	L 1.	L 5.

*L "less than".

RECEIVED

Determinations of the melting (or freezing) point were made in the apparatus shown in Figure 1. The metal in the crucible was heated inductively to a temperature about 50°C above its melting point, held molten to insure uniformity of temperature throughout the melt, and then allowed to cool slowly until the arrest in the cooling curve was reached, denoting the freezing point. The crucible was completely enclosed in thermal insulation material, now shown in the sketch. Temperature observations were made by sighting an optical pyrometer on the surface of the powdered refractory in the lower end of the sight tube. All runs were made in an atmosphere of helium which had been deoxidized by passing over heated copper turnings.

The first determination was made with an ingot of RU 557 metal in a beryllia crucible, duplicating the arrangements used in the earlier determinations. The arrest in the first cooling curve occurred at 1125°C. When the metal was remelted and a second cooling curve was run, the arrest occurred at a slightly higher temperature. This increase in the freezing point in successive cooling curves continued until the total time that the metal had been held in the molten state amounted to 15 hours and the freezing point had risen to 1131.5°C. This value was not changed by holding the metal molten for an additional 5 hours. The observed values for the freezing point are recorded in the first column of Table II.

Table II

Freezing Temperatures of Three Specimens of Tuballoy

Time held in the molten state hours	Sample RU 557 in BeO °C	Sample B 871 in ThO ₂ °C	Sample RU 557 in Graphite °C
0.	1125	1128	1128
.5	1127	1128.5	
1.	1128	1129	
2.	1129	1130	
5.	1130	1131.5	1129.5
7.			1131.
10.	1131	1133	
15.	1131.5	1133.5	1131.5
20.	1131.5	1133.5	

The next determination was made on B 871 metal in a thoria crucible, with thoria sight tube and granular thoria for thermal insulation. The results were similar to, but 2 or 3°C higher than those obtained in the first determination. The freezing temperature, 1128°C in the initial cooling curve, increased in successive determinations and finally leveled off at 1133.5°, after the metal had been in the molten state for 15 hours (see Table II).

These results indicate that the freezing temperature of modern metal is higher than the values obtained in earlier determinations with less pure metal. The small differences in composition of the two metals, and the change from beryllia to thoria crucibles did not appreciably

affect the results. The gradual rise in the freezing temperature might be the result of either an increase in impurities which raised the freezing temperature or an elimination of impurities which had lowered the freezing temperature.

After the determinations were completed, both ingots were covered with a heavy crust, grayish in color, and of approximately uniform thickness on all surfaces of contact between the metal and the crucible or sight tube. This crust apparently was formed by reaction of the metal with BeO and ThO₂, and contained essentially the same impurities as the original metal, and in approximately the same proportions. In addition to the impurities originally present in the metal, the crust in contact with BeO contained about 50 parts per million of beryllium. On the other hand, thorium was not detected in the spectroscopic analysis of the crust on the ingot which had been melted in thoria. Whatever the reaction was, its effects were confined to the production of the crust on the outer surfaces of the ingots. The underlying metal had the same oxygen content, 20 to 40 ppm, as it had originally, and there were no microstructural features to indicate a pickup of oxygen, beryllium, or thorium.

Additional evidence that the gradual increase in the freezing temperature was not due to an increase in oxygen content, from reaction with BeO or ThO₂, was obtained by determining the freezing temperature of RU 557 metal in a graphite crucible equipped with a graphite sight tube, thereby eliminating contact of the molten metal with any oxide refractory. The results obtained were practically identical with those previously obtained with RU 557 metal in a BeO crucible. As recorded in Table II, the initial freezing temperature in the graphite crucible was 1128°C; the freezing temperature increased with successive observations and finally leveled off at 1131.5°C, after the metal had been held molten for about 15 hours. The uniformity of results from all three of the determinations indicate that the nature of the crucible did not affect the results, because the same impurities could not be picked up, in the same amounts and at the same rate, from BeO, ThO₂, and graphite.

Analyses of the ingots after the freezing temperature determinations showed practically no change for many of the impurities. The iron content of each ingot increased about 15 ppm as a result of the repeated melting and freezing. The small potassium content of both original metals was eliminated as were the small contents of zinc, lead, and lithium originally present in the B 871 metal. The nitrogen content of each metal also was reduced, but all of these changes were of the order of a few parts per million and would not be expected to have much of an effect on the freezing temperature. The outstanding change in composition was the reduction in carbon contents, as shown in Table I. The carbon content of B 871 metal, melted in thoria, was reduced from 150 to 7 ppm; carbon in RU 557 metal, 350 to 500 ppm, was reduced to 5 ppm when a beryllia crucible was used. Even when a graphite crucible was used, the melting and freezing procedure reduced the carbon appreciably, to 110 ppm. for a sample representing the full cross section of the ingot.

These unusually low carbon contents were confirmed qualitatively by the results of microscopic examination. The RU 557 metal melted in beryllia was practically free from carbide inclusions. The B 871 ingot, melted in thoria, was equally free from carbides except for the extreme top of the ingot and an occasional area on the side wall, where large

carbide crystals occurred in clusters. In the RU 557 ingot melted in graphite, there was a definite concentration of small carbide particles near the sides and top of the ingot, and the analytical sample included some of the carbide-rich skin. Most of this ingot, like the other two, was essentially free from carbides, indicating that the carbon content of much of the ingot was appreciably lower than the mean value for a full cross section. Both the microscopic appearance and the analytical data indicate that these specimens are lower in carbon content than any other specimens of tuballoy examined in this laboratory.

The reduction in carbon content in the freezing temperature determinations was unexpected in view of the repeated observation, in previous work on the solubility of oxygen in molten metal, that remelting under mildly or definitely oxidizing conditions did not appreciably affect the carbon content of tuballoy. However, in these earlier experiments the metal was heated rapidly and to higher temperatures and the resulting vigorous stirring kept the carbides dispersed throughout the metal, in the freezing point determinations the metal was held quietly molten, with little or no stirring, at temperatures only slightly above the melting point. Under these conditions the carbides were free to agglomerate and migrate to the top or to the solid skin of the side walls. For example the center of the B 871 ingot contained 7 ppm of carbon, a sample near the top of the ingot contained 16 ppm, and the crust attached to the top contained 1100 ppm of carbon.

These results indicate that the solubility of carbon in tuballoy, at temperatures near the melting point is low, probably not over 5 ppm, and that carbon contents of 300 to 500 ppm, normally found in tuballoy, are the result of heating the metal to temperatures appreciably above the melting point, in contact with carbon. Holding the metal quietly molten for extended periods of time, preferably in a beryllia or thoria container, should result in the production of metal with lower carbon contents than have been obtained previously, even in biscuit metal.

Summary

1. Holding the metal barely molten for several hours resulted in a decrease in the content of several impurities, either by volatilization or by migration to the top and side walls. The most pronounced change in composition during the freezing point determinations was the virtual elimination of carbide inclusions.
2. While the metal was held molten the freezing temperature increased slowly to a final constant value, 5 or 6°C above the initial freezing temperature.
3. These results were not affected by the crucibles used, i.e., the same results were obtained in beryllia, thoria, and graphite crucibles.
4. The best result for the freezing temperature of tuballoy is 1326 ± 1°C, for metal which contains about 5 ppm of carbon, 60 ppm of iron, 20 ppm of oxygen, and lesser amounts of other constituents as recorded in Table I.