UNCLASSIFIED

I
TID-7526(Pt. 1)

METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

METALLURGY INFORMATION MEETING,
AMES LABORATORY, IOWA STATE COLLEGE,
MAY 2, 3 AND 4, 1956

February 1957
[TISE Issuance Date]

Ames Laboratory
Iowa State College
Ames, Iowa

Technical Information Service Extension, Oak Ridge, Tenn.

UNCLASSIFIED

II

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

This report has been reproduced directly from the best available copy.

Printed in USA, Price \$1.50. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

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.

TID-7526(Pt. 1)

METALLURGY INFORMATION MEETING,
AMES LABORATORY, IOWA STATE COLLEGE, MAY 2, 3 AND 4, 1956

February 1957
TISE Issuance Date

Ames Laboratory
Iowa State College
Ames, Iowa

TABLE OF CONTENTS

	Page
Nondestructive Testing of the EBWR Fuel Plates by W. J. McGonnagle and W. N. Beck, Argonne National Laboratory, Lemont, Illinois.....	1
Wetting Temperatures of Fuel Element Components With Sodium and NaK by G. G. Bentle, H. Strahl, and J. Droher, Atomics International, Canoga Park, California.....	16
Preparation of Ingots of U-Nb Alloy by O. N. Carlson, N. Ida, D. Peterson, F. Tate, and H. A. Wilhelm, Ames Laboratory, Iowa State College, Ames, Iowa.....	28
The Strengthening of Beryllium for High Temperature Use By Means of Beryllium Oxide and Beryllium Carbide Dispersions by J. Greenspan, Nuclear Metals, Inc., Cambridge, Massachusetts.....	34
On The Mechanical Metallurgy of Zircaloy-3b by D. E. Johnson, Hanford Atomic Products Operation, Richland, Washington.....	54
Mechanical Properties and Corrosion Behavior of Zircaloy-3 by F. Forscher, S. Kass, and K. Goldman, Bettis Plant, Pittsburgh, Pennsylvania.....	69
Constitution of Uranium and the Platinum Metals by J. J. Park and R. W. Buzzard.....	89
Production of Thorium-Bismuth Dispersions by J. S. Bryner, R. J. Teitel, and M. B. Brodsky, Brookhaven National Laboratory, Upton, New York.....	103
Preparation of Boron-Containing Alloys by A. P. Beard, J. W. Harrison, and C. J. Beck, Knolls Atomic Power Laboratory, Schenectady, New York.....	115
Aluminum-Boron and Aluminum-Uranium-Boron Alloys for Improved Reactor Performance by W. C. Thurber, J. A. Milko, and R. J. Beaver, Oak Ridge National Laboratory, Oak Ridge, Tennessee.....	116

VOPD
T-336

TABLE OF CONTENTS (Continued)

	Page
Radioanalysis of Krypton and Xenon and Its Use In Diffusion Experiments With Silver by J. Martin Tobin, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.....	129
Preferred Orientation in Extruded Thorium Rod by L. K. Jetter and C. J. McHargue, Oak Ridge National Laboratory, Oak Ridge, Tennessee.....	150
Morphology of Zircaloy-2 by M. L. Picklesimer and G. M. Adamson, Jr., Oak Ridge National Laboratory, Oak Ridge, Tennessee.....	165
The Microstructural Appearance and Identification of Hydrides In Zirconium and Zircaloy-2 Hydrogen Alloys by G. B. Wadsworth, M. L. Picklesimer, and G. M. Adamson, Jr., Oak Ridge National Laboratory, Oak Ridge, Tennessee.....	186
Inspection of Small Diameter Tubing By Eddy Current Methods by J. W. Allen and R. B. Oliver, Oak Ridge National Laboratory, Oak Ridge, Tennessee.....	209
Application of the Immersed Ultrasonic Technique for the Inspection of Small Diameter Tubes by R. B. Oliver and R. W. McClung, Oak Ridge National Laboratory, Oak Ridge, Tennessee.....	227
Corrosion and Mass Transfer by Lithium at Elevated Temperatures by E. E. Hoffman and L. R. Trotter, Oak Ridge National Laboratory, Oak Ridge, Tennessee.....	244
Siliconizing of Metals in Liquid NaK by E. S. Fisher, R. A. Noland, and C. Marzano, Argonne National Laboratory, Lemont, Illinois.....	268

NONDESTRUCTIVE TESTING OF THE EBWR FUEL PLATES

by

W. J. McGonnagle and W. N. Beck

Argonne National Laboratory
Lemont, Illinois

The following nondestructive testing methods are used for inspecting the EBWR fuel elements; radiography, autoradiography and ultrasonic transmission.

A radiographic technique is used to show the location of the core with respect to the end and side clad. The width of the core and side clad of the completed fuel element can be determined from the radiograph. The radiographs are also used by the shops to determine how much material should be removed from the ends and edges of the rolled fuel element.

The ultrasonic transmission technique is used to test for lack of bonding between the core and clad material and for locating blow holes, porosity and pipe in the core billets. A permanent record is made of the ultrasonic energy transmitted through the specimen being tested. A nonbond area 1/8" in diameter can be detected. A special scanner has been designed and constructed for this work.

The natural radioactivity of the EBWR core is used in an autoradiographic technique to measure the clad thickness. The beta radiation emitted by a daughter of U-238 (Pa-234) is used in conjunction with an anthracene scintillator crystal. The plate is scanned at the rate of 4" per minute. Variations in clad thickness as small as 0.0005" can be detected.

Three nondestructive testing techniques are used for testing the EBWR fuel elements. These three techniques are ultrasonic transmission, autoradiography and radiography. The ultrasonic transmission technique is used for finding porosity, blow holes in the core billet

material and for locating lack of bond in the finished fuel element. Radiography is used to locate the position of the core material with respect to the ends and side clad.

The first technique which will be described is the ultrasonic transmission technique. In this technique pulsed ultrasonic waves are sent through the specimen and the amplitude of the transmitted energy is recorded. Lack of bonding or other inhomogeneities in the specimen cause a decrease in the amount of transmitted energy.

The apparatus developed for this testing work consists of an ultrasonic generator and receiver, a scanning assembly and a recording system. Each of these components will be briefly described.

The ultrasonic generator and receiver used in this work was a commercial Sperry Reflectoscope. The instrument was modified so that: (1) a separate sending and receiving transducer could be used; (2) the pulse repetition rate could be varied; (3) a negative pulse could be taken from the pulse generator for keying the recording system.

The scanner assembly consists of a rigidly supported track, a tank, transducer carriage, two drive motors and two master Selsyn motors. Figure 1 shows the scanner with the sheet metal side panels removed.

The track consists of two rails; an inverted "V" shaped rail and a flat rail. The rails are 10-1/2 feet long and are positioned 20 inches apart. The two rails are accurately aligned and rigidly supported on a welded steel framework.

The tank is 10 feet long, 12 inches high and 14 inches wide. The tank is made of 16 gauge steel and spray coated with white Koroseal. This coating serves a twofold purpose of protecting the tank from corrosion by the couplant and acts as a sound adsorbing medium. Water is used as the couplant.

The transducer carriage is used to support and carry the two quartz crystal transducers along the sample being inspected. The transducer carriage is provided with two "V" shaped wheels and one flat wheel, which insures that the transducers will move uniformly with respect to the specimen. The transducer carriage is moved along the rails by means of a chain drive, driven by a 1/4 hp motor through a variable speed transmission. This motor is referred to as the translational drive motor. A clutch arrangement is provided to disengage the drive motor for manual scanning. The drive chain also engages a Selsyn master motor. Microswitches for stopping and reversing the drive motor at the end of a scan may be set to any desired position along the track.

The transducer assembly is a brass yoke (see Figure 2) designed to hold the two crystals in a rigid position with the faces of the transducers parallel. Adjustments in the position of the crystals can be made by means of set screws.

In addition to the transducers, a fixed speed motor for moving the transducers up and down is mounted on the transducer carriage. The transducer assembly is connected to a sliding shaft which is in turn coupled to the elevating gear train. The vertical scanning rate can be changed by changing the elevating gear train. The amplitude of the vertical motion can also be changed by changing the gear train. A master Selsyn motor is also actuated by the vertical drive motor.

The recording system consists of two parts, the electronic components and an electrosensitive paper recorder. The signal to be recorded is taken from the vertical amplifier of the Reflectoscope. The amplitude of this signal is a function of the ultrasonic transmission through the specimen - the better the transmission the greater the amplitude of this signal.

The electrosensitive paper record gives a permanent two dimensional record of the ultrasonic transmission through the specimen being inspected. Figure 3 shows this recorder. The recorder uses a moist electrosensitive paper which passes between two electrodes. The darkening of the paper is a function of the current flowing between the electrode and the writing speed. The greater the current flow the greater the darkening of the paper. The faster the writing speed the greater the current needed for satisfactory recording. Areas of good transmission appear as dark areas on the electrosensitive paper record, while areas giving poorer transmission appear as lighter areas. The electrosensitive paper must be moist for recording. The paper is sealed in plastic bags at the factory to retain moisture during storage. The paper is placed in a humidor in the recorder to prevent the paper from drying out while being used. Two kinds of electrosensitive papers have been employed, Alfax and Mufax. The Alfax paper is manufactured by the Alfax Paper and Engineering Co., Westboro, Massachusetts. The Mufax paper is manufactured by the Muirhead and Co., Ltd. Beckenham-Kent-England.

Two electrodes are used in the recorder; a fixed electrode which is the positive electrode and a movable electrode which is the negative electrode. The positive electrode is made from a strip of stainless steel $3/64$ -inch wide and equal to the width of the specimen being tested. The negative electrode is a cylindrical drum on which is wound a single turn of nichrome wire to form a helix. As the moving electrode revolves the point of intersection between the fixed electrode and the helix travels in a straight line always starting at the same edge of the paper and sweeping across it. By

proper selection of the diameter of the recording helix the width of the recording is equal to the width of the specimen.

A slave Selsyn motor actuated by the master Selsyn connected to the translational drive of the scanner is used to drive the paper feed to the recorder. Consequently, the length of the recorder trace is equal to the length of the sample being scanned. The two Selsyn motors are connected in such a manner that regardless of the direction of scanning the recording paper is always moving in the same direction. A master Selsyn motor is connected to the motor which is used to move the transducers vertically, and is connected to a Selsyn motor which drives the recorder helix. When scanning in the vertical direction, a cam, connected to the vertical drive motor actuates a microswitch arrangement so that the signal is applied to the recording helix only during the upward motion of the transducers. Figures 4 and 5 show typical recorder traces and the kind of sensitivity obtainable with this recorder using artificial defects. The upper half of Figure 4 shows a stencil from which the letters ANL had been cut. The lower half of this same figure shows how the electrosensitive paper recorder reproduced the contour of the letters. The encircled area in Figure 5 shows the record produced by an artificial defect 1/8-inch in diameter. Experiments have shown that the electrosensitive paper record accurately indicates the shape, size and location of actual nonbond or defective areas.

The electronic component of the recording system operates as follows: a negative keying pulse is taken from the synchronizer of the Reflectoscope. Because of the pulse delay in the Reflectoscope, the negative keying pulse proceeds the pulse from the ultrasonic pulse generator. The keying pulse activates a gating circuit so that the initial pulse (which carries no intelligence concerning the test specimen) is gated out from the recorder. The ultrasonic pulse transmitted through the specimen opens the electronic gate, which allows the intelligence carried by the transmitted ultrasonic beam to be passed on to the recorder. It is necessary to rectify the signal before it is applied to the electrosensitive paper. A discriminator is provided so that noise and other extraneous signals may be rejected. A control is also provided which permits the operator to vary the contrast on the electrosensitive paper.

In testing the EBWR fuel elements a linear scanning speed of four inches per minute and a vertical scanning speed of 480 inches per minute was used. A frequency of 5 Mc was used and the cross section of the beam was 5/64-inch. A pulse repetition rate of 120 per second was found to be satisfactory. Unbonded areas 1/8-inch in diameter or larger can be found using this technique.

In order to assure that the defects were not present in the core material, the billets used in making the core were also tested for

pipe, porosity and blow holes. Figure 6 shows a typical electro-sensitive paper record made of a large flat casting. This casting was so large that it was necessary to cut the casting into sections for testing. The composite record shown in Figure 6, was made from individual records. The light areas being poor transmission showing the presence of pipe, porosity and blow holes and the dark areas being areas of good transmission. After making a number of destructive tests for this nondestructive testing program, a standard was arbitrarily selected. This casting is run periodically to check on the sensitivity and resolution of the equipment and to be sure that all the electronic components are working properly.

It is possible to use the transmission technique not only to determine lack of bond but also to determine the relative degree of bonding of zirconium clad specimens. By proper selection of the amplification and recording level, the relative darkening of the paper gives a relative measure of the bond strength. The lower half of Figure 7 shows a trace of a zirconium clad specimen. The light areas represent areas of relatively poor transmission and the dark areas better transmission.

Bond strengths were determined by tensile testing. Tensile tests were performed in the following way. Zirconium studs 1/4-inch in diameter and approximately 1-inch long were percussion welded to the specimen as shown in the upper half of Figure 7. The area around each stud was machined through the cladding leaving only the bonded area under the stud. The sample was then put in the tensile machine and pulled. Comparison of the tensile test with the relative darkening of the recorder trace give a good correlation between bond strength and darkening of the paper.

The natural radioactivity of the core material is used to measure the cladding thickness of the EBWR fuel elements. U-238 decays to a second daughter protoactinium-234 through an intermediate state of thorium-234. The protoactinium decays by beta emission having an energy of 2.2 Mev. Figure 8 shows the absorption curve for zirconium aluminum and stainless steel. Each of these curves was obtained by placing sheets of varying thickness over a flat uranium source. The relative number of counts per unit time is plotted against sheet thickness.

A scintillator detector is used to record the radiation. The scintillator crystal is anthracene 1/8-inch in thickness and 1-inch in diameter. The scintillator crystal was mounted on the face of a Dumont 6292 photomultiplier tube. A cathode follower is used to feed the pulses from the photomultiplier tube to an Atomic Instruments #218 amplifier and discriminator. The shaped pulses from the discriminator were then fed to a counting rate meter of the Argonne type CRM-5B and the output of the counting rate meter was fed to a 10 Mv recorder. (See Figure 9)

Three modifications were made in the counting rate meter; (1) the zero set was expanded by use of a 100,000 ohm helipot in the cathode circuit of the output tube of the instrument. This permitted the use of a more sensitive range of the instrument so that small differences in rates could be more easily seen; (2) the time constant of the integrating circuit was increased to smooth out fast random fluctuations of the output voltage; (3) the load resistor was increased to a 5000 helipot in order to have a larger and adjustable sensitivity.

The scanning of the BER plates was carried out with a mechanical scanner designed at the Argonne National Laboratory. It consisted of roller table and a friction drive which moved the fuel elements under the scintillation counter.

Pieces of stainless steel of 2-inch width were glued to the plates as artificial variations in the clad thickness. From these experiments it was concluded that with a scanning speed of 4 inches per minute a variation of 0.0005 inch variation of clad could be detected in sections of 2-inch widths or wider; and at a scanning speed of 24 inches per minute 0.003-inch variation could be detected. With scanning speed of 24 inches per minute a 0.005 variation in widths of two inches are easily seen. For the faster scanning speed it was found desirable to reduce slightly the time constant of the counting rate meter's time constant. Choice of scanning speed depends upon sensitivity desired and time available.

The instrument is calibrated by the use of a short section cut from a typical EBWR plate. The cladding thickness at the ends of this section were measured using a microscope. Keeping the zero and sensitivity setting fixed a recorder trace was made as various thicknesses of 2 mil thick zircalloy foil were added to the section. A calibration curve was plotted using this data. A scanning speed of 4 inches per minute is used in this testing program.

All the fuel plates were radiographed using a commercial X-ray machine. The fuel plates were radiographed primarily for the purpose of locating the position of the core with respect to the ends and side cladding. The kilovoltage and exposure time used, which were determined experimentally, produced good delination between core and cladding material.

In general, the EBWR fuel elements tested have shown; (1) uniform cladding thickness, (2) uniform side and end cladding, (3) good bonding between core and clad and, (4) the thickness of the side and end clad meet the design specifications.

7

7

Figure 1 - 106-2166 Ultrasonic Scanner with Side Panels Removed

Figure 2 - 141-778 Transducer Assembly

Figure 3 - 141-797 Electrosensitive Paper Recorder

Figure 4 - 106-2487 Electrosensitive Paper Record Showing Sensitivity and Resolution of the Recording System

Figure 5 - 106-2498 Electrosensitive Paper Record Showing Sensitivity and Resolution of the Recording System

Figure 6 - 141-883 Electrosensitive Paper Record of a Large Core
Casting Showing Porosity, Pipe and Blow Holes

Figure 7 - 141-785

Tensile Specimens and Electro-sensitive Paper
Record of a Zircalloy Clad Fuel Plate

14

14

Figure 8 - 141-787 Absorption of Beta Radiation from Natural Uranium

Figure 9 - 106-2172 Scintillation Counting Equipment

WETTING TEMPERATURES OF FUEL ELEMENT COMPONENTS
WITH SODIUM AND NaK

by

G. G. Bentle, H. Strahl, and J. Droher

Atomics International
A Division of North American Aviation, Inc.
Canoga Park, California

The temperatures of wetting of stainless steel, uranium, thorium, and thorium-uranium alloys with sodium and NaK have been determined. The parameters of surface condition, wetting fluid, and composition of material have been investigated as to their effect on wetting temperatures. Cyclographic tests of fuel elements in which sodium or NaK is the bonding fluid are reported.

The assumption is made that wetting would cause more efficient heat transfer across solid-liquid interfaces. This has been indicated in a steel-mercury system.¹ However, much evidence exists which indicates that the heat transfer coefficient is the same under wetting and non-wetting conditions.²

It is thought desirable, nevertheless, to have wetting conditions in all liquid-solid interfaces in fuel elements used in the Sodium Reactor Experiment. The present study was undertaken to help establish a surface finish specification for uranium fuel, and to investigate other parameters which might affect wetting temperatures.

The observations on heat transfer refer to static and dynamic systems. In dynamic systems, Chelmer³ and others noted that "detachments" occur. These detachments affect heat transfer adversely and may account for the discrepancy between the various observers conclusions. The detachments appear to be bubbles of gas which have been entrained or adsorbed in the case of mercury.

In a mercury-steel system, measurements were made³ of the affect of individual bubbles as they passed a monitored surface. A maximum increase of about 0.5°C was noted in the heated wall as various size bubbles passed. The wall was at 100°C . The mercury was about 25°C . The flow rate was about 5 feet per minute.

In a static system such as exists within the SRE fuel element, bubbles will probably rise to the surface. The heat transfer barriers will then be the oxide coating on the fuel material and any coating on the stainless steel fuel jacket. A shiny stainless steel surface is estimated to have a film 700 to 1000 angstroms thick. The film thickness on the fuel material is a function of the composition of the material and its exposure to oxygen during the time between cleaning and canning. Judging from color change with time this film might be from a few hundred to 5000 angstroms thick.

Thermodynamically the stainless steel film would be reduced by sodium and potassium. Experiments at Atomics International with stainless steel in contact with sodium and NaK indicate no reaction after 30 days at 750°C .

Uranium and thorium thermodynamically can reduce Na_2O . This implies the scavenging of oxygen from the NaK bond and a² buildup of oxide layer on the fuel material. If the bond liquid (7.32 cubic inches of NaK) contains 100 ppm of oxygen, this oxygen would form approximately a 2 mil layer of uranium oxide on the uranium fuel. It is assumed that the effective thickness would be no more than one-half mil due to the saturation of the oxide layer with NaK. This would result in a 12°C temperature drop at maximum SRE heat fluxes. However, no oxide formation was noted on thorium and uranium samples after 30 days exposure to NaK at 750°C . The NaK was not filtered as is SRE bonding material.

Regardless of the above results it is known that "metals whose oxides are either reducible or non-reducible are wetted by sodium and do not dewet on standing unless they are subsequently exposed to oxygen".⁴

EXPERIMENTAL PROCEDURE

In the present experiment several methods to detect wetting are used. One is the spreading of a drop of sodium or NaK on the surface. In this case, the necessary criterion for wetting is satisfied in that the contact angle is less than 90° . This "contact angle" is indicated in Figure 1. Under the conditions of spreading, the contact angle becomes less than 90° .

With the second method, the liquid is applied, one drop at a

time, with an eye-dropper and then withdrawn from the surface. When part of this liquid cannot be withdrawn, wetting is assumed to occur. In the second case, the work of adhesion between liquid A and surface B is greater than the work of cohesion between liquid A and its vapor. (This quantity is numerically equal to the surface tension of the liquid.) Such a condition has been demonstrated to represent wetting.⁵

The experiments were performed in a glove box. The atmosphere was argon which had been bubbled through NaK. In some of the runs, a titanium-zirconium getter alloy was heated to 600° C to further purify the atmosphere.

The experimental apparatus is shown in Figure 2.

Measurement of the angle of contact of sodium and NaK with the surface was difficult in the glove box. Therefore, the methods described were used.

The temperatures of wetting found by the two methods were approximately the same. In both cases wetting is found to occur over a range of temperatures rather than at a specific temperature. The ranges overlap and are reported as one range of temperature.

The first work was done to find the difference in wetting temperature as a function of surface preparation. Theoretically, surface roughness reduces the apparent contact angle when the true angle is less than 90°, and increases it when the true angle is greater than 90°. This information is in Table I. The samples were outgassed in vacuum at 10^{-5} millimeters and at 350° C for one hour.

TABLE I

Wetting Temperatures as a Function of Surface Preparation

Material: Uranium

Wetting Fluid: NaK (22% sodium, 78% potassium)

<u>Surface Finish as Machined (RMS)</u>	<u>Temperature of Wetting °C</u>
5	170 - 176
40	180 - 184
125	191 - 193
250	202 - 206

It is apparent that increased roughness increases wetting temperatures in this system.

These same samples were later oxidized in air. This treat-

ment raised the respective wetting temperatures about 70° C. Other parameters were then investigated.

Table II indicates the differences due to surface condition other than roughness. The surface of this stainless steel is in the as-drawn condition. As can be seen here, wetting temperatures are lower when the surface is clean and when it is free of adsorbed gas.

TABLE II

Wetting Temperatures as a Function of Surface Condition

Material: 304 Stainless Steel

Wetting Fluid: NaK (22% Sodium, 78% Potassium)

<u>Surface Conditions</u>	<u>Temperature of wetting °C</u>
Scrubbed and degreased.	248 - 256
Oxidized at red heat for 30 minutes.	307 - 319
Outgassed in vacuum at 350° C for 1 hour.	220 - 242

Table III shows the difference as a function of composition. There is apparently no regular difference due to composition. The differences noticeable in this table are more likely a difference due to surface oxide. The time for oxide to form on the various samples indicated in this table varied.

TABLE III

Wetting Temperatures as a Function of Composition

Surface Condition: Metallographically Polished

Wetting Fluid: Sodium

<u>Material</u>	<u>Wetting Temperature °C</u>
Cast Thorium	208 - 220
Rolled Thorium	210 - 232
Thorium - 4% Uranium (powder compacted)	190 - 225
Thorium - 5% Uranium (cast)	202 - 215
Uranium (cast)	202 - 210

It has been suggested⁶ that systems which do not interact or form solid solutions, such as the systems investigated here, do not wet readily. Table IV indicates that there is no regular difference due to wetting fluid. If wetting did occur readily the potassium in the NaK should lower wetting temperatures due to its lower surface tension.

TABLE IV

Wetting Temperature as a Function of Wetting Fluid

Surface Condition: Metallographically Polished

Material	Fluid	Wetting Temperature °C
Cast Thorium	Sodium	240 - 250
Cast Thorium	NaK	235 - 245
Thorium - 4% Uranium	Sodium	190 - 225
Thorium - 4% Uranium	NaK	198 - 228
Thorium - 5% Uranium	Sodium	200 - 223
Thorium - 5% Uranium	NaK	202 - 215

Table V indicates a significant difference due to the material being previously wet. The lower wetting temperatures are probably due to a cleaner surface or tiny droplets of liquid which remain on the metal, and act as nucleation centers for spreading or both.

TABLE V

Wetting Temperatures as a Function of Previous Wetting

Surface Condition: Polished

Material	Fluid	Wetting Temperature °C
Rolled Thorium as received	Sodium	232 - 245
Rolled Thorium previously wet	Sodium	132 - 160
Thorium - 5% as received	NaK	202 - 215
Thorium - 5% previously wet	NaK	180 - 190
Uranium as received	Sodium	185 - 205
Uranium previously wet	Sodium	164 - 180

In a third method the samples were suspended by a wire, lowered into a stainless steel beaker filled with NaK, and the surface of the liquid observed. If the surface of the liquid was elevated at the wall, then the sample was considered as "wetted"; if the liquid surface was depressed near the wall, the sample was considered as "non-wetted". Surface tension forces actually pull the liquid up along the wall of a solid when it is "wetted". The glove box, in this case was evacuated to 10^{-4} millimeters and let down to one atmosphere of helium which was previously bubbled through NaK.

Samples of SRE fuel rod tubing (304 stainless steel), scrubbed, and degreased, wet between 250 and 275° C. Uranium samples with surface finishes RMS 5, 40, 125, and 250 wet between 250 and 300° C. Thus method three gives results 25 to 75° C higher than methods one and two.

A reason for this may be that the spreading or adhering of a drop of liquid to a surface can occur with a larger contact angle than can the rise of liquid up a vertical surface. An increase in temperature would be necessary to decrease the surface tension of the liquid and thereby enhance wetting.

Other anomalies were noted. The six inch long by three-quarter inch diameter slugs of normal uranium were dipped in NaK and then removed. The samples appeared bright and silvery with the oxide apparently removed from the section which was submerged in the NaK. Figure 3 is a picture of representative slugs after dipping. This oxide removal is contrary to what one would predict from thermodynamic data if the oxide is actually removed by chemical reaction with the NaK. An alternative explanation is that the oxide is merely "floated off" the surface and still exists as an oxide of uranium in the NaK.

When these slugs were removed from the hot NaK and cooled in a helium atmosphere the NaK appeared to ball up and leave areas of the slug uncovered. The slugs were reinserted and the NaK cooled to room temperature and again the slugs removed. In this case the slugs remained completely "wetted" after 48 hours in the helium atmosphere.

Conditions which could affect the complete "wetting" of the slugs are: (1) a clean surface, (2) a layer of liquid or minute drops of liquid adhering to the surface, (3) a longer time of exposure to NaK so that a semi-chemical bonding occurs at the surface which holds the NaK in place.

Experiments to detect voids in the liquid metal bond in SRE fuel rods have been performed using both sodium and NaK eutectic. (22% sodium, 78% potassium) Stainless steel tubes about eight feet long were loaded with six feet of clean uranium slugs. Sodium or NaK was introduced. After welding the tube closed, the fuel assembly was removed from the loading rig. Equivalent heat treatments were given all assemblies. They were then checked by eddy current testing. These tests indicate that fewer voids occur with NaK than with sodium as the bonding material in the 0.010 inch annulus between the uranium slugs and the stainless steel jacket. This is attributed to the lower values for both surface tension and viscosity of NaK as compared to sodium. It should be noted that there is no substantial difference between

the temperatures of wetting of a given surface with sodium and NaK.

A fundamental concept of the spreading of liquid metals on a solid may be expressed in terms of the free energies of the two phases. These energies exist as a consequence of unsaturated bonds present at the free surfaces. The surface energy of one phase may be expressed as

$$\left(\frac{\partial F}{\partial a}\right)_{P,T} = \sigma \quad (1)$$

where

- F = free energy of phase (ergs)
- a = surface area of phase (cm²)
- σ = surface free energy of the phase (erg/cm²)
numerically equal to the surface tension.

The free energy of formation of a (cm)² of interface may be looked upon as a gain in surface free energy of the wetting fluid and as a loss in surface free energy of the solid. This change may be expressed as

$$\frac{dF}{da} = \sigma_A + \sigma_{AB} - \sigma_B \quad (2)$$

where

- σ_A = surface energy of the liquid
- σ_{AB} = surface tension of the interface
- σ_B = surface energy of the solid

When $\frac{dF}{da}$ is negative spreading can occur.

Using the idealized, equilibrium expression

$$\sigma_{AB} = \sigma_B - \sigma_A \cos \theta \quad (3)$$

where θ = the contact angle in Figure 1, the interfacial tension may be investigated qualitatively. Thorium and uranium are estimated⁶ to have surface tensions of 1270 erg/cm². The assumption is made that the surface energy of the respective solids in the liquid metal vapor is half that of the metal in an inert atmosphere. The contact angle is unknown. However, employing these figures and assuming a contact angle of 0, it is evident that the interfacial tension is at least 450 ergs/cm². Empirical studies indicate that an interfacial tension of below about 300 erg/cm² is necessary for wetting to occur in such systems as bismuth-silver, tin-copper or lead-nickel. This suggests that the mechanism of wetting with the alkali metals is somewhat dif-

ferent from that of lead, bismuth or tin.

Experiments to determine some characteristics of the fundamental nature of films have been run. Electrical resistivity was found to vary with wetting and non-wetting, but did not vary directly.⁷ Epstein and Weber⁴ report that "from the variation of time necessary for sodium to rise a fixed distance up the metal grooves as wetting occurs, an activation energy of the order of 20 to 25 kcal/mole has been obtained. The rate controlling reaction has not been isolated". They refer to a sodium-stainless steel system.

The conclusions which may be drawn from this work are:

1. Sodium and NaK wet thorium, uranium and stainless steel at about the same temperature.
2. NaK is the better bonding agent for small annuli.
3. Increasing surface roughness and oxidation increases wetting temperatures of thorium, uranium and stainless steel.
4. Previous wetting lowers wetting temperatures.
5. Composition or method of manufacture do not affect thorium or thorium-uranium alloy wetting.
6. Different methods of determining wetting temperatures give different results.
7. The mechanism of wetting and spreading with the alkali metals is somewhat different from that of lead, bismuth and tin.

REFERENCES

1. Doody, T.C., and Younger, A.H., "Heat Transfer Coefficients for Liquid Mercury and Dilute Solutions of Sodium in Mercury in Forced Convection", Preprints for Heat Transfer Symposium at Forty-fourth Annual Meeting, Am. Inst. Chem. Engrs., (1951).
2. Stromquist, W.K., Effect of Wetting on Heat Transfer Characteristics of Liquid Metals, USAEC Report ORO-93.
3. Chelemer, H., Effect of Gas Entrainment on the Heat Transfer Characteristics of Mercury under Turbulent Flow Conditions, USAEC Report ORO-139.
4. Epstein, L.F., and Weber, C.E., Problems in the Use of Molten Sodium as a Heat Transfer Fluid, USAEC Report KAPL-362.
5. Burdar, R.S., "Surface Tension and the Spreading of Liquids", Second Edition, Cambridge, The University Press, 1949.
6. Taylor, J.W., The Significance of Wetting in Reactor Technology. Journal of Nuclear Energy, Volume 2, August 1955, 15-30.
7. Droher, J.J., Studies of Interfacial Effects Between Mercury and Steel, USAEC Report ORO-69.

SCHEMATIC OF WETTING
AND NON WETTING CONDITIONS

FIGURE 1

EXPERIMENTAL APPARATUS

FIGURE 2

FIGURE 3

PREPARATION OF INGOTS OF U-Nb ALLOY

by

O. N. Carlson
N. Ida
D. Peterson
F. Tate
H. A. Wilhelm

Ames Laboratory, Iowa State College
Ames, Iowa

A study was made of the preparation of a uranium-10 w/o niobium alloy by the bomb co-reduction of uranium tetrafluoride and a suitable form of niobium with calcium. A composition close to Na_2NbOF_5 proved to be most satisfactory as the source of niobium. High yields and good metal slag separations were obtained. Chemical analysis and density determinations showed the composition to be 10 ± 0.5 w/o niobium. Fifteen pounds of alloy were melted in BeO and cast into a graphite mold.

INTRODUCTION

The objective of this investigation is the development of a method for preparing a uranium-10 w/o Nb alloy of uniform composition. As reported previously¹ a few preliminary experiments were carried out in this laboratory on the preparation of some uranium-rich alloys of uranium and niobium by the bomb co-reduction of UF_4 and Nb_2O_5 with calcium. Results of these tests indicated that it might be possible to prepare the above mentioned alloy in this way.

Some work on the preparation of this particular alloy by co-melting procedures had brought out a number of difficulties which it was hoped might be eliminated by the co-reduction method. Since the co-reduction process is designed to give a uniform alloy during the reduction step any subsequent melting and casting of the alloy would be simplified. The maximum temperature to be reached in the

casting would be much less than that required for adequate alloying by co-melting. Furthermore the time at temperature before casting would be shortened because essentially no hold is needed to obtain solution and distribution of the niobium when a co-reduced alloy is employed.

EXPERIMENTAL RESULTS

Based on this previous experience, a series of reductions were attempted in which Nb_2O_5 , Nb metal powder, NbCl_5 , K_2NbOF_5 , and Na_2NbOF_5 were added to the reaction charge. Reductions were carried out in a 2 1/2 inch diameter iron pipe with a welded-in plate on one end and a threaded metal cap at the other. This reaction chamber, commonly referred to as a bomb, was lined with dolomitic oxide. The bomb was fired by heating in a gas furnace.

Attempts to prepare the 10 w/o alloy employing Nb_2O_5 were unsatisfactory. Poor slag-metal separation was encountered, which decreases the per cent of alloy recovered. Increasing the amount of calcium from 25 to 50 per cent excess over the stoichiometric amount did not noticeably improve the slag-metal separation. Similar results were obtained when niobium powder and NbCl_5 were tried in preparing the U-10 w/o Nb alloy, although somewhat better metal-slag separations were observed when NbCl_5 was used.

It was concluded from the preceding experiments that a halide salt of niobium was most desirable for preparing the U-10 w/o Nb alloy. The presence of a quantity of oxide in the slag reduces its fluidity and reduces the possibility of good slag-metal separation. Such a salt would also act as a thermal booster, thus raising the final temperature of the products. One such salt with which the authors had some previous experience was potassium oxyfluoniobate. This is easily prepared by fusing a mixture of KF , Nb_2O_5 and NH_4HF_2 in a platinum crucible at 700°C . A salt mixture having the stoichiometric composition of K_2NbOF_5 was prepared in this manner. When this compound was tried in the reduction with UF_4 , metal recovery was improved, the alloy "biscuits" were smooth, and satisfactory separation of slag and metal was observed. Analyses showed that nearly all of the niobium had alloyed with uranium. One disadvantage was the liberation of potassium in the reduction reaction. This made the task of removing the slag and alloy from the bomb an unpleasant one. In a few experiments where a graphite disc was inserted in the top of the bomb, the potassium vapors had reacted with the graphite forming an extremely pyrophoric compound.

Consequently, a sodium salt of the oxyfluoniobate was prepared by substituting NaF for KF in the above mentioned fusion reaction. By varying the amount of NaF added, salt mixtures having the stoichiometric formulae, NaNbOF_4 , $\text{Na}_3\text{Nb}_2\text{O}_2\text{F}_9$ and Na_2NbOF_5 were prepared. Reductions showed that the best results were obtained when Na_2NbOF_5

was used. In later experiments Na_2NbOF_5 was prepared by adding 70% HF to a mixture of NaF and Nb_2O_5 . This was evaporated to dryness at 110°C and then heated to 500°C to remove any volatile products.

In the reductions employing K_2NbOF_5 a 25% excess calcium was used. The slag-metal separation was good and the yields were fair. In the first four reactions with Na_2NbOF_5 a 25% excess of calcium was also used and the yields and slag metal separation were comparable to those obtained with K_2NbOF_5 . However, by increasing the calcium excess to 50%, good yields and excellent separation of metal and slag were obtained. As shown in Table I reductions were carried out in 2 1/2 and 4 inch diameter bombs. In all reductions the bomb was lined by jolting dolomitic oxide between a mandril and the bomb wall. On the larger scale reductions there was evidence of possible interaction with the dolomitic oxide liner. Packing a 1/4 inch layer of CaF_2 on the bottom of the bomb liner before the charge was added reduced this interaction.

Table I

Bomb Charge Employed in Preparation of U-10% Nb Alloy		
Ingredients	2 1/2" Dia. Bomb (grams added)	4" Dia. Bomb (grams added)
UF_4	650	1859
Na_2NbOF_5	147	420
Ca	336 (50% excess)	960 (50% excess)

The bomb generally required about ten minutes of heating in the furnace at 650°C before the exothermic reaction was initiated. The instant of firing was detected by a sudden increase in the temperature of the exterior surface of the bomb as measured by a thermocouple.

The results of several reductions are shown in Table II. As will be noted from the table, alloy recoveries in the range of 96 to 99% are obtained by this process. Chemical analyses were made on samples of alloys obtained from seven reductions. Upon adding the per cent niobium and per cent uranium for each sample one observes that the total sum exceeds 100% in five alloys. Since considerable care was exercised in sampling each alloy and since all of these values are based upon the average of several analyses, the authors feel that results of the analysis for one of the components, probably uranium, are slightly high. This opinion is corroborated by the use of density measurements to estimate the alloy composition. A density versus composition curve (Fig. 1) was determined by measuring the density of standard 50 to 60 gram samples prepared by arc-melting together

Table II

Bomb Co-Reduction Data

Reduction Experiment No.	Bomb Size	% Alloy Recovered	Composition by Chemical Analysis		Composition as esti- mated from density
			w/o Nb	w/o U	w/o Nb
1Wn ^a	2 1/2"	95%	7.85	92.56	8.45
5Wn	2 1/2"	97.6%	10.28	90.80	10.15
6Wn	4"	98%	8.91	91.09	10.05
7Wn	4"	96%	9.96%	91.87	-----
8Wn	4"	97%	9.82	89.56	9.85
9Wn	4"	97%	10.50	90.90	-----
10Wn	4"	95.9%	10.16	91.05	-----
11Wn	4"	99%	9.52	91.12	-----
12Wn	4"	95.5%	no data		
1Wn _s	2 1/2"	97%	" "		
2Wn _s	2 1/2"	97%	" "		

a Intended composition of this alloy was 8% Nb.

carefully weighed amounts of uranium and niobium. Since negligible weight changes were encountered upon preparing these standard alloys, their compositions are assumed to be quite accurate. The densities were determined by use of a pycnometer in which water was used as the immersing medium. These alloys are essentially quenched from the gamma range and the density-composition curve would not be expected to apply to alloys that have been slowly cooled. Portions of four of the co-reduced alloys were arc-melted, and their compositions were estimated from the curve as listed in the right hand column of the table.

Alloy numbers 6Wn through 11Wn were pickled in a HNO₃-HF solution preparatory to casting into ingot form. All six biscuits were placed in a BeO crucible inside a graphite heater. The crucible was equipped with a BeO disc in the bottom which could be unseated to permit pouring of the metal at the desired temperature. Casting was carried

out in a vacuum using induction heating. The melting temperature of the alloy was observed by means of an optical pyrometer to be about 1500°C. The metal was poured at 1675°C into a cold graphite mold. The cast ingot was about 16 inches in length, 1 1/2 inches in diameter and weighed approximately 15 pounds. The ingot was sampled by cutting disc-sections from the bottom, center, and top just below the pipe which extended down 4 inches into the casting. The results of chemical analysis and density measurements are shown in Table III. These results indicate that the ingot is nearly uniform from top to bottom, but shows a slight increase in niobium content from bottom to top. However, these values still lie within the specified limits of 10.0 ± 0.5 w/o Nb.

Table III

Analysis of Cast Ingot

Section of Ingot	Composition by Chemical Analysis		Composition as estimated from density
	w/o Nb	w/o U	w/o Nb
Top	10.05	89.88	10.35
Center	10.06	91.17	10.25
Bottom	9.70	90.89	9.80

The top section had a central core about 1/4 inch in diameter. This core was isolated from the rest of the section and was found to be enriched in niobium. Chemical analysis showed that it contains 11.4 w/o Nb as compared with 9.44 w/o Nb for a sample taken from near the periphery.

CONCLUSIONS

It has been demonstrated that a U-10 w/o Nb alloy can be prepared by the co-reduction of UF_4 and Na_2NbO_5 with calcium. Homogeneous alloys close to the desired composition can be prepared in this way. These may be melted in BeO and cast into an ingot of fairly uniform composition. No data are reported on the amounts of impurities such as carbon, oxygen or hydrogen. Neither has the method been applied to anything larger than a three pound reduction scale. Further work is needed on the study of these and other factors before a final evaluation of the method can be made. Such studies are currently in progress.

REFERENCE

Chiotti, P., and O. N. Carlson: Classified Research Progress Report. U. S. Atomic Energy Commission Report ISC-452, February, 1954, p. 26.

Fig. 1 - Density vs. Composition for U-Nb Alloys.

THE STRENGTHENING OF BERYLLIUM FOR HIGH TEMPERATURE USE BY MEANS OF BERYLLIUM OXIDE AND BERYLLIUM CARBIDE DISPERSIONS

by

J. Greenspan

Nuclear Metals, Inc.
Cambridge, Massachusetts

ABSTRACT

The high temperature rupture life of beryllium is extended considerably when small percentages of either oxide or carbide particles are well dispersed throughout the metal. Several alloys of each type were fabricated and tested in stress rupture at temperatures of 1200°F (648°C), 1350°F (732°C), and 1500°F (816°C). Results are plotted to compare: (1) the oxide alloys with each other, (2) the carbide alloys with each other, and (3) the oxide alloys with the carbide alloys. Correlations are shown between stress-rupture results and microstructure and particle content. In the carbide group of alloys, some stress-rupture properties are plotted as a function of carbon content.

INTRODUCTION

For altering the properties of beryllium to allow more desirable serviceability at high temperatures, say temperatures in the range of 1200°F (648°C) to 1500°F (816°C), it seems feasible to modify the beryllium microstructure by introducing in it, a dispersion of hard refractory particles. Such a modification, in the case of sintered aluminum powder,¹ for example, has proved to be fruitful, where a dispersion of aluminum oxide was introduced by means of the naturally occurring oxide coating on each powder particle. Here the aluminum oxide dispersion seems to be effective in altering the high temperature mechanical properties so that they appear to be more desirable for high temperature use.

Beryllium fabricated from powder normally contains beryllium oxide as an impurity since in air each powder particle is normally coated with oxide. Powder of -200 mesh size, when analyzed for oxide content, usually contains an amount of beryllium oxide of the order of 1% by weight. When beryllium formed from -200 mesh powder is tested in stress rupture, its rupture life does not seem to be appreciably different from that of cast beryllium,² where the oxide content is very much lower. However, when the average powder particle size is decreased, the stress-rupture life is increased, as shown later in this report. Thus, the beryllium oxide dispersion, when increased in amount, seems to be effective. Still more effective than beryllium oxide is beryllium carbide, as described later in this report.

As the dispersion content (beryllium oxide or carbide) is increased, the already existing brittleness problem in beryllium is magnified. Above a content of approximately 5% by volume, fragility is so increased that it no longer seems practical to handle, form, or machine the material with now standard techniques. This problem was somewhat alleviated by maintaining in the beryllium matrix, a texture which gives optimum ductility.³ For this, an extrusion, cross-rolling technique was adopted in fabrication, as described later. This rather large extent of hot working, besides producing the desired texture, would also be expected to produce the soundness usually characteristic of wrought metal and would also be expected to enhance dispersion of the dispersed particles. With this as a standard method of fabrication, several alloys were formed, machined into test samples, and tested in stress rupture.

PROCEDURES

For making alloys, powder-metallurgy techniques were used, employing Brush QMV powder. Powder mixtures were: (1) cold compacted in steel cans, (2) hot extruded at 1950°F (1062°C) to the shape of a flat, (3) re-jacketed, and (4) hot rolled at 1900°F (1038°C) an optimum amount transverse to the extrusion axis (see Fig. 1). This procedure yields a texture³ (see Fig. 2) which results in ductilities that are expected to minimize the brittleness problem. The product, in the form of sheet, was separated from its jacket, and from it stress-rupture samples were machined.

Samples were tested in stress rupture in apparatus shown schematically in Fig. 3. The sample was set in specially designed holders, which were inserted as a unit in the stress-rupture furnace. The furnace was sealed, evacuated, and then filled with argon gas, after which a small flow of argon was maintained through the apparatus. When desired, the sample was loaded by lowering the load support held in the Wilson seal. Strain readings were taken from Ames dial indicators coupled to top and bottom holders. The difference between the two dial

readings was taken as net strain in the sample. Strain vs. time curves were plotted to obtain minimum creep rates. Rupture times were recorded automatically when the falling load tripped a switch which stopped a timer.

Chemical analysis for oxide content was by a method based on volatilization of beryllium, while carbon content was determined by a tube furnace combustion method. For qualitative check for the presence of Be_2C and BeO , x-ray photograms were made using a 57.3 mm Debye-Scherrer camera.

Samples of concern here are conveniently divided into two groups: (1) those containing oxide, and (2) those containing carbon, presumably existing as beryllium carbide. Since -200 mesh beryllium powder was used for the carbide group, these samples contain also the amount of oxide characteristic of -200 mesh powder. The samples discussed in this report were "alloyed" or mixed as follows:

Group 1 - Oxide Alloys

- No. 1 Equal weights of -200 mesh (74 micron) QMV Brush powder and sized powder of 5 - 10 micron dia., mixed by dry tumbling. BeO content by chemical analysis, 2.06%. Carbon content as an impurity, by chemical analysis, 0.16%.
- No. 4 QMV Brush -200 mesh powder, as-received. BeO content by chemical analysis, 0.97%. Carbon content as impurity by chemical analysis, 0.15%.
- No. 5 QMV Brush -200 mesh powder, ball milled wet 24 hr and then dried in warm air. BeO content by chemical analysis, 2.71%. Carbon content as an impurity, 0.16%.
- No. 7 Mixture containing 93.5% QMV Brush -200 mesh powder and 6.5% Foote light fluffy BeO . BeO as-dispersed suspension in distilled water was added to beryllium powder, the mixture then ball milled for 24 hr and later dried in warm air. BeO content by chemical analysis, 12.95%. Carbon content as an impurity by chemical analysis, 0.10%.

Group 2 - Carbide Alloys

- No. 3 QMV Brush -200 mesh powder plus suspension of known concentration of colloidal graphite in water. Wet mixed by tumbling and then dried in warm air. BeO content by chemical analysis, 1.14%. Carbon content by chemical analysis, 0.85%.

- No. 3A Same procedure as No. 3, but with carbon content by chemical analysis found to be 0.98%.
- No. 9 Same procedure as No. 3, but with carbon content from chemical analysis estimated to be approximately 1.15%.
- No. 13 Same procedure as No. 3, but with carbon content from chemical analysis found to be 0.30%.

RESULTS

Apparently, the fracture is intercrystalline in samples tested at 1200°F (648°C) or higher. The photomicrograph in Fig. 4 of a ruptured sample of alloy No. 5 illustrates this. The remaining alloys, though not illustrated, show the same type fracture. Also visible in Fig. 4 is evidence of inclusions, many of which, significantly, are contained in grain boundaries.

Stress vs. rupture life curves for 1200°F (648°C) for the four beryllium-beryllium oxide alloys are given in Fig. 5. Correlated with the curves are photomicrographs of the various dispersion patterns. In discussing the curves, comparisons will arbitrarily be made at the 5000 psi stress level. Pertinent points with regard to fabrication history will be restated.

- a. Alloy No. 4, containing approximately 0.9% - 1% beryllium oxide by weight was formed from -200 mesh QMV Brush beryllium powder. The 5000 psi rupture life is about 2-1/2 hr, which is nearly the same as that for cast beryllium.²
- b. Alloy No. 1, containing approximately 2.06% beryllium oxide by weight, was formed from a mixture of -200 mesh (74 micron) QMV beryllium powder and an equal amount of 5 - 10 micron beryllium powder. The 5000 psi rupture life is about 12 hr, an appreciable increase over that of alloy No. 4.
- c. Alloy No. 5, containing approximately 2.71% beryllium oxide by weight, was formed from powder which was originally -200 mesh QMV and then ball milled to a finer particle size. The 5000 psi rupture life is about 6-1/2 hr, a value which, in consideration of the oxide content of alloy No. 1, is anomalous. This anomaly is tentatively associated with oxide distribution.
- d. Alloy No. 7, containing approximately 12.95% beryllium oxide by weight, was formed from a mixture of 93.5% QMV -200 mesh beryllium and 6.5% beryllium oxide. The mixture was ball milled to finer particle size. The 5000 psi rupture life is about 330 hr, an impressive increase over that of alloy No. 4. However, this material is fragile and difficult to handle.

For the carbide containing group of alloys, a similar set of stress vs. rupture life curves is given in Fig. 6. Since alloy No. 4 is taken as a standard for comparison, its curve is included. Alloys in this group were formed from mixtures of -200 mesh QMV Brush beryllium powder and colloidal graphite. Discussion is as follows:

- a. Alloy No. 13 contains 0.30% carbon, which is equivalent to approximately 0.75% beryllium carbide. The 5000 psi rupture life is about 4 hr, only slightly higher than that for alloy No. 4.
- b. Alloy No. 3 contains 0.85% carbon, which is equivalent to about 2.13% beryllium carbide. The 5000 psi rupture life is 181 hr, an impressive increase over that for alloy No. 4.
- c. Alloy No. 3A contains 0.98% carbon, which is equivalent to about 2.45% beryllium carbide. The 5000 psi rupture life is about 1180 hr, a second large increase.
- d. Alloy No. 9 contains approximately 1.19% carbon which is equivalent to about 2.98% beryllium carbide. The 5000 psi rupture life is 2495 hr. This constitutes a rupture life gain of about 1000 times over that of the standard (alloy No. 4).

In comparing the performance of the two groups of alloys with regard to percentage content of particles, it is apparent that the carbide is more effective than the oxide. In Fig. 7, stress vs. rupture time curves (1200°F) for alloy No. 3A, alloy No. 7, and alloy No. 4 are given. Table I summarizes some comparisons.

Stress vs. rupture life results show rupture life to be an increasing function of carbon content. For any particular rupture life, considered at 1200°F (648°C), the stress level also is an increasing function of carbon content. These functions for 100 hr, 1000 hr, and 10,000 hr (extrapolated) rupture lives are given graphically in Fig. 8. Table II summarizes briefly how the operating stress level is raised by increasing carbon content from 0.16% to approximately 1.2%.

Stress vs. rupture life curves were determined also for test temperatures of 1350°F (732°C) and 1500°F (816°C); all curves were shifted to lower values for higher test temperatures, but all alloys produced curves in the same relative positions. Fig. 9 illustrates how, by adding approximately 1.2% carbon, any given stress level for a 100-hr rupture life is shifted to a higher operating temperature. For example, the 2000 psi stress level is shifted from 1200°F to approximately 1450°F , an appreciable increase in operating temperature.

A Debye-Scherrer photogram, Fig. 10, confirms the presence of Be_2C in alloy No. 3. Though there is some uncertainty as to how much of the existing graphite entered into chemical reaction with beryllium,

the literature⁴ indicates that nearly all the graphite should form Be_2C during the hot-working operations at 1900°F - 1950°F (1038°C - 1066°C). Therefore, Be_2C content was estimated on the basis of carbon analysis.

The question of deterioration of the carbide alloys through hydrolysis of beryllium carbide is now considered. In alloys containing approximately 1.2% carbon or less, which were exposed to air, it is presently not obvious that deterioration occurs. Apparently, this is so because the beryllium carbide probably existing as pockets, or islands, is not exposed to air. However, when the carbon content is increased to a high enough level, the alloy deteriorates on exposure to air. This occurred in a sample containing about 1.6% carbon, presumably because the carbide now existed as a network. Apparently, the upper limit of carbon content is set by the hydrolysis problem.

SUMMARY AND CONCLUSIONS

In the beryllium-beryllium oxide alloys:

1. Practical methods for increasing oxide content in beryllium powder mixtures are: (a) by using beryllium powder of finer particle size, either sized powder or ball milled -200 mesh powder; (b) by ball milling of beryllium and beryllium oxide powder mixtures.
2. Extrusion and cross rolling is a practical way of hot working mixtures except when oxide content becomes higher than about 5% by volume.
3. Stress-rupture life at 1200°F (648°C) and higher is increased as oxide content is increased, but oxide dispersion also appears to influence rupture life. Using sized beryllium powder appears to be best in this respect. This method also provides good control in producing a desired oxide content.

In beryllium-beryllium carbide alloys:

1. A relatively easy and controllable method for introducing carbide is by adding controlled amounts of colloidal graphite in water suspension to beryllium powder and later hot working the compact.
2. Extrusion and cross rolling is a practical method for hot working alloys with carbon contents as high as 1.6%.
3. Contained graphite should almost totally react with beryllium during hot working to form beryllium carbide.

4. From a standpoint of percentage content, the carbide is much more effective in extending stress-rupture life than the oxide. This may be due to more thorough dispersion.
5. For any given stress level, rupture life appears to be an increasing function of carbon content. When carbon content is about 1.2%, the rupture life at 1200°F (648°C) for 5000 psi is increased about 1000 times. Stress levels or operating temperatures are shifted to higher levels with increasing carbon content.
6. The upper limit for carbon content seems to be set by the beryllium carbide hydrolysis problem where, above a given content, the alloy deteriorates in air.

TABLE I

Rupture Life Comparisons Showing Effectiveness
of Beryllium Carbide Content

<u>Alloy No.</u>	<u>Content</u>	<u>Rupture Life 5000 psi, 1200° F</u>
7	12.95% BeO 0.40% Be ₂ C ^a	330 hr
3A	2.45% Be ₂ C ^a 1.13% BeO	1180 hr
4	0.9% BeO 0.40% Be ₂ C ^a	2-1/2 hr

^aTotal carbon presumed to exist as Be₂C.

TABLE II

Effect of Carbon Increase on Stress Level

<u>Rupture Life (hr)</u>	<u>Stress for Rupture, psi</u>	
	<u>0.16% C</u>	<u>1.2% C</u>
100	2,100	8,000
1,000	1,100	5,200
10,000 (extrapolated)	600	3,600

REFERENCES

1. Grant, N. J.: Stress Rupture Testing. Report published in High Temperature Properties of Metals, ASM, 1951.
2. Kaufmann, A. R., P. Gordon, and D. W. Lillie: The Metallurgy of Beryllium. Trans ASM 42, 1950, p. 785-844.
3. Greenspan, J., and J. L. Klein: Ductility in Grain Oriented Beryllium. Minutes of Metallurgy Information Meeting, AEC, ORNL, 1955.
4. Theodore, J. G., W. W. Beaver, A. Dolance, and A. J. Stonehouse: The Production of High Purity Beryllium Carbide. Unpublished Report, The Brush Beryllium Company, Oct. 15, 1952.

RF 1959
Fig. 1(a) Schematic view. extrusion of beryllium powder.

44

RF 1958

Fig. 1(b) Schematic view, cross rolling of extruded beryllium powder mixture.

(0001) POLE FIGURE

RF 1929

Fig. 2 Basal plane texture in beryllium which results in high ductility in two dimensions.

RF 2658

Fig. 3 Section view of stress rupture testing furnace.

250X Pd. Lt.

A-615-4

Fig. 4 Edge view of ruptured face of beryllium-beryllium oxide sample tested in stress rupture at 1200°F (648°C). Beryllium oxide content, 2.71%.

500X (originally) Bt. Lt.

RF 2578

Fig. 5 Photomicrographs, rupture life curves for four beryllium-beryllium oxide alloys.

500X (originally) Bt. Lt.

RF 2580

Fig. 6 Photomicrographs, rupture life curves for four beryllium-beryllium carbide alloys.

500X (originally) Bt. Lt.

RF 2582

Fig. 7 Photomicrographs, rupture life comparison of beryllium-beryllium carbide alloy (No. 3A) and beryllium-beryllium oxide alloy (No. 7).

"Unalloyed" beryllium rupture life represented by No. 4.

RF 2577

Fig. 8 Stress level as a function of carbon content in beryllium-beryllium carbide alloys at 1200°F (648°C) for 100, 1,000, and 10,000 hr rupture lives.

RF 2576

Fig. 9 Stress as a function of temperature for 100 hr rupture life for unalloyed beryllium and beryllium containing about 1.2% carbon.

SAMPLE NO.3

DEBYE-SCHERRER X-RAY PHOTOGRAM
CuK α RADIATION

RF 2588

Fig. 10 X-ray photogram showing presence of Be_2C in alloy made by adding carbon to beryllium.

ON THE MECHANICAL METALLURGY OF ZIRCALOY-3b

by

D. E. Johnson

Hanford Atomic Products Operation
Richland, Washington

The tensile test properties in the rolling direction were determined for Zircaloy-3b. Tensile tests were performed with specimens in the annealed condition and in several cold worked conditions at testing temperatures of -50°C , 22°C , 100°C , 200°C and 300°C .

The effect of very short time annealing treatments on the tensile test ductility and on the microstructure of Zircaloy-3b is reported. One method for the application of short time annealing techniques to the annealing of tubular sections is described.

ON THE MECHANICAL METALLURGY OF ZIRCALOY-3b

by

D. E. Johnson

Hanford Atomic Products Operation
Richland, Washington

It is the purpose of this paper to briefly review two facets of an investigation of the mechanical metallurgy of a zirconium alloy containing 0.5% tin and 0.4% iron.

All of the test specimens used in this study were prepared from strips that were cut from hot rolled plate with their long direction parallel to the rolling direction of the plate. The strips were cold rolled to suitable thicknesses, annealed for two hours at 800°C in a vacuum of approximately 10^{-6} mm of mercury, and finally cold rolled to a thickness of 0.060". Cold reductions in area of 0% to 70% were obtained in this manner. Strips were cold rolled to a thickness of 0.040" to obtain specimens with an 80% reduction in area. Tensile specimens having a gage section one and one-quarter inches long by one-quarter inch wide were machined from the cold rolled strips.

Photomicrographs of the "as received" plate and of the rolled and annealed strip are illustrated in the first slide. It may be noted that the population density of the second phase particles appears to be greatest at or near the grain boundaries. Large stringers of this second phase were present in the hot rolled material in some areas, but are not shown in these photomicrographs. These stringers were broken up to some extent by cold working, but are still evident in the annealed material. The composition of the stringers has not been determined, but it is thought that they may be a zirconium-tin compound. Photomicrographs of Zircaloy-3b in the 50% cold-worked and 80% cold-worked conditions are also included to illustrate the effect of cold work on the structure of the material.

The second slide illustrates the tensile test data for the cold-worked material plotted as a function of the per cent cold work. Each point represents the average of the values which were determined for two specimens. The values of the tensile strength and yield strength

of 60% cold-worked Zircaloy-3b were found to be about 95,000 psi and 84,200 psi. Corresponding values of 110,000 psi and 98,000 psi have been reported by Mudge and Forscher (1) for 60% cold-worked Zircaloy-2.

The reduction of area of the 60% cold-worked Zircaloy-3b specimens was found to be about 27% while a reduction of area of about 35% has been reported (1) for 60% cold-worked Zircaloy-2. The reasons for this unexpected relationship of the ductilities of the two materials are not known at the present time. However, it is thought that the distribution of the second phase at the grain boundaries of the Zircaloy-3 and possibly a difference in the grain size of the materials for the two tests may be factors that contribute to the observed behavior.

Tensile specimens of the annealed and of the cold-worked material were also tested at temperatures of -50°C, 100°C, 200°C and 300°C, but unfortunately the specimen yield strength could not be determined for temperatures above 200°C. The third slide illustrates the yield strength of the material as a function of cold work with the test temperature as a parameter. It may be observed that the change in yield strength with temperature follows an orderly pattern and no evidence of an aging phenomena was observed. However, (fourth slide) a plot of the material tensile strength as a function of cold work for a test temperature of 200°C indicates that aging may have occurred in material that was cold-worked 15 to 20%.

Forscher has reported (2) that the normal increase in the ductility of Zircaloy-2 as measured by the tensile specimen necking strain was halted at a testing temperature of 150°C. This behavior may have been observed for Zircaloy-3b in the test temperature range reported here.

The next slide illustrates nominal stress-elongation curves for selected Zircaloy-3b tensile specimens which were tested at a temperature of 200°C. It may be observed that the maximum nominal stress occurred at about one to one and one-half per cent elongation. The uniform strain for these specimens was obtained by calculations based on the cross sectional area of the specimens outside of the necked region. The values of the uniform strain are tabulated in the chart inset and they were found in general to be about twice the magnitude of the strain at maximum load. This type of behavior has been reported by Keeler (3) for severely cold-worked crystal bar zirconium in the temperature range of 200 to 370°C, and was tentatively attributed to a combination of recovery and aging phenomena.

The annealing techniques that may be used to restore good ductility to a cold-worked structure are of particular interest to fabricators. Investigations (4, 5) which were made at Hanford have revealed that excellent ductility may be obtained by annealing zirconium and Zircaloy-2 for very short times in a salt bath. In the study of the short time annealing of Zircaloy-3 the specimens used were initially in the 50 per cent cold-worked condition. Specimens were annealed in a salt bath

containing Houghton 980 salt at temperatures of 725°C, 750°C, 775°C, and 800°C. The specimens were annealed for times of one-quarter, one-half, one, two, four and eight minutes and were then immediately quenched in a room temperature water bath. Duplicate specimens were sealed in quartz ampoules with a quantity of zirconium chips to act as a "getter". The atmosphere in the ampoules was commercial purity helium at an absolute pressure of about 20 cm. of mercury at room temperature. These specimens were heated in a muffle furnace for times of one-half, one, two, four and eight hours at temperatures of 750°C and 800°C and were then furnace cooled.

The sixth slide illustrates the tensile test elongation, uniform strain and reduction of area for the annealing study tensile specimens. From an examination of the figure the general observations may be made that the maximum elongation for the specimens that were annealed in an inert atmosphere is slightly greater than that observed for the salt bath annealed material; and that the maximum reduction of area for the salt bath annealed specimens is somewhat greater than that for the inert atmosphere annealed specimens. The reduction of area of a tensile specimen may be broken down into the reduction of area that results from the uniform strain and the reduction of area that occurs because of necking. When this analysis is applied to the data, it may be observed that the necking strain, which is illustrated in the seventh slide, is substantially greater for the salt bath annealed material than for the specimens that were annealed in an inert atmosphere.

A more detailed examination of the tensile test data for the Zircaloy-3 that was annealed in the salt bath (sixth slide) reveals that the elongation was a maximum and that the reduction of area was near a maximum for the specimens that were annealed for one-half minute at 750°C and for four minutes at 725°C. Material that was annealed at the higher temperatures does not exhibit improved ductility. In fact both the elongation and the reduction of area of specimens that were annealed at 800°C decrease markedly with increasing time at temperature. It is thought that this behavior may be attributed to an aging phenomena and probably involves the decomposition of the zirconium-iron eutectoid. (Zr Fe₂ eutectoid temperature is 800°C; the solid solubility of iron in zirconium at the eutectoid point is 2.5%)(6)

Photomicrographs of Zircaloy-3 specimens that had been given selected salt bath annealing treatments are illustrated in the eighth slide. As was expected, very little difference in the average grain diameter resulted from the various short time annealing treatments. It is of particular interest to note that recrystallization was essentially complete after only one-quarter minute at 725°C. For the samples which were annealed for relatively short times in the salt bath there appears to be a more random distribution of the second phase precipitate than was observed in the "base" material which was annealed for two hours at 800°C and furnace cooled. This observed behavior or its effect on the corrosion resistance of Zircaloy-3b has not yet been studied in detail.

The results of this annealing study illustrate that excellent ductility may be restored to cold-worked Zircaloy-3 by annealing for a relatively short time at a temperature of 725°C to 750°C. In terms of specific forming operations the test results have been tentatively interpreted as indicating that (1) for drawing a relatively long time annealing treatment at a temperature of about 750°C may be desirable; (2) for compression forming operations, such as tube reducing, a short time annealing treatment may be preferred.

A suggested schematic arrangement of the equipment that may be used for the short time annealing of tubular sections is illustrated in the last slide. The equipment consists of an induction coil, an inert gas shield assembly, and a water spray quench ring. In practice the tubular section may be advanced through the induction zone at a rate which will allow the material to remain at the required annealing temperature for the proper time interval. A supply of inert gas to the inside of the tube and to the gas shield protects the material from contamination by atmospheric gases. The water spray quench ring should be located as close as possible to the end of the gas shield to provide a minimum delay time before quenching from the annealing temperature and also to avoid exposing the hot tube wall to the atmosphere.

In summation, the following conclusions may be reached:

1. Zircaloy-3 exhibits desirable mechanical properties - although its strength is somewhat less than that of Zircaloy-2.
2. Zircaloy-3 specimens that were water quenched from an annealing temperature of 800°C exhibited evidence of a low temperature aging phenomena.
3. Excellent material ductility was obtained by annealing Zircaloy-3 for very short times at temperatures of 725°C and 750°C.
4. A method for the short time annealing of tubular products has been suggested.

REFERENCES

- (1) Mudge, W. L. Jr., and F. Forscher: Mechanical Properties of Zircaloy-2, WAPD-101, Confidential.
- (2) Forscher, F.: Effect of Cold Work on the Mechanical Properties of Zircaloy-2. WAPD-111, December 18, 1954.
- (3) Keeler, J.H.: The Tensile Characteristics of Unalloyed Zirconium at Low and Moderate Temperatures. Transactions of the American Society for Metals, Vol. XLVII, American Society for Metals, Cleveland, Ohio, 1955.
- (4) Wheeler, R.G.: Letter to W. P. Wallace, March 30, 1955.
- (5) Johnson, D.E.: A Study of the Short Time Annealing of Cold Worked Zirconium, HW-41372, February 29, 1956.
- (6) Miller, G.L.: Zirconium, Academic Press Inc., 1954, p. 264.

a. "As Received", 0.022mm

b. C. W. 50%, 2 hr. 800°C, 0.016mm

c. 50% cold worked

d. 80% cold worked

FIGURE 1.

FIGURE 2

TENSILE TEST MECHANICAL PROPERTIES OF COLD WORKED ZIRCALOY-3b

YIELD STRENGTH vs COLD-WORKED CONDITION FOR ZIRCALOY-3b
WITH THE TEST TEMPERATURE AS A PARAMETER

FIGURE 3

TENSILE STRENGTH vs COLD-WORKED CONDITION
FOR ZIRCALOY-3b WITH THE TEST TEMPERATURE AS A PARAMETER

FIGURE 4

NOMINAL STRESS-NOMINAL STRAIN TENSILE TEST CURVES FOR ZIRCALOY-3b
ILLUSTRATING THE EARLY LOAD PEAK FOR COLD-WORKED MATERIAL.
TEST TEMPERATURE, 200°C

FIGURE 5

ELONGATION, UNIFORM STRAIN, AND REDUCTION OF AREA FOR
ANNEALED ZIRCALOY-3

FIGURE 6

66

NECKING STRAIN FOR ANNEALED ZIRCALOY-3

FIGURE 7

a. 1/4M., 725°C, 0.016mm

b. 4M., 725°C, 0.013mm

c. 1/2M., 750°C, 0.019mm

d. 8M., 750°C, 0.019mm

e. 1/4M., 800°C, 0.019mm

f. 8M., 800°C, 0.016mm

FIGURE 8

SCHMATIC ARRANGEMENT OF EQUIPMENT
FOR INDUCTION ANNEALING OF TUBULAR SECTIONS

FIGURE 9

1/2 336

MECHANICAL PROPERTIES AND CORROSION BEHAVIOR OF ZIRCALOY-3

by

F. Forscher, S. Kass, and K. Goldman

Bettis Plant,* Pittsburgh, Pa.

Mechanical properties and corrosion behavior of four zirconium alloys, Zircalloys 2, 3A, 3B, and 3C, are compared. Strength and ductility properties are compared at several temperatures and in several heat treatment conditions in the transverse and longitudinal directions. Compression, impact and hardness test results are also reported. The strength properties of Zircaloy-2 are superior to any of the three alternate Zircaloy-3's. The ductility properties of the four alloys tested are not sufficiently different to favor one composition over another. Ingot size has no effect and melting practice has a minor effect on the mechanical properties.

In the 750°F steam test Zircaloy-3A is superior to Zircaloy-2 in that the post-transition rate is lower by about 20%. This alloy also continues to show better corrosion properties than do the 3B and 3C compositions. Indications based on results from transfer experiments are that a similar favorable ratio of post-transition corrosion rates exist at 680°F and 600°F. In the pre-transition region Zircaloy-2 and Zircaloy-3A, 3B, and 3C are indistinguishable. Corrosion tests are being continued.

1. INTRODUCTION

This report constitutes a summary of the mechanical properties and the latest information on the corrosion resistance of the three Zircaloy-3 compositions. It also affords a comparison of these alloys

* Bettis Plant is operated for the U.S. Atomic Energy Commission by Westinghouse Electric Corporation under Contract AT-11-1-GEN-14.

to Zircaloy-2 melted and fabricated under the same conditions. The nominal compositions of the four alloys are as follows.

	Alloy Content in Weight Percent (Balance--Sponge Zr)			
	<u>Sn</u>	<u>Fe</u>	<u>Ni</u>	<u>Cr</u>
Zircaloy-2	1.50	0.15	0.05	0.10
Zircaloy-3A	0.25	0.25	-	-
Zircaloy-3B	0.50	0.40	-	-
Zircaloy-3C	0.50	0.20	0.20	-

The three Zircaloy-3 compositions differ little among themselves and thus show only slight differences in properties, often only within statistical variation among ingots and among tests. Even the difference in composition between these alloys and Zircaloy-2 leads only to minor differences in properties, the most pronounced of which are an about 20% decrease in strength properties and an improvement of about 20% (in Zircaloy-3A) of the post-transition corrosion rate in high temperature water or steam. The corrosion tests are still in progress. The transition in 600°F water is not expected for another 800 to 1000 days, subsequent to which an additional 200 days will be needed to determine reliable post-transition corrosion rates. (The earliest Zircaloy-2 corrosion samples, after nearly 600 days in 600°F, have not yet reached the transition point.) In 680°F water the transition is reached in about 120 days.

Table I is a summary of the source material for this investigation. No results are presented for development Group I since no corresponding Zircaloy-2 ingots were melted, and thus no direct comparison is possible. Corrosion data reported herein are from development Group III only, chosen because these samples have been in test for the longest time (since March 1955). Corrosion coupons from all ingots of development Groups II, IV, and V are currently in test and will be reported on in the future.

Specimens for the mechanical tests are taken from the hot-rolled plates according to the scheme shown in Fig. 1. The heat treatment, type of test, and test temperature are shown in Table II. In the mechanical testing program, two specimens were tested per condition per ingot; four specimens per condition per ingot were used in the corrosion program.

The following is a summary of the most significant results of this investigation^{1,2} followed by a brief discussion of a few items of special interest.

2. SUMMARY OF RESULTS

2.1 Mechanical Properties

Averages of strength data from 12 tests (6 ingots) are presented in Fig. 2 and tabulated in Table III. Yield strength and tensile strength show the same trend with respect to direction of testing, testing temperature, and heat treatment. Of the three Zircaloy-3's the lowest strength is shown by Zircaloy-3A, but all three Zircaloy-3's have values below the strength of Zircaloy-2. This trend was also found to be true for the compressive strength. The relationship of longitudinal to transverse strength in the beta-quenched condition shows an opposite trend to that in the annealed or as-rolled conditions. The reason for this change in anisotropy upon heat treatment is not fully understood.

The impact strength of Zircaloy-2, particularly at 200°C, shows a definite advantage over the other compositions, which is in agreement with the findings above. The mean values of at least four tests are given in Table IV. Beta quenching improves the impact strength for all alloys and all ingot sizes tested.

The ductility of the four alloys is not greatly different (see Fig. 3). Average values from 12 tests (6 ingots) are given in Table V. Similar results were obtained in compression tests. However, some specimens did not fracture, indicative of good ductility and similar to the behavior of pure zirconium. The percent of specimens that did not fracture at 260°C was highest for Zircaloy-3C (11 out of 16) and next best for Zircaloy-3A (6 out of 15).

2.2 Corrosion Behavior

The corrosion tests are being conducted in the standard manner: i.e., specimens are degreased, etched in HF-HNO₃-H₂O to remove 2 mils per surface prior to test, thoroughly washed, and tested in deionized and degassed water or steam. Water tests are conducted at saturation pressure with 20% vapor space and specimens completely immersed in the water; steam tests are conducted at 1500 psig. Temperature is controlled to $\pm 5^\circ\text{F}$.

In 750°F steam, the four alloys exhibit similar transition times and weight gains; however, composition 3A shows the lowest post-transition corrosion rate (Fig. 4). Further evidence of the superior corrosion properties of composition 3A can be seen after 277 to 280 days exposure in 750°F steam; composition 3A possesses the thinnest oxide film, evidenced by the smallest weight gain (Table VI). A statistical "t-test" applied to the weight gains observed in 750°F steam after 193 days exposure indicates a significant difference between Zircaloy-2 and Zircaloy-3A.

In 600°F water, the post-transition corrosion rates, obtained by the transfer technique⁴ are the lowest for composition 3A. The transfer technique employs the faster corrosion rates at higher temperatures, say 750°F steam, to reach the transition point within practicable time and then continues the corrosion test at lower temperatures, say 600°F water. This technique provides reliable data if the mechanism of corrosion is the same at the two temperatures; thus only the corrosion rate is affected by the transfer from one temperature to the other.

3. DISCUSSION

3.1 Corrosion Behavior

An anomaly exists in the 750°F post-transition corrosion rate for Zircaloy-2. The rate obtained during 1952-1954 from many ingots melted at the Bureau of Mines from Bureau of Mines sponge was 1.27 mg/dm²/day. However, control specimens used in this study (melted at the Bureau of Mines, Allegheny Ludlum, and Firth Sterling from sponge zirconium produced by the Bureau of Mines and the Carborundum Metals Co.) show post-transition corrosion rates of approximately 0.50 mg/dm²/day. This discrepancy is unexplained but may be due to uncontrolled changes in the 750°F steam test technique.

Chemical analyses for impurity elements, aluminum, nitrogen, oxygen, and hydrogen, are given in Table VII. Vacuum melting lowers the hydrogen content significantly and also decreases the oxygen and nitrogen contents whereas the aluminum content does not seem to be affected. The effect of melting practice on microstructure is shown in Fig. 5 which indicates the tendency of gas-melted material to form stringers whereas vacuum-melted material appears to be free of this structural defect. Surprisingly, stringers have only a slight effect on the mechanical properties, the most pronounced of which is a decreased cold-formability (shearing or bending) in the "as-rolled" condition. After some annealing treatment or at elevated temperature this deficiency decreases to insignificant differences between vacuum-melted and gas-melted material. Stringered material shows a pronounced tendency for under-bead weld porosity.

3.2 Mechanical Properties

It is desirable to extrapolate the test results to such temperatures as are of interest to the designers of various reactors and reactor systems. An easy and reliable manner of extrapolation is shown in Fig. 6, where the logarithm of the strength value is plotted against the inverse of the absolute temperature. It must be kept in mind that this extrapolation cannot be carried to higher temperatures than are shown on the graph and that the lines represent mean values of test data with a spread of about 10% on either side of the line.

The inherent variability in addition to the pronounced effect of "hot working" on subsequent strength properties give rise to a wide spread of reported data on Zircaloy. A comparison of reported data in the as-rolled and base-annealed conditions for flat and round specimens is shown in Table XIII. The results from ingot D322, which are usually on the high side of the distribution, fall nicely in line with the averages of many ingots when base-annealed, round specimens are used. In general, annealing operations decrease the spread of data.

REFERENCES

1. Forscher, F.: Mechanical Properties Evaluation of Zircaloy-3. WAPD-143, March 26, 1956.
2. Kass, S.: Second Interim Report on the Corrosion Behavior of Zircaloy-3. WAPD-A1W(M-71), Feb. 27, 1956.
3. Forscher, F.: Pilot Run Evaluation of Zircaloy-3 Mechanical Properties. WAPD-LSR(MM)-19, May 9, 1955.
4. Thomas, D. E. and S. Kass: Effect of Prior Corrosion History on The Corrosion of Zircaloy-2 in High Temperature Water. WAPD-T-238, June 22, 1955.
5. Thomas, D. E. and F. Forscher: Properties of Zircaloy-2. J. Metals 8, 1956, 640-45.
6. Forscher, F.: Effect of Cold Work on Mechanical Properties of Zircaloy-2. WAPD-111, December 18, 1954.

TABLE I

SOURCE MATERIAL FOR ZIRCALLOY-3 MECHANICAL PROPERTIES EVALUATION

Devel. Group	Ingot weight and diam	Ingot Designation (Nominal Sn-Fe-Ni-Cr-Composition)				Source; Melting Procedure; Melting Atmosphere; Zirconium Source
		Zr-2 (150-15-5-10)	Zr-3A (25-25-0-0)	Zr-3B (50-40-0-0)	Zr-3C (50-20-20-0)	
I ³	20 lb-4 in.	-	E946	E949	E954	Bettis Plant; Nonconsumable first melt; He atm; BuM sponge
		-	E947	E955	E956	
		-	E948	E957	-	
II	300 lb-8 in. Code: 300A	5Y569 5Y570	5Y584 5Y585	5Y582 5Y583	5Y571 5Y572	Allegheny Ludlum; double consumable electrode; A atm; Carborundum sponge
III ^a	20 lb-4 in.	D199 -	E306 E278	E274 E276	E272 E302	
IV	600 lb-12 in. Code: 600A	5Y667 5Y679	5Y670 5Y678	5Y669 5Y675	5Y674 5Y676	Allegheny Ludlum; double consumable electrode; A atm; Carborundum sponge
V	600 lb-12 in. Code: 600V	FZ100 FZ99	FZ93 FZ94	FZ96 FZ95	FZ98 FZ97	

^aFor corrosion tests only

76

TABLE II
SCHEDULE OF MECHANICAL TESTS AND HEAT TREATMENTS
(Two specimens per condition per ingot)

<u>Type of Test</u>	<u>Specimen Design</u>	<u>Heat Treatment^a</u>	<u>Test Temp °C</u>
Tension (longitudinal)	3.0 in. gage length 0.253 in. diam	As rolled	R.T., 260
		Base annealed	R.T., 260
		Beta quenched	R.T.
Tension (transverse)	3.0 in. gage length 0.253 in. diam	As rolled	R.T., 260
		Base annealed	R.T., 260
		Beta quenched	R.T.
Compression (longitudinal)	1/2 in. diam x 1 in. long	As rolled	R.T.
		Base annealed	R.T., 260
		Beta quenched	R.T.
V-notch Charpy (longitudinal)	V-notch perpendicular to the rolling plane	As rolled	0,200
		Beta quenched	0,200

^a Base anneal: 750°C-20 hr-vac-F.C.
Beta quench: 1010°C-3/4 hr-helium-water quench
As rolled: Forged at 1700°F to 1-1/2 in.
rolled at 1550°F to 1/2 in. plus

TABLE III

YIELD STRENGTH AND TENSILE STRENGTH

(Each entry represents an average of 12 tests from 6 ingots)

		0.2% Yield Strength (1000 psi)				Tensile Strength (1000 psi)			
		<u>Zr-2</u>	<u>Zr-3A</u>	<u>Zr-3B</u>	<u>Zr-3C</u>	<u>Zr-2</u>	<u>Zr-3A</u>	<u>Zr-3B</u>	<u>Zr-3C</u>
<u>Room Temperature</u>									
As rolled	Long.	47.5	39.5	42.6	42.7	68.7	63.5	67.4	64.6
	Trans.	58.0	55.3	57.7	54.5	68.0	65.3	69.2	65.9
Base annealed	Long.	45.1	37.0	38.8	39.8	66.1	60.3	63.2	62.8
	Trans.	55.4	51.3	52.7	51.6	64.6	61.9	63.8	63.8
Beta quenched	Long.	82.0	70.2	75.0	65.9	97.0	88.1	94.3	85.7
	Trans.	72.5	69.3	69.7	70.5	91.2	88.0	89.1	90.3
<u>260°C (500°F)</u>									
As rolled	Long.	22.4	17.6	19.4	18.2	36.3	29.6	32.4	30.5
	Trans.	28.0	25.4	28.3	24.5	35.2	29.8	33.4	30.6
Base annealed	Long.	18.9	14.1	14.3	15.8	32.5	26.4	29.0	28.8
	Trans.	24.2	19.2	20.0	20.3	32.1	26.3	28.3	27.9

TABLE IV

V-NOTCH CHARPY IMPACT ENERGY, FT-LB

(Each entry represents an average of at least four tests)

	<u>Zr-2</u>		<u>Zr-3A</u>		<u>Zr-3B</u>		<u>Zr-3C</u>	
	<u>0°</u>	<u>200°C</u>	<u>0°</u>	<u>200°C</u>	<u>0°</u>	<u>200°C</u>	<u>0°</u>	<u>200°C</u>
As rolled								
20a	-	-	10.0	27.1	8.5	24.7	8.6	29.2
300A	5.0	13.4	5.0	8.5	4.8	7.8	5.8	12.8
600A	5.9	13.9	6.4	11.7	5.8	10.0	6.7	15.8
600V	6.4	21.2	7.0	12.4	4.8	9.4	8.3	23.4
Beta quenched								
20a	-	-	8.9	27.7	9.4	41.0	9.4	40.6
300A	13.3	30.4	13.4	31.9	12.5	29.6	13.6	30.4
600A	15.5	43.0	16.3	38.3	15.5	41.8	14.0	32.8
600V	22.5	51.0	20.5	39.5	17.5	41.0	17.1	40.4

^a Impact specimens from 20 lb ingots were broken at 260°C

70

TABLE V

DUCTILITY

(Each entry represents an average of 12 tests from 6 ingots)

		Uniform Elongation (%)				Total Elongation (%)				Reduction in Area (%)			
		<u>Zr-2</u>	<u>Zr-3A</u>	<u>Zr-3B</u>	<u>Zr-3C</u>	<u>Zr-2</u>	<u>Zr-3A</u>	<u>Zr-3B</u>	<u>Zr-3C</u>	<u>Zr-2</u>	<u>Zr-3A</u>	<u>Zr-3B</u>	<u>Zr-3C</u>
<u>Room Temperature</u>													
As	Long.	13	14	13	14	18	18	16	20	39	34	32	39
	rolled Trans.	11	12	14	11	19	19	22	18	41	40	37	43
Base	Long.	14	15	14	15	20	18	19	21	40	34	31	40
	annealed Trans.	12	12	12	11	22	20	20	19	40	39	36	44
Beta	Long.	3	7	6	7	8	12	10	10	45	48	43	40
	quenched Trans.	7	6	7	7	9	8	8	10	38	38	38	38
<u>260°C (500°F)</u>													
As	Long.	15	17	16	22	24	30	26	32	57	55	53	60
	rolled Trans.	20	19	19	22	26	27	26	29	59	59	57	58
Base	Long.	20	22	19	23	30	35	31	37	62	55	52	61
	annealed Trans.	24	24	24	24	32	34	34	35	61	58	56	64

50
TABLE VI

CORROSION BEHAVIOR OF 20-LB ZIRCALOY-3 INGOTS PREPARED BY BETTIS PLANT

Comp	Heat Treatment	Transition		Transition		Post Trans. Rate		Weight Gain, mg/dm ² after		
		Time, days		Wt. Gain		mg/dm ² /day				
		750°F	680°F	750°F	680°F	750°F	600°F	277d	280d	280d
								750°F	680°F	600°F
3A	900°C Quench	36	170 ^b	36	33 ^b	0.74	0.068 ^b	225	51	25
	775°C Fce Cool	45	168 ^b	40	34 ^b	0.34	0.042 ^b	101	57	23
3B	900°C Quench	37	170 ^b	38	38 ^b	1.05	0.065 ^b	285	58	27
	775°C Fce Cool	33	140 ^b	37	34 ^b	0.50	0.045 ^b	156	67	25
3C	900°C Quench	38	170 ^b	35	41 ^b	0.82	0.083 ^b	220	62	30
	775°C Fce Cool	39	168 ^b	38	34 ^b	0.57	0.058 ^b	154	66	30
Zr-2 ^a	775°C Fce Cool	41	112	41	34	1.27	0.065	285	98	25
Zr-2 ^c	775°C Fce Cool	41	135 ^b	41	34 ^b	0.53		150	65	26

^a Data obtained 1952-1954; average value of many Bureau of Mines ingots (still gaining weight after 2-1/2 yrs in 750°F steam)

^b Approximate values

^c Control specimens for this study

TABLE VII
CHEMICAL ANALYSIS (IMPURITY ELEMENTS, PPM)

<u>Type</u>	<u>Ingot No.</u>		<u>Al</u>	<u>N</u>	<u>O</u>	<u>H</u>
Zircaloy-2	5Y569	300A	50	44	1600	48
	5Y570	300A	62	43	1300	46
	5Y667	600A	45	39	1400	42
	5Y679	600A	49	57	1500	40
	FZ100	600V	46	30	1100	29
	FZ99	600V	44	30	1300	22
Zircaloy-3A	5Y584	300A	80	30	1600	42
	5Y585	300A	91	34	1200	40
	5Y670	600A	95	38	1500	43
	5Y678	600A	79	42	1200	41
	FZ93	600V	89	32	1200	22
	FZ94	600V	78	31	1000	27
Zircaloy-3B	5Y582	300A	75	-	1100	44
	5Y583	300A	89	-	1200	44
	5Y669	600A	78	42	1600	44
	5Y675	600A	55	43	1300	36
	FZ95	600V	60	30	1200	36
	FZ96	600V	62	34	1000	26
Zircaloy-3C	5Y571	300A	83	-	1200	45
	5Y572	300A	81	-	1100	43
	5Y674	600A	62	40	1500	45
	5Y679	600A	64	40	1500	41
	FZ97	600V	77	30	1500	27
	FZ98	600V	61	32	1000	21

82

TABLE VIII

COMPARISON OF ZIRCALOY-2 MECHANICAL PROPERTIES

Condition	Round Flat	Ref.	Longitudinal			Transverse		
			Y.S. KSI	T.S. KSI	R.A. %	Y.S. KSI	T.S. KSI	R.A. %
As-received (10 ingots)	F	5	49.4	75.6	28.3	70.0	77.5	37.1
Hot rolled (D322)	F	6	66.2	82.6	42.0	75.1	80.7	50.0
Hot rolled (D322)	R	-	50.3	71.4	43.0	63.8	72.0	47.0
As rolled (6 ingots)	R	1	47.5	68.7	39.0	58.0	68.0	41.0
Base annealed (10 ingots)	F	5	44.5	74.8	28.4	67.8	74.0	41.0
Base annealed (D322)	F	6	52.0	76.0	42.0	64.0	70.4	56.0
Base annealed (D322)	R	-	49.0	69.0	49.0	60.2	69.0	52.0
Base annealed (6 ingots)	R	1	45.1	66.1	40.0	55.4	64.6	40.0
<u>260°C</u>								
As received (10 ingots)	F	5	24.4	41.5	42.2	34.1	41.8	52.4
Hot rolled (D322)	F	6	39.5	50.8	60.0	44.1	48.7	69.0
Hot rolled (D322)	R	-	24.3	36.5	60.0	25.9	40.0	64.0
As rolled (6 ingots)	R	1	22.4	36.3	57.0	28.0	35.2	59.0
Base annealed (10 ingots)	F		no data					
Base annealed (D322)	F	6	25.4	38.8	69.0	27.5	35.0	74.0
Base annealed (D322)	R	-	19.1	33.7	66.0	23.2	31.4	65.0
Base annealed (6 ingots)	R	1	18.9	32.5	62.0	24.2	32.1	61.0

82

Fig. 1 Specimen Location in Test Plate (Plate Thickness 1/2 in. +)

54

SUMMARY OF STRENGTH DATA (EACH ENTRY REPRESENTS AN AVERAGE OF 12 TESTS FROM 6 INGOTS)

Fig. 2 Strength of Zircaloy at Room Temperature (white bars) and at 260°C (black bars)

85

Fig. 3 Ductility of Zircaloy at Room Temperature (black bars) and at 260°C (white bars)

Fig. 4 Zircaloy-3 Ingots Corrosion Behavior in 750°F Steam
 (20-lb ingots prepared at Bettis Plant, samples furnace cooled from 775°C, 4 samples from each ingot, 3 ingots each 3A and 3B, 2 ingots 3C)

Vacuum Melted

Argon Atmosphere Melted

FZ100

Zircaloy-2

5Y667

FZ93

Zircaloy-3A

5Y670

FZ96

Zircaloy-3B

5Y669

FZ98

Zircaloy-3C

5Y674

Fig. 5 Effect of Melting Practice on the Structure of 600 lb Ingots
(Longitudinal Sections 150X, As Rolled)

Fig. 6 Yield Strength and Tensile Strength of Base Annealed Zircaloy

CONSTITUTION OF URANIUM AND THE PLATINUM METALS

by

J. J. Park and R. W. Buzzard

The progress of the investigations of the constitution of uranium and the platinum metals (Ru, Rh, Pd, Os, Ir, and Pt) is presented. The solubilities of these and other transition metals in uranium are compared on the basis of radii, electronegativity, and comparable electronic structures of the ions.

The Atomic Energy Commission has for several years, sponsored a project on binary phase diagrams of uranium at the National Bureau of Standards. Previous project reports have been published on studies of the titanium-, beryllium-, silver-, and gold-uranium systems. Present studies are in progress on six of the nine Group VIII elements, specifically the Pt metals which had not previously been fully investigated. These six transition elements, i.e., ruthenium, rhodium, palladium and osmium, iridium, and platinum, exhibit many similarities in their alloying characteristics with uranium. Studies on the platinum-uranium system have been completed and are currently being prepared for publication; the ruthenium-uranium and the palladium-uranium systems are well along toward completion; and studies on the three remaining systems have only recently been initiated.

In general, the methods used have been thermal analysis, metallographic examination, and X-ray diffraction and powder methods. The alloys are melted either by induction or by arc-melting. The starting materials have been Mallinckrodt biscuit uranium and platinum metals of greater than 99.5% purity.

Thermal arrests were determined by time-temperature analysis and derived primarily from cooling curves. The thermal curves were obtained from specimens of approximately 50 g, which were heated and cooled at controlled rates of 2 deg C/min with the furnace operating under a vacuum of approximately 10 microns.

PLATINUM-URANIUM

The platinum-uranium system (fig. 1) was constructed from data obtained by thermal, microscopic, and x-ray analysis. The system is characterized by two eutectics: one of which occurs at about 11.8 weight percent of platinum and 1005°C, and the second at about 85.5 weight percent of platinum and 1350°C. There are four intermetallic compounds formed in this system; one is formed peritectoidally at 961°C having an apparent composition of UPt (45.0 W/o Pt); the second is formed peritectially at 1220°C having an apparent composition of UPt₂ (62.4 W/o Pt), which is the compound forming the terminus of the eutectic horizontal with gamma-uranium; the third is a congruently melting compound with an apparent composition of UPt₃ (70.9 W/o Pt) which has its melting point at approximately 1900°C; the fourth compound is one having the composition UPt₅ (80.1 W/o Pt) which is formed peritectically at approximately 1475°C.

The solubility of uranium in platinum appears to be between 4.4 and 6.5 weight percent, both at the eutectic temperature and at room temperature. However, due to the high cost of the materials used, there was no attempt to determine the solubility curve more exactly. The solubility of platinum in uranium was apparently 3.2 weight percent at the eutectic temperature.

The gamma-beta transformation of uranium, as determined from cooling curves, was lowered from 762° to 705°C, and the beta-alpha transformation temperature was lowered from 653° to 507°C by additions of platinum.

A hysteresis effect was noted between the uranium transformation temperatures derived from the heating and from the cooling curves. The heating curves showed reaction arrests some 40 degrees below the arrests for normal uranium but some 25 degrees above the arrests on the cooling curves. A similar type hysteresis has been observed in the other alloys of the platinum metal group.

The determinations of the freezing points of alloys melting above 1400°C were facilitated through the use of annealed molybdenum-tungsten thermocouples which, with each in a beryllia protection tube, could be lowered into the liquid alloy which was subsequently slowly cooled. An optical pyrometer was also used for determinations of the fusion point of the alloys, and was particularly useful in determining the temperature of the UPt₅ decomposition.

The compound UPt₂ was found to be reactive with the beryllia crucibles. In addition, homogenization of the alloys in this composition range indicated that this compound was very reactive with silica, which presented additional difficulties. By protecting the specimens from the silica with thin molybdenum sheet the alloys were amenable to homogenization so as to give the true two-phase structure

rather than a false single phase structure. Also, the compound UPt_5 was found to be highly reactive with both silica and molybdenum which resulted in alterations of its microstructure and also lowering of its fusion point.

RUTHENIUM-URANIUM

A tentative diagram of the partial ruthenium-uranium system has been constructed from data obtained by thermal, microscopic, and x-ray data. The liquidus of this system, determined from thermal analyses, shows a depression in the melting point of uranium with the addition of ruthenium, decreasing to 885°C at about 12 weight percent of ruthenium. The liquidus rises from this point to an as yet undetermined peak. The first intermetallic compound is formed peritectically at 948°C with the apparent composition of U_2Ru (18 W/o Ru). A second compound URu (30 W/o Ru) is also evident from the data thus far accumulated, and has an incongruent melting point, decomposing at 1180°C . A third compound is also present, having the composition URu_3 (50 W/o Ru) but its temperature of formation has not been determined.

The solid solubility of ruthenium in uranium is at a maximum at about 5 weight percent Ru at the eutectic temperature. The addition of ruthenium to uranium lowers the gamma-beta transformation temperature to 693°C and it lowers the beta-alpha transformation temperature to 618°C . (fig. 2).

Due to furnace limitations, the thermal curves for alloys with a melting point above 1400°C were determined by a hot-wire technique. In this technique, a slotted specimen of the desired alloy was hung over the tip of an annealed molybdenum-tungsten thermocouple, the tip of which had been previously coated with beryllia to prevent an alloy-couple reaction. The assembly was inserted in a tungsten radiator and heated by induction. The melting of the alloy was determined both by visual observation and by an automatic record of the couple e.m.f. An arrest was shown on the chart record and was noted to occur simultaneously with the observed melting of the specimen.

Alloys containing 57 and 71 weight percent of ruthenium melted at about 1575°C as indicated by this technique. In view of this, it appears that URu_3 is formed peritectically at this temperature.

The heat treating of the ruthenium-uranium alloys has encountered difficulties due to two reasons: (1) the loss of ruthenium on long homogenization treatments, and (2) the extreme reactivity of the alloys to the refractory materials used. The higher ruthenium alloys are sensitive to both silica and molybdenum, and are also extremely sensitive to beryllia.

PALLADIUM-URANIUM

A tentative diagram (fig. 3) of the partial palladium-uranium system has been constructed from thermal, microscopic and x-ray analyses. A series of alloys extending from 0 to 90 weight percent of palladium have been prepared; the alloys in the range 0 to 40 weight percent of palladium were made by induction melting, and the alloys of higher palladium content were made by arc melting.

The results from thermal analyses indicate that the uranium transformation temperatures are lowered by the addition of palladium, and that these transformations are detectable to at least 40 weight percent of palladium. In addition, other reaction horizontals were detected at 996°C and at 950°C. The horizontal at 996°C evidently indicates a eutectic reaction, and the horizontal at 950°C would seem to indicate the formation of a compound by a peritectic reaction. This compound is apparently located at 75 atomic percent palladium UPd_3 (55 W/o Pd).

The determination of the reaction horizontals in the high palladium alloys by thermal techniques indicated that the fusion point of the 80 weight percent palladium alloy was in the vicinity of 1300°C, and that of the 90 weight percent alloy was about 1400°C.

The addition of palladium to uranium lowers the melting point of uranium to 996°C. The gamma-beta transformation temperature of uranium is lowered to 738°C, and the beta-alpha transformation to 642°C. The solid solubility of palladium in uranium is between 0.5 and 1 weight percent of palladium at 996°C.

Due to the alloy-refractory reaction inherent in alloys containing 40 or more weight percent of palladium, the solidus temperatures of alloys in this higher composition range were determined by the hot-wire technique mentioned previously.

IRIDIUM-URANIUM

In the preparation of alloys of iridium with uranium by induction melting, a violent exothermic reaction is noted which expelled the charge from the crucible, the reaction becoming the more violent as the amount of iridium increased. When this reaction occurs it appears that the temperature of the melt increases several hundred degrees. If the melt is closely observed, and the power cut off at the point of the incipient reaction, the charge can be retained in the crucible.

An alloy containing 0.25 weight percent of iridium consisted of only a single phase after homogenization. An alloy of 2.5 weight percent was almost entirely single phase, indicating that the solid solubility of iridium in uranium is about 2 weight percent.

RHODIUM-URANIUM

The preparation of rhodium-uranium alloys by induction melting methods is possible in the range of 0 to 40 weight percent of rhodium. As contrasted to the difficulties encountered for the iridium alloys previously mentioned, there was no difficulty encountered in preparing these alloys by induction melting. However, a reaction between alloy and the beryllia crucible was apparent in the 40 weight percent rhodium melt. Alloys containing from 40 to 60 weight percent rhodium can be prepared by arc melting.

Results from thermal analysis indicated that the addition of rhodium lowers the melting point of uranium to approximately 870°C, with the formation of a eutectic at about 10 weight percent rhodium. There are indications that a reaction horizontal occurs at a temperature slightly below the 870°C eutectic horizontal. In addition, another effect of the rhodium additions is the lowering of the transformation temperatures of uranium.

OSMIUM-URANIUM

Alloys containing from 0 to 20 weight percent of osmium were prepared by induction melting in beryllia crucibles with no visible evidence of an alloy-refractory reaction. Alloys containing up to 75 weight percent of osmium can be prepared by arc melting.

Thermal analyses of alloys in the range of 0 to 20 weight percent of osmium indicate that osmium lowers the melting point of uranium to approximately 950°C to a eutectic which appears to occur at about 17 weight percent of osmium. These same results indicate that there is an appreciable solid solubility of osmium in gamma uranium. In addition, there is some evidence of a reaction horizontal at 945°C which appears to be the peritectic formation of a compound occurring in the vicinity of 8 to 10 weight percent of osmium. The gamma-beta transformation temperature of uranium is lowered to 684°C by the addition of osmium, and the beta-alpha transformation temperature is lowered to 639°C. Alloys of high osmium content may be difficult to analyze by thermal analysis methods as indicated by the fact that an alloy containing 80 weight percent of osmium exhibited no reactions below 1735°C.

In order to weigh the data just presented for these transition elements, it would be in order to review the data for the other transition elements. A consideration of the elements of the periodic table (fig. 4) shows that in the fourth period the solubility of the elements in uranium decreases from Ti to V to Cr, being the lowest at Fe and Co and increasing slightly with Ni. A similar situation appears in the fifth period except that the decrease in solubility apparently continues down to Pd. In the sixth period, Ta and W have little or no solubility in uranium whereas in the transition elements

the solubilities are comparable to those in group 5.

Some explanation of this difference exists in the electronic configurations of the elements. All the elements from group 4 through group 8 of these three series ionize to leave vacancies in the outer d band except Ta and W which lose the d band electrons first and hence their outer bands are the s bands which are not favorable to solubility. However, the outer bands of the balance of the group are comparable, being d bands, and it is logical to treat them as a group.

One rule of thumb in regard to solubility states that the size relationship is a criteria of solubility. This is indicated by plotting the solubilities of some elements in uranium on the vertical axis, with the difference in radius divided by the radius of uranium, expressed as percent, plotted on the horizontal axis (fig. 5). The vertical line represents a 15% deviation of the solute radius from the radius of the solvent. Hence the zone of small radius deviation which is the postulated favorable area is at the left of the chart. The data depicted by crosses shows the relationships calculated on the basis of the atomic radii. Although the bulk of the transition elements have very low solubilities, they all fall within the favorable zone; only five of the elements plotted show a solubility greater than 10 percent, and the magnitude of the percentage difference of atomic radii appears to have little bearing on the order of the solubility. However, if the same elements are considered on the basis of the ionic radii, as indicated by the circles, those elements of low solubility are placed outside of the favorable zone and the pattern appears to be more in line with the respective solubilities. Moreover, even though the ionic data alone appear to present the more accurate picture, in neither case is it possible to make accurate predictions of the solubilities.

A second rule of thumb often applied to solubility data is given by a comparison of the electronegativity versus the respective radii (fig. 6). The degree of solubility is theoretically shown by the location of the solute in respect to the solvent metal. The atomic radii are indicated by crosses, and on this basis a circle which includes all the elements of high solubility also includes Ag, Cr, Co, and W which spans the low solubility area to almost complete immiscibility in solid and liquid. Consideration on the basis of ionic data as shown by the circles presents a more clearly defined picture but still includes Cr and W. By comparing the platinum metals it is seen that no conclusion whatever could be drawn other than that their relationships are apparently similar. However, by their location it might be assumed that their solubilities might be comparable to Fe, Co, and Ni - a condition which the data presented previously does not confirm. It therefore is apparent that neither of these rules concerning the favorable radius or the electronegativity individually presents a clearly defined pattern.

However, by the application of direct ionic analysis (1) to this transition series, all the elements having outer unsaturated d bands may be grouped together and analyzed according to their solubilities (fig. 7). This graph shows the results of an ionic analysis of these elements. It will be noted that a direct and fairly accurate separation of the elements on the basis of their solubility in uranium has been accomplished by this method. Thus the platinum metals have been grouped with elements having known solubilities and the experimental data previously presented agrees with the predicted solubilities as shown by this chart.

(1) Buzzard, R. W., National Bureau of Standards Report 4032 (1955).

Figure 1. Tentative platinum - uranium phase diagram.

Figure 2. Tentative uranium-50 w/o ruthenium phase diagram.

Figure 3. Tentative uranium-40 w/o palladium phase diagram.

PERIODIC ARRANGEMENT OF THE METALLURGICAL ELEMENTS

	I	II	III	IV	V	VI	VII	VIII	VIII	VIII	I	II	III	IV	V	VI	VII	
2	3 Li 1524 534 6940 184 □ 196 □ 117 □ 186 1s ² 2s	4 Be 1115 9013 233 ○ 1283 1s ² 2s ²	5 B 1082 227 □ 2000 2s ² 2p	6 C 1201 3500 ○ 3500 2s ² 2p ²														
3	11 Na 185 971 22997 174 □ 977 2p ³ 3s	12 Mg 160 2432 2699 2696 242 ○ 650 2p ³ 3s ²	13 Al 143 2696 242 □ 660 3s ² 3p	14 Si 117 2809 182 ◇ 1430 3s ² 3p ²	15 P 30975 957 32066 □ 441 3s ² 3p ³	16 S 106 119 □ 119 3s ² 3p ⁴												
4	19 K 231 87 391 □ 63 3s ² 3p ⁴ 4s	20 Ca 196 155 4008 25 □ 450 □ 610 □ 850 3s ² 3p ⁴ 4s ²	21 Sc 160 45.1 4.5 □ 1400 3d 4s ²	22 Ti 146 4790 6.11 □ 882 □ 1690 3d 4s ²	23 V 131 5095 7.1 □ 1860 □ 1875 3d 4s ²	24 Cr 125 5201 72 □ 1095 □ 1134 □ 1245 3d 4s ²	25 Mn 112 720 □ 1095 □ 1134 □ 1245 3d 4s ²	26 Fe 124 5493 787 □ 910 □ 1388 □ 1495 3d 4s ²	27 Co 125 5894 8.9 □ 420 □ 1455 □ 1083 3d 4s ²	28 Ni 124 5869 8.9 □ 420 □ 1455 □ 1083 3d 4s ²	29 Cu 128 6354 6.4 □ 419.5 □ 298 3d ¹⁰ 4s	30 Zn 133 6538 5.91 □ 419.5 □ 298 3d ¹⁰ 4s ²	31 Ga 122 6972 5.36 □ 298 4s ² 4p	32 Ge 122 7265 5.73 ◇ 937 4s ² 4p ²	33 As 125 7491 4.8 ◇ 811 4s ² 4p ³	34 Se 116 7896 ◇ 209 4s ² 4p ⁴		
5	37 Rb 244 153 8548 254 □ 39 4s ² 4p ⁵ 5s	38 Sr 215 8763 5.51 □ 605 □ 770 4s ² 4p ⁵ 5s ²	39 Y 180 8892 6.5 □ 1475 □ 1860 4p 4d 5s ²	40 Zr 158 9122 8.4 □ 863 □ 1860 4p 4d 5s ²	41 Nb 143 9291 10.2 □ 2415 □ 2622 4p 4d 5s ²	42 Mo 136 9595 □ 2622 □ 3395 4p 4d 5s ²	43 Tc 99 122 □ 2500 □ 1966 4p 4d 5s ²	44 Ru 132 101.7 24.4 □ 2500 □ 1966 4p 4d 5s ²	45 Rh 134 1029 2.16 □ 1966 □ 1554 4p 4d 5s ²	46 Pd 137 1067 10.49 □ 1554 □ 9605 4p 4d 5s ²	47 Ag 144 10788 □ 9605 □ 321 4d ¹⁰ 5s	48 Cd 148 11241 7.28 □ 321 □ 155 4d ¹⁰ 5s ²	49 In 162 11476 7.29 △ 155 △ 231.9 5s ² 5p	50 Sn 151 118.7 6.691 △ 13 △ 231.9 5s ² 5p ²	51 Sb 145 121.76 6.24 ◇ 630.5 5s ² 5p ³	52 Te 143 12761 ◇ 450 5s ² 5p ⁴		
6	55 Cs 262 1873 132.91 35 □ 28 5p ⁶ 6s	56 Ba 217 87.3 6.73 □ 704 □ 1950 5p ⁶ 6s ²	57 La 187 6194 138.92 6.78 □ 920 5d 6s ²	58 Ce 182 140.13 6.776 140.92 6.998 14427 □ 804 4f 6s ²	59 Pr 182 67.6 6.776 140.92 6.998 14427 □ 935 4f 6s ²	60 Nd 181 61.6 6.776 140.92 6.998 14427 □ 1024 4f 6s ²	61 Pm 145 6.93 15043 5224 52.0 7948 □ 1052 4f 6s ²	62 Sm 62 15043 5224 52.0 7948 □ 1150 4f 6s ²	63 Eu 158 52.0 7948 □ 1350 4f 6s ²	64 Gd 178 56.9 8.332 159.2 8.562 162.46 8.764 164.94 9.164 □ 1450 4f 6s ²	65 Tb 173 56.9 8.332 159.2 8.562 162.46 8.764 164.94 9.164 □ 1450 4f 6s ²	66 Dy 173 56.9 8.332 159.2 8.562 162.46 8.764 164.94 9.164 □ 1450 4f 6s ²	67 Ho 174 56.9 8.332 159.2 8.562 162.46 8.764 164.94 9.164 □ 1450 4f 6s ²	68 Er 173 56.9 8.332 159.2 8.562 162.46 8.764 164.94 9.164 □ 1450 4f 6s ²	69 Tm 172 56.9 8.332 159.2 8.562 162.46 8.764 164.94 9.164 □ 1450 4f 6s ²	70 Yb 173 56.9 8.332 159.2 8.562 162.46 8.764 164.94 9.164 □ 1450 4f 6s ²	71 Lu 172 56.9 8.332 159.2 8.562 162.46 8.764 164.94 9.164 □ 1450 4f 6s ²	
7	87 Fr 223 5.0 226.05 □ 960 6s ² 6p ⁴ 7s	88 Ra 226 5.0 226.05 □ 960 6p ⁴ 7s ²	89 Ac 227 5.0 226.05 □ 1050 6d 7s ²	90 Th 180 61.6 6.776 140.92 6.998 14427 □ 1690 6d 7s ²	91 Pa 231 61.6 6.776 140.92 6.998 14427 △ 1300 5f 6d 7s ²	92 U 138 61.6 6.776 140.92 6.998 14427 □ 680 5f 6d 7s ²	93 Np 237 61.6 6.776 140.92 6.998 14427 □ 278 5f 7s ²	94 Pu 239 61.6 6.776 140.92 6.998 14427 □ 278 5f 7s ²	95 Am 241 61.6 6.776 140.92 6.998 14427 □ 278 5f 7s ²	96 Cm 247 61.6 6.776 140.92 6.998 14427 □ 278 5f 7s ²	97 Bk 247 61.6 6.776 140.92 6.998 14427 □ 278 5f 7s ²	98 Cf 249 61.6 6.776 140.92 6.998 14427 □ 278 5f 7s ²						

□

cubic

□

b.c. cubic

□

f.c. cubic

□

hexagonal

○

c.p. hexagonal

2

4

1

3

5

6

7

8

9

1 Element

2 Atomic Number

3 Atomic Radius

4 Density

5 Atomic Weight

6 Crystal Formation

7 Transformation Temperature (°C)

8 Melting Point (°C)

9 Electronic Configuration

◇ diamond cubic

◇ rhombohedral

◇ orthorhombic

◇ tetragonal

△ f.c. tetragonal

◇ monoclinic

Prepared by

Chemical Metallurgy Section

NBS

1955

- cubic
- b.c. cubic
- f.c. cubic
- hexagonal
- c.p. hexagonal

2	1	3
4		5
6	7	
8		9

- 1 Element
- 2 Atomic Number
- 3 Atomic Radius
- 4 Density
- 5 Atomic Weight
- 6 Crystal Formation
- 7 Transformation Temperature (°C)
- 8 Melting Point (°C)
- 9 Electronic Configuration

- ◇ diamond cubic
- ◇ rhombohedral
- orthorhombic
- △ tetragonal
- △ f.c. tetragonal
- ◇ monoclinic

Prepared by
Chemical Metallurgy Section

NBS

1955

Figure 4. Periodic arrangement of the metallurgical elements.

Figure 5. Relation between atomic and ionic radii and solubility of certain elements in uranium.

Figure 6. Relation between electronegativity and solubility of certain elements in uranium.

Figure 7. Influence of the number of compatibility factors on the solubility of certain elements in uranium.

PRODUCTION OF THORIUM-BISMUTH DISPERSIONS

by

J. S. Bryner
R. J. Teitel
M. B. Brodsky

Brookhaven National Laboratory
Upton, New York

Methods by which dispersions of equiaxed particles of thorium bismuthide in liquid bismuth have been produced on a laboratory scale will be described. These methods include various modifications of the reaction of solid thorium with liquid bismuth and a new method by which the dispersions can be produced from a solution of thorium in liquid bismuth. The scale-up of these methods to produce large batches will be discussed.

INTRODUCTION

The current design for Brookhaven's proposed Liquid Metal Fuel Reactor includes a breeder blanket for generating U-233 from Th-232. The proposed breeder blanket material is an alloy of approximately 10 weight per cent thorium in bismuth, in which the thorium is present as an intermetallic compound, tentatively identified as Th_3Bi_5 , uniformly dispersed in bismuth. The compound has a specific gravity of approximately 10.5, which is slightly higher than that of molten bismuth. The bismuth will be molten at reactor temperature, and the alloy fluid, so that it can be circulated into and out of the blanket region for processing to remove the bred products, Pa-233 and U-233.

During study of the Th-Bi system, it was observed that Th_3Bi_5 precipitates from a saturated solution of thorium in liquid bismuth upon cooling at normal rates in the form of platelets whose maximum dimension can exceed 1 cm. Such platelets are shown in Fig. 1. These platelets might plug small openings in a piping system. In addition, it has been observed that dispersions of the platelet form of the compound are very viscous at compositions as low as 4 wt. per cent

thorium. For these reasons, the platelet form of the compound is considered undesirable. Efforts have been directed toward developing methods for producing thorium-bismuth dispersions in which the thorium-bismuthide has a more nearly equiaxed shape. Several successful methods have been discovered.

METHODS OF PRODUCTION

A. Exfoliation - One method is to heat thorium in the form of thin chips or powder in contact with liquid bismuth at temperatures below the liquidus but above 420°C . This method produces equiaxed particles of thorium-bismuthide. It has been called the "exfoliation" method because of the nature of the reaction. Fig. 2a shows the reaction of a thorium chip in bismuth at 500°C for fifteen minutes. The reaction product at the thorium surface is a layer of indefinite structure. At high magnification (Fig. 2b), it is seen to be made of tiny particles less than $1/2$ micron in diameter. Where the thorium surface is fairly flat, the particles remain tightly packed together and the layer appears to protect the thorium from further reaction. Where the surface is convex with a suitably small radius of curvature, the particles separate as the layer grows thicker and exfoliate in ostrich-plume-shaped aggregates, exposing fresh thorium surface.

At the outer boundaries of these aggregates, the tiny particles which are presumably the compound, ThBi , react with the bismuth to form crystals of Th_3Bi_5 . These grow very rapidly at the expense of the smaller particles until the supply in the immediate vicinity is exhausted. Beyond this time they grow at a very much slower rate.

The overall rate of reaction is, therefore, controlled by the rate of exfoliation from the thorium surface, and hence increases as the convex radius of curvature of the thorium surface decreases. This point can be demonstrated by several examples.

Thorium powder of -100 mesh size reacts completely with bismuth in less than a minute as soon as the alloy is heated above 420°C , evolving appreciable heat. Thorium chips about .010 inch thick require heating in bismuth at 500°C for 2 hours for complete reaction. Thorium chips about .020 inch thick require heating at 500°C for 12 hours for complete reaction. Thorium plate about .050 inch thick heated in bismuth at 500°C for 2 hours showed formation of a surface layer but only a few Th_3Bi_5 particles. The effect of temperature upon the rate of reaction has not been studied.

The size of the largest Th_3Bi_5 particles produced is a function of the size of the "ostrich plume" aggregates and the number of simultaneously growing nuclei at the surface of each. Aggregates exfoliated from thorium surfaces with smaller radii of curvature are smaller and less dense, and produce smaller Th_3Bi_5 particles. Thus the Th_3Bi_5 particle size is affected somewhat indirectly by the thorium particle

size. This effect is not proportionate when the thorium particle size exceeds 40 microns, as can be seen by comparing Fig. 3a and 3b. These photomicrographs show alloys containing 5 per cent Th prepared by heating at 500°C for 2 hours using -325 mesh thorium powder (44 microns) and .010 inch thick thorium chips (254 microns) respectively. The maximum dimensions of the largest particles are 35 microns and 60 microns respectively. These dispersions contain the smallest average particle sizes normally produced. There has been some evidence that the average particle size can be decreased by agitation during the reaction, and by increasing the thorium concentration.

The compound particle size increases with the temperature of production because of precipitation of dissolved thorium upon the particles during cooling. If the liquidus temperature is approached too closely, the number of particles of undissolved compound may be insufficient to serve as nuclei for all such precipitation, and formation of platelets on cooling will result. Also, it is necessary to agitate the dispersion on cooling from higher temperatures to 500°C to keep the solid particles suspended. Otherwise, the particles will settle out, allowing platelets to form in the supernatant liquid. By observing these precautions, dispersions containing particles of satisfactory size and shape have been produced at temperatures up to 1000°C.

Dispersions can be produced using thorium chips by mixing the ingredients and heating under inert atmosphere. Although batches thus produced to date have been smaller than 1000 grams, the method should be applicable to production on a tonnage scale.

Production of dispersions using powder is more difficult. When thorium powder produced from thorium hydride or by electrolysis of fused salts reacts with bismuth, gas is evolved. The rising gas bubbles sweep the solids toward the top of the melt increasing the viscosity to the point where the bubbles cannot escape. The resulting froth, which contains a high percentage of thorium, may overflow the container unless special precautions are taken.

The frothing problem has been solved by adding the thorium powder a little at a time to the surface of the molten bismuth which is violently agitated by an impeller which forces the powder down into the melt. The smaller amount of froth which forms is broken up by periodically changing the gas pressure above the melt and continuing the surface agitation after all of the thorium has been added. By this method, batches of up to 70 pounds of dispersion containing up to 9 weight per cent thorium have been produced. The method could be scaled up to tonnage production by enlarging the equipment.

B. Electrolytic Method - Another method of making Th-Bi dispersions is based on a process for the production of metallic thorium by electrolysis of fused salts developed by Horizons, Inc. At Brookhaven's request, Horizons, Inc. has been attempting to produce suitable

dispersions by using electrolysis to introduce finely divided thorium into molten bismuth.

1. Direct Electrolysis - First attempts to electrodeposit thorium directly into molten bismuth using bismuth as the cathode were not successful. The initial thorium deposit reacted with the bismuth at the interface to form a hard crust of thorium-bismuthide which prevented the subsequent deposit from getting into the melt. Further work is planned to discover whether agitation of the bismuth surface will eliminate this difficulty.

2. Dummy cathode Method - Dispersions with satisfactory particle size and shape were produced by electrodepositing loosely adherent fine particles of thorium upon a dummy cathode in the salt above the molten bismuth, and then plunging the deposit into the bismuth, and agitating during the reaction. Basically, this method is a modification of the exfoliation method previously described.

C. Formation from Solution by Quenching and Reheating - Since virtually all of the thorium in these dispersions is in the solid thorium-bismuthide particles, the bred products, Pa-233 and U-233, are generated mostly within the solids. If, in processing the breeder blanket material for removal of bred products, it should be necessary to dissolve the solids by heating to a temperature above the liquidus in order to release the bred products, the problem arises of platelet formation on cooling and the resultant loss of fluidity.

It has been found possible to break up the larger platelets by mechanical stirring at 300-400°C and thus restore some of the fluidity. This procedure is being considered only as a last resort because it apparently requires extremely long stirring times to produce particles of satisfactory size and shape.

A method has been developed whereby dispersions of small relatively equiaxed particles of thorium-bismuthide can be produced from solutions of up to at least 10 weight per cent thorium in bismuth. In this method, the solution is rapidly quenched from a temperature above the liquidus by pouring into a cooled graphite crucible, thus producing extremely fine short platelets of Th_3Bi_5 . This fine platelet dispersion is then reheated for a short time at a temperature below the liquidus. This treatment causes the platelets to thicken without growing appreciably longer, thus approaching an equiaxed shape. By suitably modifying the conditions, particles of the desired size and shape can be produced.

The effect of quenching the solutions is shown in Fig. 4a and 4b. Fig. 4a shows an alloy containing 10 weight per cent thorium (soluble at 1060°C) quenched from 1100°C, and Fig. 4b shows an alloy containing 5 weight per cent thorium (soluble at 950°C) quenched from 1000°C, both by pouring into water cooled graphite crucibles. The layered structure

in Fig. 4a shows how the individual drops of solution flattened and froze in the fraction of a second before the following drops landed, and emphasizes the rapidity of the quenching rate necessary to produce the small platelets. The increases in particle size from the bottom to the top of each layer demonstrates the sensitivity of the dependence of particle size upon cooling rate.

Fig. 5a and 5b show two alloys of 5 per cent thorium which were heated to 1000°C and poured into crucibles heated at 300°C and 500°C respectively and then slowly cooled. The average size of the platelets is larger than in the alloys poured into water cooled crucibles because of slower cooling through the temperature range in which most of the compound precipitates. The very small platelets which can be seen in Fig. 5a indicate that under proper conditions platelets of suitable size can be produced without freezing the bismuth.

The effect of the time and temperature of reheating the small platelets is shown in Fig. 6a, 6b, and 6c. All three of the dispersions shown were produced by reheating pieces cut from an alloy of 5 per cent thorium in bismuth poured from 1000°C into a water cooled crucible like the one shown in Fig. 4b. The dispersion shown in Fig. 6a was heated at 600°C for 5 minutes. The platelets have thickened without an appreciable increase in length. Although many of the particles are elongated, the approach to equiaxiality is apparent. This dispersion has satisfactory fluidity.

The observed thickening is too great to be explained on the basis of solution on heating and precipitation on the undissolved particles on cooling, for the solubility of thorium in bismuth at 600°C is only 0.26 per cent. The explanation must be in fact that solubility increases as the radius of curvature of the solid surface decreases according to the relationship, $\ln S_r/S = K/r$, at constant temperature. S_r is the solubility at the surface of radius of curvature r , S is the solubility at a flat surface, and K is a constant for the system. This relationship demands that material dissolve from the edges of the plates and from smaller equiaxed particles and precipitate on the flat surfaces of the plates.

Fig. 6b and 6c, showing alloys which were reheated to 900°C for 5 minutes and one hour respectively, indicate that the degree of approach to equiaxiality increases with temperature and with time.

This method has been demonstrated on batches of up to 250 grams. The problem of scaling up the operation appears to be formidable because of the difficulty in rapidly cooling large batches. At Brookhaven's request, the American Metal Company, Ltd., is attempting to determine whether this might be accomplished by a shotting technique. Such a technique offers the possibility that, even if the cooling rate is not fast enough, the droplet size may be small enough to limit the platelets to a desirable size.

D. Ultrasonic Method - Another method has been conceived for producing equiaxed dispersions from thorium-bismuth solutions which uses ultrasonic vibrational energy to disrupt platelet formation during cooling from the solution temperature or to break up the platelets at lower temperatures. Ultrasonic vibration causes fragmentation of solids suspended in liquids by inducing cavitation at the liquid-solid interface. Cavitation has been observed in Brookhaven's High Velocity Loop which circulates bismuth. It has been demonstrated that the larger thorium-bismuth platelets can be broken up by mechanical stirring. Therefore, the method must be regarded as promising. Aeroprojects, Inc. is planning to study this method.

CONCLUSIONS

Several methods have been developed and others conceived for the production and reconstitution of dispersions of equiaxed fine particles of thorium-bismuthide in bismuth for use as a fluid breeder blanket material in a thermal nuclear reactor. Each of these methods has its peculiar advantages and disadvantages. Each shows enough promise to warrant further development to the point where the relative merits of each may be more accurately assessed.

Fig. 1-11 Per cent Th in Bi. Cooled from 1100°C at Moderate Rate. 3X

a. 15 minutes at 500°C. 150 X.

b. 5 minutes at 500°C. 2000 X.

Fig. 2 - Thorium chip in Bi.

a. 325 mesh powder. 150 X.

b. 0.01 inch thick chips. 150 X.

Fig. 3-5 Per Cent Th in Bi. 2 Hours at 500°C.

a. 10 per cent Th in Bi. Quenched from 1100°C. 150 X.

b. 5 per cent Th in Bi. Quenched from 1000°C. 150 X.

Fig. 4 - Th-Bi Solutions Quenched into Cold Crucibles.

a. Into crucible at 300°C. 150X.

b. Into crucible at 500°C. 150 X.

Fig. 5-5 Per Cent Th in Bi. Quenched from 1000°C.

150 X.

a. Reheated for 5 minutes at 600°C.

150 X.

b. Reheated for 5 minutes at 900°C.

c. Reheated for 1 hour at 900°C. 150X.

Fig. 6-5 Per Cent Th in Bi. Quenched from 1000°C into Cold Crucible and Reheated.

PREPARATION OF BORON-CONTAINING ALLOYS

by

A. P. Beard, J. W. Harrison, C. J. Beck

Knolls Atomic Power Laboratory
Schenectady, New York

Stainless steel base boron alloys with nominal compositions of 18 weight percent chromium, 14 weight percent nickel and 0.4 to 3.2 weight percent boron were successfully cast into ingots by vacuum induction melting. Alloy ingots containing up to 2.4 weight percent were fabricated into 0.100 inch strip by forging and rolling at 1140 to 1175°C. An ingot containing 3.2 weight percent boron could not be fabricated by the same procedure. Chemical analyses on as-cast ingots and rolled strip indicated very high boron recovery and good homogeneity. Brinell hardness numbers of the alloys were directly proportional, and measured densities were inversely proportional to boron content. Details on this work are available in KAPL-1371.

Zirconium base boron alloys with nominal boron compositions of 0.2 to 3.0 weight percent were prepared and fabricated by hot extrusion, hot rolling, and cold swaging. Chemical analyses on as-cast ingots, extruded rods and rolled strip indicated high boron recovery and good homogeneity. Brinell hardness numbers were directly proportional, and measured densities were inversely proportional to boron content. Details on this work may be obtained from KAPL-1555.

ALUMINUM-BORON AND ALUMINUM-URANIUM-BORON ALLOYS
FOR IMPROVED REACTOR PERFORMANCE

by

W. C. Thurber, J. A. Milko and R. J. Beaver
Oak Ridge National Laboratory
Oak Ridge, Tennessee

The problems associated with melting and casting homogeneous aluminum and aluminum-uranium alloys with borides of aluminum and nickel are reviewed. The results reported include pertinent physical and corrosion properties of these alloys; extent of segregation; irradiation testing program; and manufacturing procedures established for incorporation of boron into aluminum fuel elements.

The addition of boron to aluminum-uranium alloy fuel elements is desirable for the improvement of reactor performance. The boron, a burnable poison, reduces flux perturbation during the initial stages of reactor operation and enhances fuel element life. Three possibilities exist for incorporating boron into these fuel elements: (1) as an aluminum-uranium-boron ternary fuel alloy, (2) as an aluminum-boron binary cladding alloy, and (3) as a binary alloy in the side plates. Only the first two possibilities were considered in this investigation with the ultimate goal being development of a homogeneous ternary fuel alloy--intimate mixing of the boron with the fuel alloy being more desirable from a reactor physics standpoint.

The present work describes casting techniques for adding boron to both the cladding and core of MTR-type fuel elements. Physical and corrosion properties as well as irradiation performance of some of these boron-containing materials are also discussed.

Boron has no known solubility in solid aluminum, and the reported solubility in molten aluminum at 950°C is only 0.35%.⁽¹⁾ Two high-melting intermetallic compounds, hexagonal AlB_2 and tetragonal/graphitic AlB_{12} , are known to exist in the system. The lack of solid solubility coupled with the high melting point of the intermetallics create marked deterrents in the casting of homogeneous aluminum-base boron alloys.

Initially, a series of 7 aluminum-boron alloys, containing from 0.18% to 2.11% boron, were prepared by inert-gas arc-melting cold-pressed compacts of aluminum and boron powders. These alloys were remelted several times in an attempt to obtain maximum homogeneity. Figure 1 shows the microstructure (500X) of the 0.18% boron alloy. Scattered throughout the aluminum matrix are small rectangular platelets which have been identified by X-rays as AlB_2 . Figure 2 shows a similar alloy containing 0.55% boron. The important feature illustrated here is that, even after repeated remelting and rolling, microscopic inhomogeneity exists. In addition to this microscopic inhomogeneity, boron analyses taken of both ends and the center of each of these arc castings revealed that non-uniform distribution of boron also existed on a macroscopic scale.

Sheet metal tensile specimens were machined from each of these arc-melted alloys after rolling. The average properties of these specimens are summarized in Figure 3.

After the preliminary work on small arc melts, attention was directed to the production of slabs of aluminum-uranium alloy weighing about 1750 grams and containing 0.2% boron. Nine rectangular slabs having the nominal composition 17% U, 0.22% B, balance Al were cast, using finely-divided AlB_{12} (40-200 mesh) as the boron addition. All heats were prepared by open-air induction melting using graphite crucibles and molds. The boron recovery was extremely erratic and often low as is shown in Table I. Recovery was important not in terms of absolutes but merely as a measure of consistency in casting. Non-uniform distribution of boron with some tendency toward top segregation was also observed. The index of segregation of each of these castings, also included in Table I, establishes a relative basis of comparison for the segregation existing in each slab. This comparison is limited in that it does not show segregation trends but merely divergence from the mean boron content.

Dross samples taken from several melts were boron-rich, indicating that the AlB_{12} was being entrapped on the surface of the melt. Apparently the difference in densities of the AlB_{12} (2.58 gms/cc), and the aluminum-uranium solution (3.12 gms/cc) coupled with deleterious surface tension effects, allowed the aluminum boride to rise to the surface of the melt where it became absorbed by the oxide skin present.

To obtain improved wetting of the boron addition by the melt, blended, cold-compacted, and sintered mixtures of aluminum and AlB_{12} powders (5 parts Al to 1 part AlB_{12}) were examined. Favorable results were obtained with aluminum-boron binary alloys both from the standpoint of recovery and homogeneity (see Table I), but attempts to extend the use of the type of addition to aluminum-uranium-boron ternary alloys met with little success.

A cursory glance at the possible use of compacted mixtures of aluminum-amorphous boron rather than aluminum- AlB_{12} as addition agents indicated that no advantages were accrued.

Since powder metallurgy additions appeared to be inherently unsuitable for use in preparation of aluminum-uranium-boron alloys, other boron-containing master alloys were next investigated. With massive additions of this latter type it was felt that adverse surface tension effects could be overcome and losses of boron in the dross minimized. Experimentation with these materials substantiated this conjecture.

Previous work had indicated that arc-melted aluminum-boron master alloys of high boron content ($>20\%$) were difficult to dissolve in aluminum alloy melts. Therefore, master alloys of less than 5% boron were selected for study. Two such commercially available materials were investigated.

A complementary investigation of a nickel-boron master alloy was undertaken at the same time. The reported eutectic melting point of a 13% boron-nickel binary alloy is 900°C (2) and, therefore, such a material should readily dissolve in aluminum at moderate temperatures. Nickel-boron master alloys were prepared by arc-melting blended, cold-compacted and sintered mixtures of nickel and boron powders. The resultant alloys were extremely brittle and could be readily fractured into sizes suitable for addition to the melt.

The primary disadvantage of nickel is that it has a high thermal neutron cross section of 4.50 barns/atom. However, the nickel is present in such minor amounts that it increases the total absorption cross section of a standard MTR fuel element with 0.22% boron in the fuel alloy core by less than 0.2%.

As is illustrated in Table I, improvement in both homogeneity and recovery are manifest when a master alloy of either Al-B or Ni-B is used. However, nickel-boron additions are superior in both aluminum and aluminum-uranium alloys--the recovery being excellent in every case although the segregation tends to be somewhat erratic. Work is currently in progress to determine whether segregation anomalies can be minimized by cropping the castings prior to fabrication. Figure 4 illustrates the microstructure (500X) of an aluminum-boron-nickel alloy containing 1.5% nickel and 0.18% boron. The primary grains of aluminum are surrounded by a eutectic phase. Within the primary aluminum rectangular platelets similar in form and appearance to those found in aluminum-boron binary alloys (i.e. AlB_2) are observed. These particles may possibly be a complex aluminum-nickel-boride.

Table II shows the comparative mechanical properties of aluminum-boron alloys with and without nickel. An increase in tensile strength

of about 16% was realized by the addition of 0.78% nickel.

Preliminary corrosion data on 0.071% boron-aluminum and 0.079% boron, 0.75% nickel-aluminum was obtained both in boiling water (18 days) and in the MTR for one cycle (3 weeks) of irradiation. This initial work, which is being performed by Phillips Petroleum Company, is summarized in Table III. Although both materials tested were within tolerable limits, the material containing nickel-boron appears to be somewhat more corrosion resistant.

During this investigation three experimental MTR-type fuel elements containing enriched uranium were fabricated; two contained boron in the aluminum-uranium alloy core and one had boron incorporated into the cladding alloy. Standard fabrication techniques were applicable in preparation of these assemblies. A sound metallurgical bond between the boron-containing clad and the aluminum-uranium alloy core was readily obtained as is shown in Figure 5. However, fuel plates containing boron in the cladding were more prone to blistering and required special precautions to minimize this defect.

To briefly summarize then—the production of satisfactory boron-containing alloy involved overcoming, (1) segregation and (2) loss of boron during melting and casting. Nickel-boron master alloys appear only slightly more satisfactory than compacted Al / AlB_{12} powders or Al-B master alloys for producing boron-containing binary alloys. However, the nickel-boron master alloy is the only material investigated that has real potential as an addition to aluminum-uranium alloys.

References:

1. Metal Handbook. American Society for Metals, Cleveland, 1948,
p. 1155.
2. W. L. Bridges: Boron & Borides, Fairchild Engine & Airplane Corp.
Report NEPA-177-SCR-9, March 30, 1948.

As Polished

Figure 1. Al / 0.18% Boron Alloy Showing Rectangular Platelets of AlB_2 in Aluminum Matrix.

As Polished

Figure 2. Al $\neq$ 0.55% Boron Alloy Showing Non-Uniform Distribution of AlB_2 in Aluminum Matrix.

ORNL-LR-DWG 12107
 Y-18301

Figure 3. Mechanical Properties of Aluminum-Boron Alloys as a Function of Boron Content.

Etchant - 5% HF

Figure 4. Aluminum with 1.5% Ni and 0.18% Boron, Section Taken Perpendicular to Rolling Direction. Rectangular Borides Visible Within Primary Aluminum Grains.

As Polished

Figure 5. Cross Section of MTR-Type Fuel Plate with Al-B Cladding Illustrating Core/Clad Bond Integrity.

Table I.

ORNL-LR-DWG. 13300

**BORON RECOVERY AND SEGREGATION IN CAST ALUMINUM
AND ALUMINUM-URANIUM ALLOYS**

	TYPE OF ADDITION	RECOVERY - %	INDEX OF SEGREGATION*
1	AlB ₁₂	17	88
2		50	86
3		68	78
4		26	70
5		45	58
6		43	61
7		93	20
8		32	68
9		54	78
10	COMPACTED Al + AlB ₁₂	85	98
11		75	97
12		100	24
13		84	83
14		42	22
15		54	25
16		39	33
17		27	20
18		25	39
19	COMPACTED Al + B	86	33
20		70	73
21	Al-B MASTER ALLOY	74	90
22		100	66
23		74	76
24	Ni-B MASTER ALLOY	94	93
25		92	74
26		91	88
27		83	78
28		91	92

} WITH 17% U

} WITH 17% U

} WITH 17% U

} WITH 17% U

*100 = PERFECT HOMOGENEITY.

TABLE II
COMPARISON OF MECHANICAL PROPERTIES
OF Al-Ni-B AND Al-B ALLOYS

ALLOY	TENSILE STRENGTH (psi)	YIELD STRENGTH (0.2% OFFSET) (psi)	ELONGATION (2-in. G.L.) (%)
Al + 0.78% Ni + 0.13% B	10,170	2680	49.4
Al + 0.13% B*	8740	2570	44.8

* DATA INTERPOLATED FROM FIG. 3

TABLE III
CORROSION PROPERTIES OF CLADDING ALLOYS.

ALLOY	CORROSION RATE (INCHES PENETRATION PER YEAR)	
	BOILING WATER - 18 DAYS	MTR - 1 CYCLE
2S Al	$+ 2.9 \text{ TO } 5.3 \times 10^{-4}$	$- 4.0 \times 10^{-4} *$
0.079% B - 0.75% Ni - Al	$+ 2.9 \text{ TO } 5.3 \times 10^{-4}$	$- 3.9 \times 10^{-4}$
0.071 % B - Al	$+ 24 \times 10^{-4}$	$+ 7.8 \times 10^{-4}$

* IRRADIATED IN LITR

RADIOANALYSIS OF KRYPTON AND XENON
AND ITS USE IN DIFFUSION EXPERIMENTS WITH SILVER

By

J. Martin Tobin

Hanford Atomic Products Operation
GENERAL ELECTRIC COMPANY
Richland, Washington

ABSTRACT

A method has been evaluated which is capable of analyzing relative concentrations of krypton and xenon gases whose total concentration is in the range of 10^{-10} to 10^{-8} gram atoms. The necessary gas collection and gas transfer apparatus is described. Krypton-85 and xenon-133 are produced by neutron irradiation and their activities are counted with a gamma spectrometer. The isotopes are identified by the energy of their gamma radiation and their disintegration half-lives.

The use of the radioanalysis technique for the determination of diffusion coefficients of krypton in silver has proven successful. The equipment used in diffusing the gas, collecting the gas samples, and analyzing them are described. The values of diffusion coefficients at 500, 600, 700, 735, and 800 C are given. The values can be represented by the following equation,

$$D = 1.05 \exp^{-35,000/RT} \text{ cm}^2/\text{sec}$$

Thus, the activation energy for the diffusion of krypton in silver is 35 kilocalories per gram atom.

INTRODUCTION

In the ordinary sense of the word, the inert gases are chemically inert; however, under special conditions compound formation has been reported.¹ For example, under conditions of electron bombardment or electrical discharge in inert gas atmospheres, comparatively stable compounds of the gases with metals have been produced.^{2,3,4} Tolansky⁵ reports that considerable quantities of argon gas are absorbed in the hollow cathode discharge.

Several reports also exist in which the insolubility and lack of diffusivity of the inert gases are cited in metals.^{6,7,8} In the latter experiments, however, the inert gases were used under conditions of high temperature and pressure without ionizing the gas.

An interesting study of the diffusion of argon in silver has been reported by LeClaire and Rowe.⁹ Argon was introduced into the surface of silver sheet by means of a hollow cathode discharge. A sandwich was then prepared by cold welding two sheets of the silver together with their argon laden faces adjacent. The silver was irradiated in a nuclear reactor in order to form radioargon. Then the sandwich was heated to a high temperature, and the radioargon which diffused out of the center was counted. The diffusion coefficient for argon in silver derived from analysis of the gas activity data is given by the following equation:

$$D = 0.12 \exp^{-33,600/RT} \text{ cm}^2/\text{sec}$$

LeClaire and Rowe concluded that the argon atoms are quite mobile in silver metal and will diffuse through silver, provided they are first introduced into the metal by an energetic process such as gaseous discharge in the hollow cathode. If the inert gas atom must be chemically activated before it can enter the metal lattice, the activation step represents an extremely high energy barrier to diffusion under ordinary conditions. For example, unpairing the 1 s electrons in the helium atom and promoting one of these to the 2 s state should produce a helium atom having some chemical activity. This particular activation of the helium atom would require 460 kilocalories per gram atom of helium. Similar situations exist for all the inert gas atoms.

Based on a comparison of the rate of diffusion of argon in silver with the rates of various other atoms in silver, LeClaire and Rowe⁹ have decided that argon diffuses substitutionally by a vacancy mechanism; however, some doubt does exist as to the contribution of other diffusion and permeation mechanisms as the values of the diffusion coefficients which they obtained were not constant. The coefficient decreased with each successive anneal of the same silver specimen. In any case, it is quite evident that the main contributory diffusional process is that of volume diffusion because of the agreement with the space-time diffusion relationship as the authors pointed out.

OBJECTIVE

The mechanism of diffusion of the inert gases is of considerable theoretical interest in the field of gas-metal systems. The present paper deals with the study of the diffusion of krypton in silver. Any difference in the mobility of the two gases may be attributed to the difference in their atomic or ionic sizes since there is very little difference in chemical activity.

SUMMARY AND CONCLUSIONS

A method of irradiation and analysis of krypton and xenon was developed which is sensitive to relative changes in concentration in a range of total concentration of 10^{-10} to 10^{-8} gram atoms with less than 5 per cent error. The use of this method of analysis of the gas in the diffusion experiment is important because it eliminated the necessity of irradiating the silver metal and the resultant radiation damage to the metal.

The diffusion coefficients for krypton in silver were determined at 500, 600, 700, 735, and 800 C. Four separate annealing periods were used on the same silver specimen at each temperature without a change in the space-time diffusion relationship. The logarithm of the diffusion coefficient was found to be a linear function of the reciprocal absolute temperature obeying the following equation:

$$D = 1.05 \exp^{-35,000/RT} \text{ cm}^2/\text{sec}$$

Thus, the activation energy for diffusion of krypton within silver is 35 kilocalories per gram atom. The large pre-exponential term suggests a complex diffusion mechanism. The close agreement with the space-time diffusion equation indicates that krypton diffuses through the bulk of the silver and under the conditions of this experiment there was very little contribution from structurally sensitive diffusion processes such as grain boundary, crack, or void diffusion.

DISCUSSION

A. Preparation of the Silver-Krypton Sandwich

Krypton gas was introduced into the silver in nearly the same manner that LeClaire and Rowe⁹ used for argon. However, a few conditions were necessarily changed because of the discharge characteristics of krypton. The pressure of krypton was adjusted to 1.5 to 2 mm. The discharge began at about 240 volts DC (from a filtered full-wave rectifier). Discharge was conducted at a constant current of 30 milliamperes. The voltage across the tube varied between 420 and 500 volts depending upon the temperature of the cathode region of the tube.

High purity (99.99%) silver sheet of 0.010-inch thickness was rolled into a hollow cylinder about 1/2-inch in diameter by 2 inches long. This cylinder was slipped into a second one made of silver which served to protect the inner cylinder in the gaseous discharge. The bottom of the cylinder was a silver disc.

After an hour or two of discharge, the silver is found to contain krypton by the method of analysis which will be described later. It is quite uniformly distributed over most of the length of the cathode, but very little is found near the base where the metal has been sputtered. Since the gas seemed to be associated with the sputtered metal, a short period of discharge was used in order to keep the krypton concentrated in a very thin layer.

Pieces of the silver cathode were cut in order to prepare the silver krypton sandwiches. The silver pieces were placed together with the krypton laden faces adjacent and the sandwich was reduced 50 per cent in thickness down to 0.010-inch in a precision rolling mill. The sandwich was heated for 24 hours at 200 C (392 F) in order to produce a good metallurgical bond and the edges were trimmed. The sandwich was then ready for the diffusion experiment.

B. Diffusion of Krypton Out of the Silver

The cold-welded silver sandwich was then placed in the vacuum apparatus shown schematically in Figure 1. The silver was suspended above the tube furnace and could be raised and lowered by a magnet. The furnace was brought to temperature with the silver outside of the furnace. The apparatus was then evacuated and filled with helium to a pressure of roughly 2 mm of mercury. This was repeated several times in order to purge the system. The system was then isolated from the evacuation pumps and helium source by a mercury trap not shown in Figure 1.

Before the silver was heated, a sample of the helium gas in the closed system was taken for subsequent analysis of its krypton content. This was accomplished by starting up the mercury diffusion pump and the Toeppler pump. The helium was compressed into the quartz ampules. One of the ampules was then sealed off. It contained a volumetrically determined aliquot portion of the helium gas. The remainder of the gas was allowed to expand back into the furnace tube by raising the check valve magnetically.

The silver sandwich was lowered into the tube furnace for a known length of time at a constant, controlled temperature, and then raised out of the furnace. The helium gas was then pumped into the quartz ampules and another ampule was sealed off containing an aliquot portion of the gas. Subsequent analysis of the gas showed that the helium

now contained a small amount of krypton which had diffused out of the silver at the high temperature and was swept along with the helium through the pumps.

This procedure was repeated four times at the same temperature with the same silver sandwich. Each time the silver was annealed, more krypton diffused out of the metal. The four ampules were sealed off at varying lengths of time.

The silver sandwich was relowered into the furnace, and the temperature of the furnace was raised until the silver fused and released all the krypton remaining in the metal. The helium and krypton gases were again pumped into the sixth and last quartz ampule.

Analysis of the gas contained in the six ampules showed the fraction of the total amount of krypton present initially in the center of the silver sandwich that had diffused out of the metal in time, t ; this fraction is defined as γ .

C. Irradiation and Radioanalysis of the Gas Samples

A detailed drawing of the ampules before sealing is shown in Figure 2. Each of the ampules is about 1/2-inch in diameter by two inches long after sealing. The six ampules used in the diffusion experiment were packed into an aluminum capsule about 1-1/2 inches in diameter by 8 inches long. Aluminum wire was used as a packing material. The arrangement was spherically symmetrical and resulted in a uniform flux of neutrons when the capsule was placed in a reactor.

After irradiating the capsule for a short time, the capsule was opened and the ampules were delivered to a semi-hot lab where the irradiated gas was transferred to unirradiated glass ampules. The apparatus used is shown schematically in Figure 3. Each quartz ampule has a thin-walled blister blown in its side which serves as a break-seal.

The irradiated quartz ampule was sealed into the gas transfer apparatus. The apparatus was then evacuated and sealed off at the stopcock. The iron nail was dropped into the quartz blister and the irradiated gases were released. The volume of the Toeppler pump was large enough so that 99.7 per cent of the gas was transferred to the glass ampule in seven cycles of the pump. The glass ampule was then sealed and detached at a glass ball joint.

The six samples of gas were delivered to a counting laboratory which measured the activity of the gas with a gamma pulse height spectrometer. Typical spectrograms for irradiated krypton and xenon are shown in Figures 4 and 5, respectively. The xenon spectrogram is included because the method works at least as well for xenon as for krypton.

The presence of krypton or xenon in the helium carrier was determined both by the energy of the gamma radiation and by the half-lives of the radioisotopes. The relative amount of krypton or xenon was determined by comparing the integrated activities under a particular energy peak on the spectrogram for different samples of gas.

This analytical procedure was checked with ampules containing helium containing known amounts of krypton and xenon gases. The results of the calibration runs are given in Appendix A. It was found that the method was sensitive to relative changes in concentration of the inert gases, krypton or xenon, in a range of total concentration from 10^{-10} to 10^{-8} gram atoms, with less than 5 per cent error.

D. Results and Discussion

The data showing the fraction of gas, gamma, out of the metal in time, t , was used to find the diffusion coefficient D_T , at that temperature.

LeClaire and Rowe⁹ analyzed the Fick's Law of Diffusion for the boundary conditions existing in the silver sandwich. They obtained the following relationship between gamma and t :

$$\text{gamma} = 1 - \frac{4}{\pi} \sum_{s=1}^{\infty} \frac{(-1)^s}{2s-1} \exp^{-(2s-1)^2 \frac{\pi^2 Dt}{h^2}} \quad (1)$$

where h is the sandwich thickness and s is a summation index. The development of this equation is repeated in Appendix B.

Using equation (1), the diffusion coefficients were determined at 500, 600, 700, 735, and 800 C. The values are listed in Table I.

TABLE I

Diffusion Coefficients (D_T) for Krypton in Silver

Temperature °C °F		D_T (cm ² /sec)
500	932	3.8×10^{-10}
600	1112	3.3×10^{-9}
700	1292	2.2×10^{-8}
735	1355	4.3×10^{-8}
800	1472	1.2×10^{-7}

A graph of $\log D_T$ as a function of the reciprocal temperature is shown in Figure 6. The linear relationship is best represented in the following equation:

$$D = 1.05 \exp^{-35,000/RT} \quad (2)$$

This is the correct relationship for volume diffusion through a pure metal with a small concentration gradient. If diffusion occurs by means of imperfections such as vacancies, then the probability of an atom making an elementary diffusion jump, P_D , is proportional to the product of the probability of an imperfection existing adjacent to the atom by the probability of the diffusing atom jumping into the imperfection (rather than another atom bordering the imperfection). That is,

$$P_D = (P_E)(P_J) \quad (3)$$

For diffusion over distances very large compared to the mean distance between sources of imperfections, the diffusion may be assumed to occur under conditions of thermal equilibrium. The probabilities in Equation 3 may then be treated by Boltzmann statistics. The diffusion coefficient is found to be

$$D = r_0^2 U \exp^{-(E_f + E_M)/KT} \quad (4)$$

where r_0 is the jump distance, U the vibrational frequency of the diffusing atoms in the lattice, E_f the energy required to form an imperfection, E_M the energy barrier for the movement of the atom into the imperfection, K the Boltzmann's constant, and T the absolute temperature. This equation is usually written in the form of the Arrhenius equation:

$$D = D_0 \exp^{-H/RT} \quad (5)$$

because it is difficult to separate r_0 and U in the so-called frequency factor, D_0 ; and difficult to separate E_M and E_f in the activation energy, H .

The experimentally measured dependence of the diffusion coefficient D upon the temperature, T , in Equation 1 is of the form as Equation 5. It is assumed that the krypton diffuses through silver by a mechanism involving an imperfection created in thermal equilibrium in the silver, probably a vacancy mechanism. Also, it is shown that there is very little contribution from structurally sensitive diffusion processes since such mechanisms limit the rate of flow and diffusion is quite irregular. Structurally sensitive diffusion is very responsive to subtle changes in crystalline imperfections.

The comparable equation for the diffusion coefficient for self-diffusion in silver is given by Tomizuka and Slifkin,¹⁰

$$D = 0.57 \exp^{-45,500/RT} \text{ cm}^2/\text{sec} \quad (6)$$

A comparison of frequency factors shows that the frequency factor, D_0 , for krypton in silver is quite high. It is unusual that it be higher than that for self-diffusion in the solvent metal. This is an indication of a complex diffusion mechanism. The activation energy for krypton diffusing in silver is 35 kilocalories per gram atom. This is much lower than the 45.5 kilocalories found for silver self-diffusion. The difference can be expected from the difference in Goldschmidt's radii. The radius for krypton is 2.00 Å, which is much larger than the 1.44 Å radius of silver.

Evidently, there is little error caused by diffusion of krypton from the edges of the silver sandwich. A plausible explanation is given in Appendix C.

ACKNOWLEDGEMENT

The author wishes to acknowledge the help he obtained in numerous discussions with Dr. Spencer H. Bush, and the technical assistance of the Analytical Chemistry and Special Irradiations Units at Hanford.

REFERENCES

1. Moeller, T.: Inorganic Chemistry. John Wiley and Sons, Inc., New York, 1952, p. 378.
2. Manley, J. J.: Nature, 114, 1924, 861. 115, 1925, 997. Phil. Mag. [7], 4, 1927, 699.
3. Boomer, E. H.: Nature, 115, 1925, 16.
4. Kraft, H., and Rompe, R.: Z. Physik, 73, 1932, 681.
5. Tolansky, S.: High Resolution Spectroscopy. Methuen and Company, Ltd., London, 1947, p. 64.
6. Urey, W. D.: J. Amer. Chem. Soc., 55, 1933, 3242.
7. Henning, F.: Temperaturmessung. Handbuchder Physik, Berlin, 1926, p. 535.
8. Smithells, C. J., and Ramsley, C. E.: Proc. Roy. Soc., 150, 1935, 172.

9. LeClaire, A. D., and Rowe, A. H.: Revue de Metallurgie, 52, 1955, 94.
10. Tomizuka and Slifkin: To be published.

APPENDIX A

Analysis of Known Samples of Krypton and Xenon

Ampules were prepared containing helium at about 15 mm of mercury of pressure mixed with known quantities of krypton or xenon gases. Two sets of six were prepared. They were irradiated for a short time in a reactor. The samples of gas were transferred and counted according to the procedure outlined in the body of the article. The resultant activities of the gases are listed in Table II.

TABLE II

Post-Irradiation Activity of Krypton and Xenon
in Helium Carrier at Known Concentrations

Ampule	Gas Content	Activity* (0.150 Mev)
B1 - Krypton	none (vacuum)	0 counts/min.
B2 - Krypton	4.1×10^{-8} gram atoms	4.6×10^4
B3 - Krypton	6.2×10^{-11}	7.0×10^1
B4 - Krypton	2.6×10^{-9}	3.0×10^3
B5 - Krypton	2.5×10^{-8}	2.8×10^4
B6 - Krypton	none (He alone)	not detectable
J1 - Xenon	3.62×10^{-10}	1.4×10^2 (0.190 Mev)
J2 - Xenon	1.56×10^{-9}	6.1×10^2
J3 - Xenon	1.19×10^{-8}	4.62×10^3
J4 - Xenon	3.27×10^{-8}	1.24×10^4
J5 - Xenon	4.20×10^{-8}	1.63×10^4
J6 - Xenon	none (He alone)	not detectable

* All activities corrected to $t = 0$

An interesting fact determined from these data is that the integrated gamma activity under the energy peaks noted in the table are directly proportional to the known quantities of krypton or xenon added to the gas sample. The error is less than 5 per cent. The analytical procedure is sufficiently accurate to be used to determine gamma, the fraction of the gas diffusing out of the metal in time, t .

Secondly, the tank helium gas contains no measurable amounts of krypton or xenon gas.

Some evidence obtained when air leaked in to the diffusion apparatus indicates that the analytical method would also work for argon.

APPENDIX B

Space-Time Diffusion Relationship

Equation 1 in the article was taken directly from the LeClaire and Rowe⁹ article. The derivation was probably similar to the one that follows.

A mathematical model was used in order to set up coordinates and interpret the boundary conditions into the equations. The gas is assumed to be contained at time zero in a thin concentration zone in the center of the sandwich, which is presumed to be of infinite area. (The edge effect is discussed qualitatively in Appendix C) It is also assumed that the gas leaves the metal on reaching the surfaces of the sandwich and cannot re-enter.

The thickness of the zone of original concentration, c_0 , at time, $t = 0$, is taken to be $2b$. The thickness, x , goes from zero at one surface to h at the other surface of the sandwich. At all times, t , the concentration, $c = 0$ at $x = 0$ and at $x = h$.

Fick's Law of Diffusion is

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (1')$$

where D is the diffusion coefficient.

$$\text{If } c = X(x) T(t) \quad (2')$$

$$\text{then } \dot{X}T = D\ddot{X}T \quad (3')$$

$$\text{or } \frac{1}{D} \frac{\dot{T}}{T} = \frac{\ddot{X}}{X} = \text{a constant} = -k^2$$

$$(a) \dot{T} = -k^2DT; \quad (b) \ddot{X} - k^2X = 0$$

A solution of Equation 3'a in exponential form is

$$T = \exp \left[-k^2DT \right] \quad (4')$$

A solution of the harmonic Equation 3'b is

$$A \sin kx = X \quad (5')$$

To satisfy the boundary conditions, let $k = \frac{n\pi}{h}$

$$\text{From (1')} \quad c = \sum_{n=1}^{\infty} A_n \exp \left[-\left(\frac{n}{h}\right)^2 Dt \right] \sin \frac{n\pi}{h} x \quad (6')$$

At $t = 0$,

$$c = \sum_{n=1}^{\infty} A_n \sin \frac{n\pi}{h} x$$

$$c_0 = \int_{\frac{h}{2}-b}^{\frac{h}{2}+b} \sin \frac{n\pi}{h} x \, dx = A_n \int_0^h \sin^2 \frac{n}{h} x \, dx$$

$$A_n = \frac{2 c_0}{h} \left(\frac{h}{n\pi} \right) \left[\cos \frac{n}{h} \left(\frac{h}{2} - b \right) - \cos \frac{n}{h} \left(\frac{h}{2} + b \right) \right]$$

$$A_n = \frac{4 c_0}{n\pi} \left[\sin \frac{n\pi}{2} \sin \frac{n\pi}{h} b \right]$$

$$A_s = \frac{4 c_0}{(2s-1)\pi} (-1)^{s-1} \sin \frac{(2s-1)\pi}{h} b \quad (7')$$

Substituting (7') into (6')

$$c = \frac{4 c_0}{\pi} \sum_{s=1}^{\infty} \frac{(-1)^{s-1}}{(2s-1)} \exp \left[- \left\{ \frac{2s-1}{h} \right\}^2 Dt \right]$$

$$\sin \frac{2s-1}{h} \pi x \quad \sin \frac{2s-1}{h} \pi b$$

The amount of gas remaining in the foil after time t is

$$Q(t) = \int_0^h c \, dx \quad (8')$$

At $t = 0$,

$$2bc_0 = Q; \quad \gamma = 1 - \left[\frac{Q(t)}{Q(0)} \right]$$

$$\text{Thus, } \gamma = 1 - \frac{4h}{b\pi^2} \sum_{s=1}^{\infty} \frac{(-1)^{s+1}}{(2s-1)^2} \exp \left[- \left\{ \frac{2s-1}{h} \right\}^2 \pi^2 Dt \right] \sin \frac{2s-1}{h} \pi b \quad (9')$$

For small b

$$\gamma = 1 - \frac{(4)}{\pi} \sum_{s=1}^{\infty} \frac{(-1)^{s+1}}{2s-1} \exp \left[- \left\{ \frac{2s-1}{h} \right\}^2 \pi^2 Dt \right] \quad (10')$$

A graph of this function is shown in Figure 7. It can be seen from Figure 7 that the region of the greatest differential slope is the most sensitive and involves reasonable annealing times.

APPENDIX C

Side Diffusion From the Sandwich

The gas diffusing out of the sides of the sandwich apparently does not cause a large error since the diffusion coefficients followed the space-time diffusion equation. The side effects would act upon the diffusion coefficient in somewhat the same manner as structurally sensitive diffusion.

A reasonable explanation for this can be given if one considers that the diffusion path length will be shorter than one-half of the sandwich thickness only when it diffuses from a depth of about 0.005-inch or less. Thus, for a sandwich measuring one inch by two inches, only 0.030 square inches of the krypton concentration layer is affected. Since the concentration of the gas is uniform, less than 1.5 per cent of the krypton can diffuse out the sides and much of that will diffuse slowly.

Figure 1. Schematic drawing of the diffusion annealing apparatus.

144

QUARTZ AMPULES

Figure 2. Drawing of the quartz ampules before sealing.

144

Figure 3. Schematic drawing of gas transfer apparatus.

GAMMA SPECTROGRAM
KRYPTON 85
(4.4 HOUR)

Fig. 4. Gamma spectrogram of krypton 85. (4.4 hour half-life)

GAMMA SPECTROGRAM
XENON 125
(18 HOUR)

Figure 5. Gamma spectrogram of xenon 125. (18 hour half-life)

Figure 6. Temperature dependence of the diffusion coefficient, D , for krypton in silver.

Figure 7. Fraction of gas diffusing out of metal in time, t .

PREFERRED ORIENTATION IN EXTRUDED THORIUM ROD

by

L. K. Jetter and C. J. McHargue

Oak Ridge National Laboratory
Oak Ridge, Tennessee

Complete fiber axis distributions have been determined for thorium rods extruded at rates from 1 to 600 fpm at 850°C and for these rods annealed at 750°C. Slow extrusion speeds resulted in duplex $\langle 111 \rangle$ - $\langle 001 \rangle$ fiber textures with the amount of the $\langle 001 \rangle$ component corresponding to the amount of recrystallized material in the as-extruded rod. Annealing treatments at 750°C produced duplex $\langle 115 \rangle$ - $\langle 235 \rangle$ or $\langle 013 \rangle$ - $\langle 4,10,13 \rangle$ textures in these rods. Fast extrusion speeds resulted in $\langle 114 \rangle$ fiber textures which were unaffected by the annealing treatments.

The mechanical properties were determined and a correlation between properties and texture was established.

INTRODUCTION

Because of the crystallographic nature of plastic flow, processes used to produce wire, rod or sheet also produce textures in which certain orientations are preferred with respect to the principal applied or flow stresses. In rods or wires fabricated by a variety of procedures, the texture is referred to as a "fiber" -- in the ideal case, a definite crystallographic direction is aligned with the rod axis, but all other directions have a random distribution around the rod.

The deformation fiber textures of face-centered cubic metals have been reported to have $\langle 111 \rangle$ directions parallel to the wire or rod axis or varying ratios of $\langle 111 \rangle$ and $\langle 001 \rangle$.¹ The relative ratio of the components of the duplex texture has been considered characteristic of the individual metal and fabricating procedure.

Annealing deformed metals does not destroy preferred orientations, but gives rise to a variety of textures -- some similar to the deformation texture and some entirely different. The literature on face-centered cubic metals contains reports of a number of annealing components, i.e., $\langle 111 \rangle$, $\langle 001 \rangle$, $\langle 112 \rangle$, $\langle 013 \rangle$, and $\langle 012 \rangle$; ¹ however, the fundamental principles controlling texture formation are not yet known, and many of the early data are inadequate.

In order to obtain experimental data to serve as a basis for development of theories, a quantitative study of the textures of face-centered cubic metals and alloys has been undertaken. As a part of this program, the fiber axis distributions were determined for thorium rods having a variety of histories.

PROCEDURE AND RESULTS

Ames thorium containing 0.04 and 0.12% carbon was used in this study. Extrusions were made with billet temperatures of 850°C. Billets containing the lower amount of carbon were extruded to a rod diameter of 0.875-in. (a reduction area of 92.2%) using speeds of 2.3 and 588 fpm. The rods were die-quenched in order to retain, insofar as possible, the as-extruded structure. A portion of each rod was vacuum annealed one hour at 750°C.

Billets with the higher carbon content were extruded to 1-in. (reduction in area of 89.8%) using speeds of 1 and 600 fpm. A portion of each rod was vacuum annealed 30 minutes at 750°C.

On 0.20-in. spherical x-ray diffraction specimens, pole distribution data were obtained by a spectrometric method.² The technique developed for the purpose of getting quantitative data is illustrated in Fig. 1. A spherical specimen is mounted in the spectrometer plane of a conventional focusing spectrometer by means of a special goniometer. The specimen orientation is varied by rotating about an axis parallel to the reference direction (angle α) and about an axis perpendicular to the reference direction in the spectrometer plane (angle ϕ). Each axis passes through the center of the sphere. The Geiger counter, held stationary at the appropriate Bragg angle, measures an intensity which is proportional to the fraction of the irradiated volume of the sphere properly oriented to diffract. Since the specimen is spherical, diffraction geometry is the same for all values of the angles ϕ and α ; therefore, geometrical corrections in the recorded intensity are not required. Since the method employs a reflected x-ray beam, it can be used satisfactorily with metals of high absorption coefficients.

The pole distribution charts, normalized diffracted x-ray intensity, I vs ϕ , for a number of planes were used as a basis for determining axis distribution charts.³ On the latter charts, the contours indicate angular positions of equal normalized fiber axis density. A value of unity corresponds to a random distribution.

The axis distribution chart for the as-extruded rod containing 0.04% carbon fabricated at 2.3 fpm and given a reduction in area of 92.2% is shown in Fig. 2. The texture is duplex - $\langle 111 \rangle$ and $\langle 001 \rangle$ are the more preferred crystallographic directions of the fiber axis. The axis density at first falls off symmetrically from both peaks but then asymmetrically to form a low saddle along the $\langle \bar{1}10 \rangle$ zone. The $\langle 111 \rangle$ component was found to be associated with 75% of the volume and the $\langle 001 \rangle$ component with 25%. A metallographic examination showed a number of well developed recrystallized grains in a deformed matrix.

In Fig. 3 is shown the axis distribution chart for the as-extruded rod containing 0.04% carbon extruded at 588 fpm. A single $\langle 114 \rangle$ fiber texture was developed with a fairly symmetrical distribution about the position of maximum density. The microstructure showed this rod to be completely recrystallized in the as-extruded condition.

Annealing the slowly extruded rod for one hour at 750°C produced the texture shown in Fig. 4. The more preferred crystallographic directions of the fiber axis are $\langle 236 \rangle$ and a position 2° from $\langle 115 \rangle$. Note the asymmetry toward $\langle 012 \rangle$ which will be referred to later. The microstructure indicated complete recrystallization to a fairly uniform grain size. Neither of these components has been reported in the literature, although the $\langle 112 \rangle$ annealing texture reported in some cases may be nearer to $\langle 236 \rangle$ than $\langle 112 \rangle$.

Annealing the rod extruded at the faster speed produced no significant changes in either the $\langle 114 \rangle$ or the microstructure.

The axis distribution chart for the as-extruded rod containing 0.12% carbon extruded at a rate of 1 fpm to give a reduction in area of 89.8% is shown in Fig. 5. The texture is duplex - $\langle 111 \rangle$ and $\langle 001 \rangle$ - as in the case of the other rod extruded at a slow speed; however, the $\langle 111 \rangle$ component is associated with 96% of the material and the $\langle 001 \rangle$ component with 4% as compared to 75% and 25%, respectively. The distribution about the peak at $\langle 001 \rangle$ is quite asymmetrical although that about $\langle 111 \rangle$ is symmetrical. The microstructure consisted of a few small recrystallized grains in a deformed matrix.

Figure 6 shows the axis distribution chart for the as-extruded rod containing 0.12% carbon extruded at a rate of 600 fpm. The texture was a single $\langle 114 \rangle$ fiber as in the case of the higher purity rod extruded similarly. Again the microstructure indicated complete recrystallization.

The axis distribution chart for the rod extruded at 1 fpm and annealed 30 minutes at 750°C is shown in Fig. 7. The duplex texture can be described as near $\langle 013 \rangle + \langle 4,10,13 \rangle$ which is quite different from Fig. 4, ($\langle 115 \rangle + \langle 236 \rangle$). The asymmetry toward $\langle 012 \rangle$ noted in Fig. 4 may indicate a tendency for the formation of the $\langle 013 \rangle$ component in that specimen. The differences in these annealing textures are not understood at present. The obvious differences in the specimens are purity, annealing times and the ratio of

$\langle 111 \rangle$ to $\langle 001 \rangle$ texture components in the as-extruded material.

Annealing the rod extruded at the faster rate produced no significant change in the $\langle 114 \rangle$ texture nor the microstructure.

DISCUSSION OF RESULTS

Textures -- The "ideal" texture components as noted from the fiber axis distribution charts are summarized in Table I. The deformation texture of extruded thorium rod appears to be $\langle 111 \rangle$. The $\langle 001 \rangle$ component which was present with the $\langle 111 \rangle$ component is thought to be associated with grains which recrystallized during the fabrication process. This has been shown to be so in extruded aluminum rod; however, the evidence in the case of thorium is less direct. The relative amount of $\langle 111 \rangle$ and $\langle 001 \rangle$ components correspond to the relative amount of deformed and recrystallized material as determined metallographically.

TABLE I

Y-18673

Textures Found in Thorium Rod

Fabrication History	Fiber Textures
0.04% C	
As-extruded 2.3 fpm	75% $\langle 111 \rangle$ + 25% $\langle 001 \rangle$
Annealed 1 hour at 750°C	$\langle 236 \rangle$ + $\langle 115 \rangle$
As-extruded 588 fpm	$\langle 114 \rangle$
Annealed 1 hour at 750°C	$\langle 114 \rangle$
0.12% C	
As-extruded 1 fpm	96% $\langle 111 \rangle$ + 4% $\langle 001 \rangle$
Annealed 30 min. at 750°C	$\langle 013 \rangle$ + $\langle 4, 10, 13 \rangle$
As-extruded 600 fpm	$\langle 114 \rangle$
Annealed 30 min. at 750°C	$\langle 114 \rangle$

If the $\langle 001 \rangle$ component is accepted as having occurred due to a thermal process rather than a deformation process, six different texture components were noted in this study which had such origins -- $\langle 001 \rangle$, $\langle 114 \rangle$, $\langle 115 \rangle$, $\langle 236 \rangle$, and $\langle 4, 10, 13 \rangle$. Two of these components $\langle 001 \rangle$ and $\langle 114 \rangle$, appear when recrystallization occurred during the fabrication process and may have been influenced by strains or constraints connected with the process. Moreover, because of the speed of deformation, the temperature of the rods which developed the $\langle 114 \rangle$ component was higher than any other temperature in this study. This suggests the possibility that the $\langle 114 \rangle$ texture may be associated with a very high temperature process.

It has been found instructive by many investigators to relate the deformation and recrystallization texture components in terms of a rotation about some axis which moves one orientation into the other. The most commonly reported relationship for face-centered cubic metals has been rotations of 25-40 deg about $\langle 111 \rangle$ axes, although there have been a few reports of rotations about $\langle 001 \rangle$ and $\langle 011 \rangle$ axes.¹ It has also been reported that in

a number of instances the growth rates of grains related to a matrix by such relationships were higher than for other orientations. The physical basis for such relationships is unknown at the present time, but such observations have been taken as evidence for both the "oriented nucleation" and "oriented growth" theories of recrystallization texture formation.

Some possible retational relationships for the textures were observed in the present study and are shown in Fig. 8. These are summarized in Table II. On the basis of such rotational relationships, it appears that the $\langle 001 \rangle$, $\langle 115 \rangle$, and $\langle 013 \rangle$ components may originate in materials having a $\langle 111 \rangle$ texture and that the $\langle 236 \rangle$ and $\langle 4,10,13 \rangle$ components come from material having a $\langle 001 \rangle$ texture. It is striking that rotations about $\langle 011 \rangle$ axes may be more common than previously supposed and may be operative in three of the above cases.

Table II
Rotational Relationships Between Components of
Deformation and Recrystallization Textures

Y-18674

Recrystallization Component	As-Extruded Component	Angle of Rotation	Axis of Rotation
001	111	54°44'	$\bar{1}10$
115	111	38°30'	$\bar{1}10$
	001	19°30'	$\bar{1}11$
236	001	38°	$\bar{1}11$
013	111	45°	$\bar{1}11$
4,10,13	001	56°	101

CORRELATION OF PROPERTIES AND TEXTURES

Because of the crystallographic nature of deformation mechanisms, the mechanical properties of metals should be expected to depend upon the texture. Conventional tensile test specimens were taken from the extruded rods and data were obtained on the mechanical properties. These are shown in Table III.

Relative resolved shear stresses were calculated from the peak position of each texture component using the relationship $s = N \cos \chi \cos \lambda$ where χ and λ are the angles between the stress (rod) axis and the slip plane normal and the slip direction, respectively. The yield strength of a specimen would be expected to vary as the inverse of the resolved shear stress. In other words, the more of the applied stress that is resolved in shear on a slip system the more likely is slip to occur for a given applied stress level.

The ratio of the yield strength of the specimen having essentially all $\langle 111 \rangle$ texture to that having a $\langle 114 \rangle$ texture is 1.9 and the reciprocal of the resolved shear stresses is 1.7. The ratio of yield strength of the

155

TABLE III

Mechanical Properties and Textures of Thorium Rod^a

Condition	Texture	Yield Strength (psi)	Tensile Strength (psi)	Ultimate Strength (psi)	Elong. in (%)	Reduction in area (%)	Modulus of Elasticity (psi)	Cos χ cos λ
As-extruded (slow)	$\langle 111 \rangle$ $\langle 001 \rangle$	49,645	50,621	58,234	21	37	1.34×10^6	$\langle 111 \rangle - 0.27$
Annealed	$\langle 4,10,13 \rangle$ $\langle 013 \rangle$	31,250	39,000	78,500	49	69	8.05×10^6	$\langle 4,10,13 \rangle - 0.46$ $\langle 013 \rangle - 0.47$
As extruded	$\langle 114 \rangle$	26,234	30,496	66,628	42	70	7.65×10^6	0.45

a. 0.12% C

specimen having $\langle 111 \rangle$ to that having $\langle 013 \rangle + \langle 4,10,13 \rangle$ is 1.6 and the ratio of the reciprocal shear stresses is 1.7. The ratios for $\langle 013 \rangle + \langle 4,10,13 \rangle / \langle 114 \rangle$ are 1.2 and 1.05, respectively. The good agreement between yield strengths and calculated relative resolved shear stress indicates that in rods fabricated at these temperatures the texture markedly influences yield strengths.

REFERENCES

1. Barrett, C. S., Structure of Metals, 2d Ed. 1952, McGraw-Hill Book Company, New York, New York.
2. Jetter, L. K., and Borie, B. S., J. Appl. Physics, 24 (1953) 532.
3. Jetter, L. K., and McHargue, C. J., and Williams, Ro. O., J. Appl. Physics, 27 (1956) 368.

Fig. 1 Photograph of the preferred orientation goniometer containing a spherical diffraction specimen mounted in a Norelco High-Angle Spectrometer.

ORNL-LR-DWG 12961

Fig. 2 Axis distribution chart for thorium rod (0.04% C) reduced 92.2% in area by extruding at 2.3 fpm at 850°C.

ORNL-LR-DWG 12962

Fig. 3 Axis distribution chart for thorium rod (0.04% C) reduced 92.2% in area by extruding at 588 fpm at 850°C.

ORNL-LR-DWG 10111

Fig. 4 Axis distribution chart for thorium rod (0.04% C) reduced 92.2% in area by extruding at 2.3 fpm at 850°C and annealed 1 hour at 750°C.

ORNL-LR-DWG 4208

Fig. 5 Axis distribution chart for thorium rod (0.12% C) reduced 89.8% in area by extruding at 1 fpm at 850°C.

Fig. 6 Axis distribution chart for thorium rod (0.12% C) reduced 89.8% in area by extruding at 600 fpm at 850°C.

ORNL-LR-DWG 13183

Fig. 7 Axis distribution chart for thorium (0.12% C) reduced 89.8% in area by extruding at 1 fpm at 850°C and annealed 30 minutes at 750°C.

GRNL-LR-DWG 13182

Fig. 8 Some rotational relationships between the texture components observed in thorium rod.

MORPHOLOGY OF ZIRCALLOY-2

M. L. Picklesimer and G. M. Adamson, Jr.

Metallurgy Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee

ABSTRACT

Zircaloy-2 specimens were given a wide variety of conventional heat treatments. The microstructures show the effect of cooling rates on the beta to alpha transformation, the effect of annealing time and temperature on the beta quenched structure, the development of a partially randomizing heat treatment, and grain growth in the alpha and beta phases. The microstructure of a multipass weld is shown and compared to the conventionally heat treated structures.

INTRODUCTION

The nuclear requirements of the two-region reactor of the Homogeneous Reactor Project at the Oak Ridge National Laboratory have necessitated the use of a zirconium base alloy as the constructional material for the core tank. Consideration of the other requirements for the vessel caused the selection of the zirconium alloy known as Zircaloy-2, a sponge zirconium base alloy containing 1.5% Sn, 0.1% Fe, 0.05% Ni, and 0.1% Cr. Considerable developmental work was involved in the construction of the core tank, such as fabrication techniques for the alloy plate, forming techniques for the shaping of the sections of the vessel, and welding techniques for the fabrication of the formed sections into the vessel. Sufficient microstructural and physical testing work was done to insure the soundness and satisfactory operation of the core tank, but no extensive morphological and mechanical testing program was carried out to determine the optimum properties of the alloy for the present application.¹

A fairly extensive investigation of the microstructures characteristic of the various heat treatments and the resulting mechanical and corrosion properties was initiated to determine the optimum properties of Zircaloy-2, and to provide a background of information for the understanding and interpretation of the weld structure and radiation damage studies that are being carried out at the present. This report presents a portion of the morphological studies that have been carried out to date. No mechanical properties, as correlated to microstructure, have been determined, but such determinations are scheduled in the very near future.

RESULTS

The starting material for this experiment was 5/16-in Zircaloy-2 plate in the "as-received" condition, that is, after hot forging the arc cast ingot to a 4-in x 16-in x 16-in billet, and hot rolling from 816°C to 5/16-in plate with two reheats, the last reheat being to 11420°F. All fabrication was done in air with surface grinding, sand blasting, and pickling preparation of the plate during the hot fabrication to prevent an excessive buildup of oxide and surface defects. The microstructure of the "as-received" material is shown in Fig. 1, exhibiting a fine grained equiaxed alpha structure with intermetallics precipitated in the grain boundaries and as stringers. The specimen was manually ground through 400 grit wet emery paper, chemically polished with a solution of 50 parts water, 40 parts nitric acid, 20 parts hydrochloric acid, and 5 parts hydrofluoric acid, and anodized at 20 volts for 2 to 5 seconds in a solution of 60 ml ethyl alcohol, 35 ml water, 20 ml glycerine, 5 ml phosphoric acid, 10 ml lactic acid, and 2 grams citric acid, a modification of the procedure used on titanium by Margolin and Ence.² The anodized film is ZrO_2 , sufficiently thin to show interference colors. The oxide film increases the contrast in bright field and polarized light examination and may be used, in certain circumstances, to identify microconstituents by color.

That the small spherical precipitates and the stringers are intermetallics is demonstrated by the microstructure of Fig. 2. The specimen was held at 840°C for 30 minutes and water quenched. The microstructure shows that approximately 15% beta was present at temperature, and that the beta phase was formed from the alpha grains and the precipitate. No precipitate can be seen in any of the grain boundaries. The beta phase was not retained on quenching but a partitioning of the alloying elements causes a difference in composition between the alpha that was beta at temperature and the alpha that was unchanged, sufficient to cause a difference in color on anodizing. A specimen held for two weeks at 840°C showed essentially the same structure. Cathodic etching of the "as-received" material has verified the conclusion that the stringers are intermetallics by showing continuity between the stringers and the alpha grains, a stringer showing up only because it serves as a common boundary for several grains.

Specimens were water quenched, air cooled, and furnace cooled from 1050°C, a temperature within the beta field. The resulting structures are shown in Figs. 3, 4, and 5, respectively. The structure of transformed beta is essentially the same, for the different cooling rates, differing primarily in the size of the acicular alpha needles and the formation of an intermetallic precipitate in the boundaries between the alpha needles in the specimens which were not water quenched.

Specimens were held at a series of temperatures from 700°C to 1100°C and water quenched. Examination of the microstructures of these specimens established the alpha/alpha plus beta temperature as 810°C and the beta/alpha plus beta temperature as 970°C.

An attempt to remove the highly oriented texture of the "as-received" material was made by annealing the water quenched beta structure at a series of temperatures. The microstructure shown in Fig. 6 was the result of annealing the beta quenched structure at 600°C for two hours. The acicular needle structure has only sharpened. Annealing at 700°C caused a recrystallization of the beta quenched structure which was not complete in two hours. Very large almost equiaxed alpha grains absorbed the acicular needles formed on quenching. Annealing at 800°C for 15 minutes resulted in a smaller equiaxed alpha grain size and a greater absorption of the acicular alpha needles. This structure is shown in Fig. 7.

Cold working the beta quenched structure resulted in the microstructures shown in Figs. 8, 9, 10, and 11. The specimens were water quenched or air cooled from 1000°C and cold rolled 10 and 20% before annealing at 800°C for 15 minutes. The slower quench (air cooling) and the smaller amount of cold work resulted in a larger grain size for the material. Cold rolling 20% is required in order to cold work the center of the plate sufficiently to prevent the very large grain size found for the 10% cold worked specimen. Texture determinations on the water quenched and 20% cold rolled specimen indicate that the texture is somewhat more randomized than the initial texture but that a completely random texture still has not been obtained.

A macrograph of a weld section in 5/16-in Zircaloy-2 plate is shown in Fig. 12 and the related microstructures in Figs. 13, 14, 15, and 16. The weld was made by tack welding a root insert in place, fusing, and making three filler passes. Figs. 13 and 14 show the microstructure at the fusion line in bright field and polarized light respectively. The intermetallic stringers, which are very thin in the parent material, have partially dissolved and have opened up, forming elongated voids near the fusion line. The beta grains have grown across the fusion line with no appreciable increase in grain size. A thorough examination of the weld shows that the only clear marker for the fusion line is the disappearance of the stringers. Fig. 15 shows the microstructure of the parent metal side of the heat affected zone

of the weld. One diagonal of the micrograph crosses the structures from the cold worked parent metal through a zone of recrystallization of the cold worked structure, through a zone of structures of alpha plus beta, and to the all beta structure zone, all within a distance of not more than 0.05 inches in the weld. The structure of the deposited weld metal in the center of the weld is shown in Fig. 16. The grain size is from 0.5 to 1 mm in diameter.

CONCLUSIONS

The study of the heat treated structures of Zircaloy-2 has allowed the following conclusions to be drawn as to the morphological characteristics of Zircaloy-2.

- (1) The rate of grain growth of equiaxed alpha grains is very slow, once the grains have become equiaxed.
- (2) The rate of grain growth of beta grains is very slow once the specimen has transformed to the all beta structure, the grain size for a specimen held at 1080°C for 2 hours being not more than 10% larger than that for one held at 980°C for 15 minutes, and both being approximately the size of beta grains in deposited weld metal.
- (3) The very large beta grain size observed is formed during the heating through the alpha plus beta temperature range, the grain size for the all beta structure being very little larger than the beta grain size for a 95% beta-5% alpha structure.
- (4) The alpha/alpha plus beta temperature of Zircaloy-2 is 810°C and the beta/alpha plus beta temperature is 970°C.
- (5) The intermetallic stringers present in the "as-received" material can be almost completely dissolved in 30 minutes at 1000°C, leaving less than 10% of any one stringer undissolved. Holding for 2 hours at 1080°C did not cause the complete solution of the stringers.
- (6) The structure of transformed beta is essentially the same whether the beta is water quenched, air cooled, furnace cooled, or isothermally transformed, differing primarily in the size of the acicular alpha needles and the formation of an intermetallic precipitate in the boundaries between the alpha needles in the specimens which were not water quenched.
- (7) The preferred orientation texture of the "as-received" material is not randomized by any simple combination of heat treatments, and is only partially randomized by cold working the water quenched beta structure.
- (8) The transformed beta structure can be recrystallized by annealing above 700°C. A higher temperature of annealing results in a finer grain size.

REFERENCES

1. Elder, G. E., E. C. Miller, L. F. Bledsoe, and F. V. Daly: Fabrication of a Large Zirconium Tank. Jnl. Metals, May, 1956.
2. Margolin, H. and E. Ence: Cumulative Etching of Titanium Specimens for Phase Identification. Jnl. Metals, March, 1954.

Fig. 1 (Y-18559). As Received Zr-2. Zr-2-1. 500X. Polarized Light.

Fig. 2 (Y-17721). Zr-2 840°C 30 Minutes, Water Quenched, Anodized at 80 Volts.
Zr-2-58. 200X. Bright Field.

Fig. 3 (Y-18560). Zr-2 1050°C 30 Minutes, Water Quenched. Zr-2-2. 500X. Polarized Light.

Fig. 4 (Y-18561). Zr-2 1050°C 30 Minutes, Air Cooled. Zr-2-3. 500X.
Polarized Light.

Fig. 5 (Y-18563). Zr-2 1050°C 30 Minutes, Furnace Cooled. Zr-2-4. 500X.
Polarized Light.

Fig. 6 (Y-17720). Zr-2 1000°C 30 Minutes, Water Quenched, Annealed 600°C 2 Hours, Water Quenched. Zr-2-43. 200X. Polarized Light.

Fig. 7 (T-9355). Zr-2 1000°C 30 Minutes, Water Quenched, Annealed 800°C 15 Minutes, Water Quenched. Zr-2-51. 100X. Polarized Light.

Fig. 8 (Y-18570). Zr-2 1000°C 30 Minutes, Water Quenched, Cold Rolled 10%, Annealed 800°C 15 Minutes, Water Quenched. Zr-2-88. 100X. Polarized Light.

Fig. 9 (Y-18573). Zr-2 1000°C 30 Minutes, Air Cooled, Cold Rolled 10%, Annealed 800°C 15 Minutes, Water Quenched. Zr-2-92. 100X. Polarized Light.

Fig. 10 (Y-18569). Zr-2 1000°C 30 Minutes, Water Quenched, Cold Rolled 20%,
Annealed 800°C 15 Minutes, Water Quenched. Zr-2-84. 100X.
Polarized Light.

Fig. 11 (Y-18575). Zr-2 1000°C 30 Minutes, Air Cooled, Cold Rolled 20%, Annealed 800°C 15 Minutes, Water Quenched. Zr-2-93. 100X. Polarized Light.

Fig. 12 (Y-18924). Zr-2 Weld Structure. Al103. 2X.

Fig. 13 (Y-18553). Zr-2 Weld, Fusion Line. Al103. 50X. Bright Field.

Fig. 14 (Y-18554). Zr-2 Weld, Fusion Line. Al103. 50X. Polarized Light.

Fig. 15 (Y-18557). Zr-2 Weld, Heat Affected Zone, Parent Metal Side.
Alloy 1103. 100X. Polarized Light.

Fig. 16 (Y-18556). Zr-2 Weld, Center of Weld Deposit. All03. 100X.
Polarized Light.

THE MICROSTRUCTURAL APPEARANCE AND IDENTIFICATION OF HYDRIDES IN ZIRCONIUM AND ZIRCALOY-2 HYDROGEN ALLOYS

G. B. Wadsworth, M. L. Picklesimer, and G. M. Adamson, Jr.

Metallurgy Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee

ABSTRACT

A procedure for the positive identification and location of hydrides in crystal bar zirconium and Zircaloy-2 has been found. Hydrogen was added to vacuum annealed specimens to give specimens of known hydrogen contents and exact heat treatments. These specimens were used to develop and prove the identification procedure of anodizing the polished and etched surface of the specimen in a highly buffered bath to produce a thin film of ZrO_2 showing interference colors. The hydrides are colored a golden yellow while the matrix metal is colored purple to blue, depending primarily on composition and heat treatment. The microstructures for the crystal bar zirconium specimens containing 23 to 500 ppm H_2 and slow cooled from $900^\circ C$ are shown. The microstructures of Zircaloy-2 specimens containing 30 to 870 ppm H_2 and slow cooled from $900^\circ C$ are shown. Two crystal bar zirconium specimens containing approximately 500 ppm H_2 were oil and mercury quenched. The mercury quenched specimen retained considerable amounts of H_2 in supersaturation. The hydride identification technique has been applied to specimens used for mechanical property determinations and radiation damage evaluations.

INTRODUCTION

The sensitivity of zirconium and titanium alloys to hydrogen content as demonstrated by their impact transition curves has caused considerable concern in their use as a constructional material for

reactors. The maximum hydrogen content acceptable has been determined for several of the titanium alloys and for crystal bar zirconium, but no such determination has been made for Zircaloy-2, so far as the authors are aware.

There has been initiated a program of study at the Oak Ridge National Laboratory to determine the effect of hydrogen content and the distribution of the hydrides on the various mechanical properties, as affected by heat treatment, and heat treatment and radiation damage. One of the primary problems in this study is the positive identification and location of the hydrides within the microstructures of the specimens. This report concerns the metallographic procedure that has been developed for such identification and location of the hydrides.

PROCEDURE

Specimens of crystal bar zirconium (Grade I) and Zircaloy-2 were vacuum annealed at 900°C for 24 hours to reduce the hydrogen contents to less than 5 ppm H₂. A modified Sievert's apparatus was used to add known amounts of hydrogen to the specimens at 900°C. The specimens were homogenized at 900°C in their equilibrium pressure hydrogen atmosphere and, in most cases, step cooled by turning down the furnace controller 100°C every 30 minutes. Some specimens were quenched out in Octoil-S or in mercury from 900°C in the hydrogen atmosphere. All specimens were analyzed for hydrogen by vacuum fusion analysis. The metallographic procedure used was to grind through 400 wet emery paper by hand, to polish on coarse, medium, and fine diamond paste wheels successively, and then to alternately electropolish in a perchloric-acetic bath and mechanically polish on a fine diamond paste wheel until the specimen was free of scratches and distorted surface metal. All types of chemical etchants and chemical polishes tried left the hydrides standing in relief too great for examination in a microscope. The final electropolish was very short and etched the specimen sufficiently for detailed examination after anodizing. The electropolished specimen was then anodized at 20 volts for 2 to 5 seconds in a bath composed of 60 ml ethyl alcohol, 35 ml water, 20 ml glycerine, 5 ml phosphoric acid, 10 ml lactic acid, and 2 grams citric acid, a modification of the technique used on titanium by Margolin and Ence.¹ The bath should be fairly fresh, not more than a few hours old. The composition of the bath and the voltage for anodizing are not too critical. The specimen should be anodized for a time sufficiently long to develop the thickness of oxide characteristic of the applied voltage. Times shorter than this will not give a sufficient reproducibility of the interference color. The hydrides are colored a golden yellow while the matrix metal is colored purple to blue, depending primarily on composition and heat treatment and only slightly on the anodizing voltage. The hydrides may be identified by their characteristic color at any magnification at which they can be clearly resolved without requiring a microscope objective using an oil immersion lens (the color is lost in oil immersion examination).

RESULTS

A typical microstructure of a crystal bar zirconium specimen containing 23 ppm H_2 and step cooled is shown in Figs. 1 and 2. No massive hydrides were observed in this specimen. The striations in one grain in the microstructure of Fig. 1 may be very small hydrides, but they are not resolvable at 1500X and did not color the characteristic yellow. The microstructure of a specimen containing 160 ppm H_2 is shown in Figs. 3 and 4, revealing the appearance of the hydrides within the grains of crystal bar zirconium with only an occasional hydride in a grain boundary. The addition of 500 ppm H_2 to crystal bar zirconium, as shown in Figs. 5 and 6, causes the hydrides present to be more massive. Only when approximately 1000 ppm H_2 is present do the hydrides appear to any extent in the grain boundaries. This is probably due to the large volume of hydride present plus the tendency of hydrogen to stabilize beta phase rather than a change in the preference of location.

In contrast to the location of the hydrides within the alpha grains of crystal bar zirconium, the hydrides in Zircaloy-2 have a very decided preference for the grain boundaries, with only an occasional needle of hydride penetrating an alpha grain when the hydrogen content is near 1000 ppm H_2 . A content as small as 30 ppm H_2 causes the appearance of hydrides in the grain boundaries of slowly cooled Zircaloy-2, as shown in Figs. 7 and 8, where the more massive rounded white (yellow in the specimen) particles in the grain boundaries are the hydrides and the remainder of the grain boundary material is formed of the Fe, Ni, and Cr intermetallics. The appearance of the hydrides in the grain boundaries, both as films and as massive particles, is more clearly shown in Figs. 9 and 10, the microstructures of a specimen containing 100 ppm H_2 and step cooled from 900°C. At 230 ppm H_2 , Figs. 11 and 12, the hydride occupies a considerably greater amount of the grain boundaries and appears still more massive. A content of 870 ppm H_2 , Figs. 13 and 14, causes the retention of considerable amounts of beta phase to a temperature sufficiently low to give a very coarse type eutectoid decomposition structure on step cooling from 900°C. The massive clumps of hydride are a result of the eutectoid decomposition while the films of hydride are located between neighboring alpha needles.

Crystal bar zirconium specimens containing approximately 500 ppm H_2 were quenched from 900°C into Octoil-S and into mercury in the hydrogenating apparatus. The resulting microstructures are shown in Figs. 15, 16, 17, and 18. The hydride needles have formed as a Widmanstätten type precipitate in the oil quenched specimen, and as a very distorted Widmanstätten type precipitate in the mercury quenched specimen. It is evident that the faster quenching rate in mercury has caused the retention of a considerable amount of hydrogen in supersaturated solution. Many of the hydride needles occurring in this microstructure are too small to be clearly resolved even at high magnification.

and do not have the characteristic yellow color on anodizing. It may also be that only the ZrH_2 hydride is colored yellow by the anodizing process and that the remainder of the needles are the proposed ZrH hydride.

CONCLUSIONS

The progressive appearance of larger and larger amounts of the phase which anodizes to the golden yellow color, with increasing hydrogen content combined with the reproducibility of the structures and colors is proof that the stated anodizing procedure will give a positive identification and location of the hydrides in the microstructures of zirconium and Zircaloy-2, provided they are large enough to be clearly resolved without requiring the use of an oil immersion objective in the microscope.

The technique of hydride identification reported herein has been successfully used to locate and identify the hydrides appearing in irradiated and unirradiated Zircaloy-2 and crystal bar zirconium specimens in an attempt to evaluate, microstructurally, the effects of irradiation on the amount and the appearance of hydrides present in the specimens. The data are, as yet, too sparse to permit any conclusions other than that the method of identification of the hydrides is successful.

REFERENCES

1. Margolin H. and E. Ence: Cumulative Etching of Titanium Specimens for Phase Identification. Jnl. Metals, March, 1954.

Fig. 1 (Y-18530). X-Bar Zr 23 ppm H₂ Step Cooled. B-3. 500X. Bright Field.

Fig. 2 (Y-18531). X-Bar Zr 23 ppm H_2 Step Cooled. B-3. 500X. Polarized Light.

Fig. 3 (Y-18528). X-Bar Zr 160 ppm H₂ Step Cooled. B-11. 500X. Bright Field.

Fig. 4 (Y-18529). X-Bar Zr 160 ppm H₂ Step Cooled. B-11. 500X. Polarized Light.

Fig. 5 (Y-18304). X-Bar Zr 500 ppm H₂ Step Cooled. B-5. 500X. Bright Field.

Fig. 6 (Y-18305). X-Bar Zr 500 ppm H₂ Step Cooled. B-5. 500X. Polarized Light.

Fig. 7 (Y-18526). Zr-2 30 ppm H₂ Step Cooled. D-3. 500X. Bright Field.

Fig. 8 (Y-18527). Zr-2 30 ppm H_2 Step Cooled. D-3. 500X. Polarized Light.

Fig. 9 (Y-18265). Zr-2 100 ppm H₂ Step Cooled. D-5. 500X. Bright Field.

Fig. 10 (Y-18267). Zr-2 100 ppm H₂ Step Cooled. D-5. 500X. Polarized Light.

Fig. 11 (Y-18269). Zr-2 230 ppm H₂ Step Cooled. D-6. 500X. Bright Field.

Fig. 12 (Y-18271). Zr-2 230 ppm H_2 Step Cooled. D-6. 500X. Polarized Light.

Fig. 13 (Y-18277). Zr-2 870 ppm H_2 Step Cooled. D-8. 500X. Bright Field.

Fig. 14 (Y-18279). Zr-2 870 ppm H₂ Step Cooled. D-8. 500X. Polarized Light.

Fig. 15 (Y-18532). X-Bar Zr 480 ppm H_2 Oil Quenched from $900^{\circ}C$. J-2. 500X.
Bright Field.

Fig. 16 (Y-18533). X-Bar Zr 480 ppm H_2 Oil Quenched from 900°C. J-2. 500X.
Polarized Light.

Fig. 17 (Y-18536). X-Bar Zr 530 ppm H₂ Mercury Quenched 900°C. J-3. 500X.
Bright Field.

Fig. 18 (Y-18537). X-Bar Zr 530 ppm H_2 Mercury Quenched $900^{\circ}C$. J-3. 500X. Polarized Light.

INSPECTION OF SMALL DIAMETER TUBING
BY EDDY CURRENT METHODS

J. W. Allen and R. B. Oliver

Metallurgy Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee

ABSTRACT

The basic principles of eddy current testing are discussed as they apply to the problem of inspecting small diameter tubing. Both encircling coils and probe coils are considered and the relative advantages of each presented. The inspection problem is described in terms of separation and classification of defect types rather than in terms of mere sensitivity to defects. As a possible means of defining defect types the "impedance analysis" concept introduced by Förster is examined in detail, and it is shown that although this method holds great potential for future development, present day instrumentation is not sufficient to allow satisfactory utilization of the approach.

The use of an encircling coil instrument known as the Cyclograph is discussed with regard to its unique property of variable frequency, and curves relating its parameters of operation are presented. The usefulness of this instrument is illustrated with the inspection results of several thousand feet of small diameter tubing. A detailed description of what can be accomplished with this type of test is given.

A newly developed instrument utilizing probe type coils is presented and its salient features discussed. Test results which correlate its indications to the initiating defects are given.

General statements are made as to what can be accomplished with an eddy current test on small diameter tubing at present, and what may be expected in the future.

In recent years the field of Nondestructive Testing has seen a continuous parade of electronic instruments constructed for the purpose of inspecting materials by eddy current methods. In some instances many of these eddy current tests have produced remarkably gratifying results, while in other instances the very same instruments have failed to produce adequate results. This has led to conflicting opinions and a great deal of confusion as to what can and what cannot be accomplished with an eddy current test. The purpose of this paper is to establish what can be accomplished with the eddy current testing of small diameter tubing according to present day methods. A brief review of eddy current testing in general is thought to be of value before discussing its application to tubing.

In essence the method consists of inducing eddy currents into the metal part to be inspected by bringing it into the electromagnetic field of a coil which is being supplied with an alternating current. The coil may encircle the part, or be placed on the surface of the part in the form of a probe. Also in the case of tubular shapes, a coil may be wound to fit inside the tube. In any event, the original field of the coil is altered according to the magnitude, phase, and distribution of the induced eddy currents. All of the eddy current methods attempt to measure by some means this alteration in the field. If the coil is excited with a current of constant amplitude, the voltage at its terminals is a measure of the change in the field. Also, a second coil coupled to the first may be utilized to measure the same thing. This second coil is often used as a convenience and is called the "sensing" or "pick-up" coil.

In general the alteration of the field produced by the induced eddy currents is a function of the frequency of the exciting current, the electrical conductivity and magnetic permeability of the part, the physical dimensions of the part and its location in the field, and the presence and location of discontinuities or "inhomogeneities" within the part. Since the degree of cold work or heat treatment of the part influences its electrical conductivity (and its magnetic permeability in the case of the austenitic stainless steels), they also become influencing factors.

The largest single contribution to the field of eddy current testing has been made by Dr. Fritz Förster¹ in his proposal of a method for separating some of these variables. The changes in the field of the testing coil just described take place not only in amplitude but also in time phase. A plot of the variations in amplitude and phase of a testing coil's impedance, which is directly related to its field, is called an "impedance plane" for the coil. Such a plot for a coil encircling a cylindrical metal tube or rod is shown in Fig. 1.² In this

plot the amplitude-phase values have been broken into two quadrature components: the reactive component and the resistive component. The values are normalized to the pure reactive impedance of the coil in absence of the metal part. By making use of the frequency ratio f/f_c , this plot can be used for materials of any conductivity, permeability, and diameter. Note that the number f_c is determined only by the part itself. The solid lines for varying f/f_c ratio are plotted for solid rod for three different values of $\nu = D_p/D_c$ or "filling factor". The dotted curves departing from rod curves are for varying diameters of the part for the several values of f/f_c . The other solid curves are for tubular shapes and the percent parameters represent the wall thickness in percent of the outside diameter D_p .

Examination of the rod curves shows that if phase sensitive detectors are employed and a frequency chosen to give a reasonable value of f/f_c , say $f/f_c = 16$, then certainly variations of D_p and of conductivity may be separated.

Examination of the tube curves shows that another parameter is introduced in the selection of an operating frequency--the thickness of the tube wall. Consider a tube having a wall thickness of 10 percent of its outside diameter. From the impedance plane it is seen that a value of 25 for f/f_c would give adequate phase separation between varying D_p and varying tube wall thickness. Thus by operating at this point on the impedance plane and employing phase sensitive detectors (impedance analysis method), wall thickness measurements could be made in the presence of varying D_p .

Another factor enters into the selection of frequency or the f/f_c ratio. The eddy currents do not distribute themselves uniformly throughout the wall of the tube, but decrease exponentially with the depth below the surface. In terms of the ratio f/f_c the eddy current density at the inside wall of the tube as a fraction of the density on the outside surface of the tube is approximately

$$\left| \frac{i \text{ inside}}{i \text{ outside}} \right| = e^{-\sqrt{2} t \sqrt{f/f_c}}$$

t being the wall thickness as a fraction of the O.D. In the case just sighted of $t = 1/10$ and $f/f_c = 25$, the eddy current density at the inside surface will be

$$\left| \frac{i \text{ inside}}{i \text{ outside}} \right| = e^{-\sqrt{2} (0.1) \sqrt{25}} \cong 1/2$$

of the density at the outside surface. Although there is no exact criterion for determining what the allowable attenuation shall be,

experience has indicated that the figure of $1/2$ used in the illustration is a reasonable standard.

With these basic eddy current relationships well in mind, let us examine the problem of testing small diameter tubing by eddy currents. At the Oak Ridge National Laboratory there exists a tubing inspection problem very similar to that of many other consumers of small diameter tubing. There is a need for a relatively fast method of inspecting large amounts of tubing having diameters from 1 inch down to $3/16$ inch, having wall thicknesses ranging from 5 to 20 percent of the O.D., and electrical conductivities ranging from 0.70×10^6 mho/meter to 1.5×10^6 mho/meter (all non ferro-magnetic alloys). Also since the tubing is to be used in critical applications where failures are apt to be disastrous to large and expensive installations, the inspection requirements are rather stringent. It is desired to inspect the tubing for cracks, pin holes, non-metallic inclusions, gouges and other mechanical defects, and dimensional tolerance.

In approaching this problem encircling coils, surface probe coils, and inside probe or "bobbin" type coils have been considered. The latter has been rejected because of the mechanical problem in scanning long lengths of the smaller diameters. Of the other two, the encircling coil method has received primary consideration due to the relative ease of mechanical handling and the inspection speed. A considerable amount of work has also been done with surface probe coils, and will be discussed later.

In employing an encircling coil to inspect tubing, the problem is more than simply one of sensitivity to variations in the tube. As suggested previously, the eddy currents will in general be influenced by almost any possible variation that may occur in the tube, and by exercising a little ingenuity one may contrive several instrument types which will have a very sensitive response to these variations. The problem is one of separation and classification of these variations as to their nature and extent. For instance, how may an I.D. crack be distinguished from a decrease in wall thickness? Or an area or intergranular attack from a perturbation in the diameter?

The most obvious approach to finding a solution to this problem is the one of employing phase sensitive detectors in the manner prescribed by Dr. Förster.¹ In order to utilize this method to advantage, a frequency must be selected to give an operating point on the impedance plane such that adequate phase separation is achieved between diameter and wall thickness variations. For tubing having wall thicknesses of about 10 percent, $f/f_c = 25$ would be a good choice; for thicker walls a lower value of f/f_c would be advantageous; for thinner walls a higher value of f/f_c would be advantageous.

The range of tubing sizes and conductivities just mentioned yield values of f_c which vary from about 525 to about 32000. For the chosen

value of $f/f_c = 25$ this means the operating frequency of the instrument used must be variable from 13.1 kc to 800 kc. For thicker walls (up to 20 percent of the O.D.) the lower frequency limit needs to be moved down to about 4.7 kc, and for thinner walls (down to 5 percent of the O.D.) the upper frequency limit needs to be moved up to 3200 kc. This is the range of frequencies which an impedance analysis type instrument must cover if it is to be utilized over the limited range of tubing sizes and conductivities mentioned here. The only instruments of this type which have been built to date operate at a single, fixed frequency. With a fixed frequency impedance analysis instrument adequate phase separation between diameter and wall thickness variations can be accomplished for only a few selected tubing sizes and conductivities. Most of the time this is inadequate in a production inspection situation.

Experimental investigations with an impedance analysis type instrument under ideal conditions have indicated that the condition of phase separation between diameter and wall thickness variations is not sufficient for truly definitive inspection. In general, discontinuities near the inside wall of the tube give signals which are very nearly in phase with wall thickness variations, and discontinuities near the outer surface will give signals which are very nearly in phase with diameter variations. Thus if circuits are adjusted to discriminate against diameter signals, they will also discriminate to a large extent against signals from surface pits and shallow cracks. Another undesirable feature is that there are no adequate means by which to distinguish between signals from I.D. cracks or intergranular attack and those from wall thickness variations.

The impedance analysis concept offers the only promising avenue toward a truly definitive eddy current test for small diameter tubing in the future. At its present stage of development, however, it offers no advantage to the inspector of tubing over other eddy current methods.

Although eddy current tests on small diameter tubing leave much to be desired in the definition of flaw types, it should not be assumed that such tests are not of value. On the contrary, an encircling coil eddy current test can be invaluable in sorting very faulty tubing from sound tubing, and obtaining an inspection for dimensional tolerances.

The encircling coil eddy current instrument known as the Cyclograph has been utilized (in a slightly revised form) to inspect several thousand feet of tubing in the range of sizes and materials previously mentioned with a considerable amount of success. This instrument measures the resistive component of changes in the impedance of the testing coil, and its operating frequency is determined solely by this coil. Although this instrument is incapable of an impedance analysis, its unique property of changeable frequency has considerable advantage. By selecting the proper frequency, optimum O.D. and I.D. sensitivity can be obtained regardless of the diameter, wall thickness,

or material of the tubing. Also by using a consistent method of choosing the frequency, the same relative sensitivity can be maintained regardless of the properties of the particular tube.

Fig. 2 is a plot of the Cyclograph reading (at a reduced sensitivity) as a function of tube wall thickness, with the ratio f/f_c as a parameter. This readout is a distorted inverse measure of the resistive component on the impedance plane of Fig. 1. The distortion is due to the non-linear characteristic of this instrument near the zero or "quench" point, which also accounts for its extreme sensitivity. Experience has indicated that the optimum O.D. and I.D. flaw sensitivity is obtained for an f/f_c which causes the curve to peak near the wall thickness under question. Since flaw signals move along the curve from the operating point in the direction of decreasing wall thickness, the operating point is selected on the left side of a peak to avoid confusing signals that are sometimes obtained in the immediate vicinity of the peak. Fig. 3 is a graph of the f/f_c values for which the curves of Fig. 2 have their peaks.

Although the Cyclograph signals in themselves are not definitive, interpretation of these signals can be enhanced by utilizing a properly designed mechanism to feed the tubing through the coil at a constant speed, and recording the resultant signals. Signals from tube wobble in the coil, which is by far the greatest offender in producing spurious signals, have been all but eliminated by utilizing a feeding mechanism such as shown in Fig. 4 in which the coil is allowed to move with freedom on the tube. Relatively large discontinuities are usually very easily separated from dimensional variations in the tube because of their very abrupt nature. This is indicated by the Cyclograph trace in Fig. 5 of a 1/4 inch x .049 inch Hastelloy B tube having a large radial crack. A photomicrograph of this crack is shown in Fig. 6. The other trace of Fig. 5 is indicative of the small defects that may be detected in the absence of dimensional variations in the tube. The intergranular attack causing the flaw signal at the point 34Ra is shown in the photomicrograph of Fig. 7. By utilizing reference standard tubes of known dimensions, successful inspection for dimensional tolerances has been achieved on a comparison basis.

In general, discontinuities may be resolved by this method if they penetrate much deeper than the background of dimensional variations in the tube, and have lengths of the order of 1/16 inch. Clusters of much smaller defects are, of course, detectable.

The need for a more precise and definitive method for the inspection of tubing has prompted the study and development of a probe type surface coil and instrument. The probe is made to mechanically scan the surface of the tube and signal variations are displayed on a persistent screen oscilloscope as a function of tube rotation as indicated schematically in Fig. 8. The probe is composed of two coils, the exciting coil which is fed by an alternating current of constant

amplitude, and the pick-up coil which is closely coupled to the exciting coil. The voltage from the pick-up coil is compared to that of adjustable balance circuits in the instrument, the difference being amplified and fed to the oscilloscope.

Probe coils as small as $1/16$ inch in diameter have been constructed and found to be sensitive to minute defects. This small size, however, results in very slow scanning rates, and elongated probes are now being utilized. Although the sensitivity to minute discontinuities is reduced in proportion to the increased length, it has been established that the coils could be elongated to about $1/4$ inch without seriously compromising the sensitivity. The construction of an early version of the probe and its holder is shown in Fig. 9.

The great advantage of the probe coil method is its inherent ability to be definitive. Because it is a surface probe it is not affected by changes in diameter. Changes in wall thickness are indicated by changes in the over-all height of the oscilloscope pattern, and eccentricity is indicated by a pattern having a sinusoidal envelope. Discontinuities within the wall of the tube, because of their abrupt nature, cause spiked indications in the pattern. The oscilloscope pattern obtained from the cracked tube of Fig. 6 is shown in Fig. 10.

This method is mechanically more difficult to utilize and is inherently a slower method than that of the encircling coil. Its vastly superior definitive ability, however, may more than offset this disadvantage in critical inspection applications.

In general eddy current techniques as they exist today can, if properly utilized, perform valuable inspections on small diameter tubing. Already information on the quality of tubing is being obtained with this method which cannot be gained by any other nondestructive test, such as the detection of intergranular attack on the I.D. of tubing and a continuous gaging of the dimensions of the tubing. Eddy current methods have the potential of becoming a truly definitive means of inspecting tubing. These potentialities will become realized with the continued development of techniques and instrumentation.

REFERENCES

1. Förster, F. and K. Stambke: A Method of Non-Destructive Testing Employing a Slip-Over Coil. Zeitschrift Für Metallkunde, Vol. 45, 1954, No. 4, pp 171-179.
2. This graph is essentially a composite of two graphs presented in the above paper.

Fig. 1 (ORNL-LR-DWG.-12972)

Impedance Plane for a Coil Encircling a Metal Tube or Rod.

218

218

Fig. 2 (ORNL-IR-DWG.-11105)

Cyclograph Reading Vs. Tubing Wall Thickness with f/f_c as a Parameter.

Fig. 3 (ORNL-IR-DWG.-11106)

Frequency Vs. Tubing Wall Thickness for Maximum Resistive Coil Impedance.

Fig. 4 (ORNL-IR-DWG.-11015)

Cyclograph Coil Assembly and Feed Mechanism for Tubing Inspection.

2

CYCLOGRAPH TRACE OF REJECTED $\frac{1}{4}$ X 0.049-in.
HASTALOY B TUBING AT 160 kc

R586A-1-1: O.D. RADIAL CRACK 0.027-in. DEEP
(PHOTOMICROGRAPH: Y17292)

CYCLOGRAPH TRACE OF REJECTED
 $\frac{1}{4}$ X 0.025-in. INCONEL TUBING AT
200 kc

34RA: I.D. INTERGRANULAR ATTACK
MAXIMUM PENETRATION = 0.002 in.
(PHOTOMICROGRAPH: Y17293)

34RC: I.D. INTERGRANULAR ATTACK
MAXIMUM PENETRATION = 0.001 in.
(PHOTOMICROGRAPH: Y16605)

Fig. 5 (ORNL-LR-DWG.-11104)

Cyclograph Traces of Defective Tubing.

Fig. 6 (Y-17292)

Radial Crack on the Outside Diameter of a $1/4$ inch x 0.049 inch
Hastelloy B tube.

Fig. 7 (Y-17293)

Intergranular Attack on the Inside Diameter of a $1/4$ inch x 0.025 inch Inconel Tube.

Fig. 8 (Y-16980)

Eddy Current Inspection of Tubing with a Probe Coil.

Fig. 9 (ORNL-LR-DWG.-11079)

Eddy Current Probe Coil and Holder for Scanning Small Diameter Tubing.

Fig. 10 (ORNL Photo #16155)

Oscilloscope Pattern of Eddy Current Probe Obtained from Cracked Tube.

APPLICATION OF THE IMMersed ULTRASONIC TECHNIQUE
FOR THE INSPECTION OF SMALL DIAMETER TUBES

R. B. Oliver and R. W. McClung

Metallurgy Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee

ABSTRACT

The criteria for the selection of equipment to inspect tube sizes less than 1/2 inch in diameter are presented and the testing procedure is described. Collimation of the ultrasound beam and the mode of sound propagation are discussed. The capabilities and limitations of this inspection method and typical defects detected are presented. The method has proven to be satisfactory for the detection of defects at least 1/16 inch long and at a scanning rate of 12 feet per minute.

Nuclear power reactors, in common with other types of thermal power generators, require a vast quantity of pipe and tubing. This is inherent since thermal energy is generated in one locality and must be transferred to some fluid for transport to another location to be converted into mechanical energy. Most of the uses of pipe and tubing are in regions of critical application, in hazardous regions, or in non-accessible, non-repairable locations. Hence soundness must be guaranteed. In view of the great footage of tubular shapes and the quality required, special techniques were indicated. Pulse-echo ultrasonic methods were selected as promising the earliest solution to this inspection problem with the minimum requirement for instrument development.

Since the sizes required ranged from 3/16 inch O.D. x 0.025 inch wall to 8 inch schedule 80 pipe, the design criteria included instrument characteristics compatible with the thin sections of the small tubing and mechanical designs flexible enough for adaptation to pipe

sizes. Inspection rate was important so additional investment was made in instrumentation to insure the detection of defect signals at high inspection speeds.

The basic instrument selected was the Model 424 Immerscope (Curtis-Wright Company, Caldwell, New Jersey) which can be used for either contact scanning or immersed scanning. This line of equipment is shown in Fig. 1. The instrument, when used with a highly damped Li_2SO_4 crystal, has a pulse length of no more than one microsecond--equivalent to 1/4 inch--travel in the metal. The instrument contains circuits to provide for: (1) a gated alarm system, (2) attenuation correction, and (3) the necessary synchronization signals to provide for the use of a "B" scan attachment. Immersed scanning was selected because of several inherent advantages:

1. The method allows the use of a highly damped piezoelectric crystal having a very high signal strength.
2. No special adaptors or shoes are required when changing the size or shape of the object being inspected.
3. Simple continuous adjustment of the incident angle of the sound beam is permitted.
4. It does not require the continuous application of a coupling liquid nor is contact pressure a variable.
5. Since intimate contact is not required, this limitation on inspection speed is eliminated.
6. Immersed technique is independent of the ovality, surface conditions, or of dimensional variations.
7. The 2 inch water column provides a delay line that allows the very strong initial signal to pass through the amplifier before the weaker inspection signals return to the instrument. This point is particularly advantageous with the small tube sizes.
8. The method permits collimation of the sound beam. Thus the defect signal is compared with the signal from the front surface of the test object rather than with the very strong signal transmitted by the crystal.

Contact scanning has the advantage of portability, though this can be partially offset by the use of a jet of water to couple an immersed type transducer with the work. Regardless of the scanning method, the handling of pipe and tubing in mill lengths and in large quantities requires considerable mechanized equipment to rotate the tubular shape and to translate the transducer along the axis of the pipe or tube. These facts make portability impracticable. The design of the mechanical handling equipment is essentially the same for any of the scanning methods except for the minor problem of surrounding the scanning equipment with a light metal tank for immersed work. The mechanical equipment must hold the pipe or tubing straight as it is rotated around its axis, it must hold the transducer in proper alignment at all times, and it must translate the transducer along the length of the tube at such a

rate that the entire surface of the test object is covered by the sound beam. As performed at Oak Ridge National Laboratory, the tube is rotated at approximately 200 rpm and the 3/4 inch transducer is moved at about 0.3 inches per revolution. This gives a scanning speed of about 5 feet per minute. Rotational speeds of 300 rpm or greater are possible and if defects less than one inch long are acceptable, the scanning pitch could be increased to 0.7 inches per revolution. Under these conditions, scanning speed up to 18 feet per minute would be possible. The scanning equipment designed and fabricated at the Laboratory is illustrated in Fig. 2.

The conventional or "A" scan presentation found on most ultrasonic flaw detection instruments presents the instantaneous signal intensity as a function of the time-of-travel or distance traveled by the sound. Since for the inspection of pipe and tubing the sound is channeled around the circumference in the wall of the object, the signal from a defect in the rotating pipe or tubing travels across the "A" scan oscilloscope. With high rotational speed it is difficult to detect these rapidly moving defect signals and impossible to evaluate their magnitude. The "B" scan instrument samples the "A" scan pattern 300 to 1,000 times per second and presents this information on the vertical sweep of the "B" scan oscilloscope. The horizontal sweep of the oscilloscope is driven by some position signal supplied from the mechanical scanning equipment. This method of presentation is analogous to a stroboscope and as such is nearly independent of scanning speed. If a plate is being inspected, the "B" scan would present an instantaneous cross section of that part. Fig. 3 compares the principal types of data presentation from a laminate-like defect. If, when scanning tubing and pipe, a rotational signal is used to actuate the horizontal sweep, any defect moving with the pipe wall will produce a signal which moves across the screen. This moving defect is also changing its distance from the transducer, which will show on the vertical sweep. The combination of these two sweeps is a defect signal which is an inclined line on the face of the "B" scan oscilloscope. The length and brilliance of this inclined line are indicative of the depth and size of the defect. A block diagram of this method of ultrasonic inspection appears in Fig. 4.

Discontinuities such as surface scratches and crack-like defects, when they are located near the incident sound, will give about the same signal intensity, but as they are moved further from the incident beam the signal from the scratches drops off very rapidly, while the defect will produce a detectable signal even when rotated 90° or more from the incident beam. If a gated alarm circuit is adjusted some distance in time from the signal caused by the front surface, then only signals from defects will actuate the flaw alarm. At this position in time, defects of the same size on both the inner and outer surface produce signals of comparable magnitude. The sensitivity time control circuit, which corrects for attenuation by increasing the amplification

as a function of the distance from the front surface, is an additional aid in separating superficial indications from defect signals.

For the inspection of tubular shapes the transducer is aligned so that the beam of sound produces a range of incident angles from 10° to 30° as illustrated in Fig. 5. The sound upon entering the wall of the tubular object is refracted to larger angles and travels around the wall of the pipe or tube in a saw-tooth pattern. The sound beam should be collimated to remove that part of the beam having an incident angle of less than 10° to eliminate the direct reflections from the inner surface of the tube wall. For maximum coverage the sound originating from the diameter of a round crystal should make a 15° incident angle and a collimator should then be adjusted to limit the incident angle to more than 10° . This point is particularly important if the crystal size is greater than the radius of the object being inspected as in the case with tubing. Fig. 6 presents the subject of collimation in graphic form. A crack-like defect returns the maximum signal only if the plane of the longitudinal defect contains a radius of the tubular shape. If this condition does not obtain, the defect is detectable when the sound beam is propagated around the tube in one direction, but the same defect may not be detectable if the sound is propagated in the other direction. For this reason all tubular objects should receive a double inspection to insure the detection of non-radial defects.

The proper alignment of the transducer with reference to the axis of rotation of the tubular object should be performed on a sample length of the same size having similar longitudinal notches milled on both the inner and outer surface to a depth comparable to that of a rejectable defect. The transducer should be positioned to "see" each of the notches with comparable signal strength when the reference defect signals are the same distance from the front surface signal. This adjustment may not give the maximum signal from either defect, but it does present defects in their relative size regardless of their location in the tube or pipe wall. The defects located on the inner surface are the most difficult to detect, so it is considered necessary to "prove" the technique on reference defects located on the inner surface.

Due to the non-linearity of the various electronic circuits, none of the ultrasonic instruments give a linear relation between signal strength and defect size over a range of sizes. Also unless a properly adjusted sensitivity time control circuit is used, the signal received from similar defects at various depths will vary as a function of the distance below the front surface of the test object. For these reasons any evaluation of defect size should only be a comparison with a known defect in the same material having a similar mechanical and thermal history, and the known defect should simulate the defect being evaluated. Since the common defect in pipe and tube is a longitudinal crack, a very narrow longitudinal notch having a length less than the maximum length of the transducer is used. At best, this is only a go-no-go

gage to tell whether the defect appears to be larger or smaller than the reference notch.

The sound is propagated around a pipe wall in a saw-tooth or zig-zag pattern and the mode of propagation is generally considered to be the shear or transverse vibration. The saw-tooth pattern is fairly sharp and a defect is only detected when its position coincides with each of the nodes. The part of the beam that has an incident angle of about 30° produces a Rayleigh or surface wave which in turn gives a signal from a scratch that is of the same magnitude as the signal from a deep crack. Proper alignment of the transducer can minimize the surface wave and the proper adjustment of the instrument assists in the rejection of signals resulting from the surface wave. It is the opinion of this group that the sound is propagated around the thin wall of the small diameter tubing as a severely retarded and distorted longitudinal wave. As the wall gets thinner, the reflection nodes get progressively less sharp until with very thin walls the sound floods around the very narrow metal annulus or wall. The two concepts of the travel pattern are depicted in Fig. 6.

The $3/16$ inch x 0.025 inch and the $1/4$ inch x 0.025 inch tubing inspected for reactor application is rejected on the basis of any detectable defect as an internal standard. Rejections for return to the vendor are based on the negotiated purchase specification. Piping is inspected on the basis of a longitudinal defect $1/2$ inch long having a depth of 3 percent or 0.004 inches, whichever is the greater. Rejection rates on some lots of commercial grade tubing have run as high as 90 percent and on some special purchases the rejections were as low as 1 percent. It appears that any inspection effort by the vendor results in a marked reduction in the rejections by the consumer.

It is currently indicated that the confidence to detect a 3 percent defect on the inner surface of pipe up to 4 inch IPS is quite high if an adequate gated alarm system is employed, and if an overlap of approximately 50 percent of the crystal size is maintained while scanning the pipe. The "B" scan assists in the detection of the defect and makes possible a rapid evaluation of the defect. Existing gated alarm systems have not been reliable for the inspection of small diameter tube, so the inspector is dependent on the "B" scan for both detection and evaluation. Also the transducer alignment is critical, hence the confidence in the detection of longitudinal defects 0.0015 inches deep by 0.060 inches long on the inner surface is probably not over 50 percent. Longitudinal defects 0.003 to 0.005 inches deep by 1 inch long are certain of detection.

Fig. 7 is a "B" scan from a $1/4$ inch x 0.025 inch tube containing one large O.D. crack and three defects that are very small and probably located on the inner surface. The larger defect was probably more than $1/2$ inch long and 0.008 to 0.010 inches deep similar to the larger crack in Fig. 8, while the smaller defects are representative of the

small crack in Fig. 9 which was 0.0015 inches deep by about 0.060 inches long. Figs. 10 and 11 are respectively a crack greater than one inch long and penetrating at least 50 percent of the tube wall, and the "B" scan presentation of the signal from that defect.

Evaluation of the confidence for the detection of various types and sizes of defects in the wide range of sizes will only come with the inspection of large quantities of tubular shapes.

Fig. 1 (Y-16377)

Ultrasonic Test and Data Presentation Equipment. Left to right: "B" Scan, Recorder, and Immerscope. The small box is the audible alarm.

Fig. 2 (Y-16211)

Tube Scanning Equipment Featuring Variable Speed Drive, Moving Slotted Guides and Transducer Mounting.

LAMINATION IN PLATE

"A" TRACE OF DEFECT

"B" TRACE OF DEFECT

"C" TRACE (PLAN VIEW)

SHOWS AREA OF FLAW AS
SEEN FROM ABOVE

THE ENTIRE SURFACE OF THE PLATE MUST BE
SCANNED TO PRODUCE THE PLAN VIEW

Fig. 3 (Y-10996)

Comparison of the Several Methods of Ultrasonic Flaw Indication From a Lamination-Like Defect.

Fig. 4 (DWG-11163)

Alignment of Tubing and Crystal for the Inspection of Small Diameter Tubing.

Fig. 5 (DWG-11112)

Technique of Collimation of the Ultrasound Beam for the Inspection of Tubing.

238

238

PROPAGATION OF SOUND IN TUBE WALL.

Fig. 6 (DWG-11111)

Graphic Representation of the Patterns Followed by the Ultrasound Traveling Around a Pipe Wall and Around a Tube Wall.

Fig. 7 (Y-16453)

"B" Scan of a Small Diameter Tube Indicating Three Very Small Defects and One Large Defect. (See Figs. 8 and 9.)

Fig. 8 (Y-16967)

Cross-Section of Cracks 15% of the Wall Thickness, Representative of the Larger Defect Signal in Fig. 7.

Fig. 9 (Y-18167)

Cross-Section of a Crack 0.0015 inches Deep on the Inner Surface of a Tube, Representative of the Defects Causing the Weak Defect Indications in Fig. 7.

242

242

Fig. 10 (Y-16454)

"B" Scan Presentation of the Signal from a Large Deep Crack in a Small Diameter Tube.

Fig. 11 (Y-17292)

Cross-Section of a Crack Approximately 60% of the Wall Thickness, Representative of the Defect Causing the Indication in Fig. 10.

CORROSION AND MASS TRANSFER BY LITHIUM AT ELEVATED TEMPERATURES

E. E. Hoffman and L. R. Trotter

Oak Ridge National Laboratory
Oak Ridge, Tennessee

In recent years there has developed a considerable interest in the possible application of lithium metal as a heat transfer medium, especially as a nuclear reactor coolant. The major problem encountered, and one which is yet to be resolved, is the inability of commercially available metals and alloys to withstand the corrosive effect of lithium in dynamic systems at temperatures in excess of 1000°F. This report discusses several of the more important corrosion processes; a general review of the results of static, isothermal tests; and recent results on seventeen thermal convection loop tests conducted on iron- and nickel-base alloys. None of these alloys tested in dynamic systems with temperature differentials present were found to be satisfactory container materials at temperatures in excess of 1100°F. Plans for further tests are mentioned.

Lithium and several other liquid alkali metals, notably sodium and potassium, have been considered as nuclear reactor coolants because of their very attractive heat-transfer properties.^(1,2) Sodium and the various sodium-potassium alloys have found fairly wide use while lithium has not been used to date as a heat transfer medium at elevated temperatures except in experimental systems. The principal reasons for this are as follows:

1. The inability of commercially available alloys to withstand the corrosive action of high temperature lithium.
2. The necessity of separating the high thermal absorption cross section lithium-6 isotope (950 barns)⁽³⁾ from the low cross section lithium-7 isotope (0.033 barns) before lithium could be used as a primary coolant in a thermal reactor. The high absorption cross section of naturally occurring lithium (92.5% Li-7, 7.5% Li-6) is a most undesirable property and could be

eliminated only by isotopic separation. Otherwise, the very high cross section of the lithium-6 would lead to inefficient consumption of neutrons produced by the fission process.

Some of the important properties of lithium and several other potential coolants which must be considered are listed in Figure 1. Those properties which are considered quite undesirable insofar as concerns their application as coolants in high temperature thermal reactors are indicated. The most important difficulty which bars the use of lithium today, however, is its corrosiveness in dynamic non-isothermal metal container systems.

The results of two types of lithium corrosion tests will be discussed. These tests are as follows:

1. Static tests in which there is no movement of the lithium and there is no temperature differential present.
2. Dynamic tests in which flow is maintained and in which a temperature differential is present.

Static tests conducted under isothermal conditions are easy to perform and are very useful in screening out those materials which have little probability of withstanding the more corrosive action of lithium which is encountered in dynamic test systems.⁽⁴⁾ No attempt will be made to cover in detail the many corrosion mechanisms and only the most important points will be discussed.⁽⁵⁾ As with all very active liquid alkali metals it has been found to be very important to keep the metal under a protective inert gas atmosphere during handling operations if contamination is to be minimized. Exposure of lithium to the atmosphere leads to the formation of lithium nitride chiefly and additions of this material to lithium have been shown to have a detrimental effect on the corrosion resistance of several container materials (see Figure 2). The addition of 0.1% Li_3N to lithium has led to complete intergranular penetration of an austenitic stainless steel tube wall (32 mils) while under similar test conditions in a standard test with no nitride addition, approximately 3 mils of attack occurred. Another corrosion phenomenon which occurs quite frequently in static systems is dissimilar metal mass transfer. This may occur when two or more container materials are in contact with the same liquid metal. Even though the solubility of the two solid metals may be very low in the liquid lithium, the lithium may act as a carrier in transferring atoms of one of the solid metals to the surface of the other solid metal. Figure 3 illustrates the extent to which this phenomenon may affect the corrosion on type 304 stainless steel specimens when a dissimilar iron container is used. Nickel is preferentially leached from the surface of stainless steels when exposed to high temperature lithium. This leaching action occurs to a depth of approximately 2 mils when both specimen and container are type 304 stainless steel. The very heavy attack (15 mils) which occurred when an iron container was used is due to leaching of nickel from the stainless steel specimen and

subsequent alloying of the nickel in solution in the lithium with the walls of the iron container allowing the corrosion process to continue.

For containing lithium in static, isothermal, monometallic systems at temperatures up to 1500°F for periods of 1000 hours, there are several satisfactory container materials. The austenitic and ferritic grades of the stainless steels are the most satisfactory structural materials for this type of service provided grain boundary precipitation of carbides is minimized. The corrosion resistance of the refractory metals in general in lithium is good at elevated temperatures in static systems (See Figure 4). However, many other problems such as the poor oxidation resistance of molybdenum and niobium must be solved or circumvented before utilization of these metals is practical.

The dynamic corrosion tests which will be covered in this paper are of two types:

1. Seesaw and Tilting Furnace Tests - A sealed tube partially filled with lithium metal is tilted up and down, while a temperature differential is maintained between the ends of the tube.
2. Thermal Convection Loop - A sealed loop filled with lithium is heated in certain sections and cooled in others to cause circulation due to differences in density of the liquid metal between the hot and cold leg of the loop.

These tests simulate to some extent the conditions which might exist in an actual system where liquid lithium is flowing through a plumbing system in which temperature differences are present. The most important information to be gained from these types of tests is the susceptibility of the system to suffer temperature gradient mass transfer (See Figure 5). Since the solubility of most container materials is temperature dependent, and generally solubility increases with increase in temperature, solution in the hot section and subsequent deposition in a cooler section may occur. The seesaw test apparatus is shown in Figure 6, and the mass transfer revealed by such tests is illustrated in Figure 7.

A thermal convection loop test is shown in Figure 8. Flow velocities of approximately five feet per minute are induced by maintaining sections of the loop at different temperatures. The results of seventeen thermal convection loop tests conducted to date are listed in Table I. No attempt will be made to discuss these tests individually, but the conclusions which may be derived from examination of the data will be presented. The most important information contained in this table is whether or not the loop plugged during the test, the weight of metal crystals recovered from the cold leg of the loop following test, and the depth of attack in the hot leg of the loop.

Inconel (nominal composition 77 Ni-15 Cr-7 Fe) showed extensive mass transfer and hot leg attack even at temperatures as low as 1300°F (cold

leg - 1200°F), and this result is typical for the nickel-base alloys exposed to lithium under these conditions.

Six type 316 stainless steel (nominal composition 68 Fe-17 Cr-12 Ni-2 Mo) loops have been tested and have shown less mass transfer and tendency to plug in three tests conducted at hot leg temperatures of approximately 1500°F than in other tests conducted at hot zone temperatures of approximately 1400°F and 1300°F (See Figures 9, 10 and 11). One type 316 stainless steel loop completely plugged in 290 hours when tested at a hot leg temperature of 1310°F (cold leg - 1058°F).

Type 321 stainless steel (nominal composition 70 Fe-18 Cr-10 Ni-0.5 Ti), when tested at a hot leg temperature of 1500°F, completely plugged with crystals in 204 hours (See Figure 12). Type 347 stainless steel (nominal composition 70 Fe-18 Cr-10 Ni-1 Nb) loops showed results similar to those of type 321 stainless steel tests, with plugging occurring in 280 hours with a 1500°F hot leg temperature. A 3000 hour test of a type 347 stainless steel loop at a hot leg temperature of 1000°F (See Figure 13) indicated that this material would be satisfactory for operation at temperatures in this range for very long time periods.

A type 430 stainless steel (nominal composition 83 Fe-16 Cr) loop operated at a hot leg temperature of 1500°F (cold leg - 1220°F) for 1500 hours without plugging, but did show considerable mass transfer (See Figure 14).

Two type 446 stainless steel (nominal composition 74 Fe-25 Cr) loops tested at hot leg temperature of 1500°F (cold leg - 1200°F) completely plugged in less than 900 hours and had 6.8 and 9 grams of metal crystals in the cold legs (See Figure 15). The wall-crystal interface on the cold leg surface may be seen in Figure 16. The bulk of the crystals are ferrite (composition 90 Fe-6 Cr), while those attached to the surface of the type 446 stainless steel wall have been identified by x-ray analysis as Cr₂₃C₆. The relative hardnesses of these two phases may be noted in the photomicrograph.

The results of chemical analysis of the mass transfer crystals from the nickel-iron-chromium and iron-chromium alloy loops tested show that all three metals are transferred in appreciable quantities. If the alloy contains nickel, the mass transfer crystals are richer in nickel than the container alloy. In iron-chromium alloy loop tests, the crystals deposited are richer in iron than the container alloy. Of the three metals -- nickel, iron and chromium -- chromium has the least tendency to mass transfer, but is still found to be present to the extent of 5 to 10 per cent in the mass transfer crystals found in stainless steel-lithium tests.

In summarizing these thermal convection loop data, it is obvious that further work needs to be done to resolve the apparent discrepancies which exist between the results on type 316 stainless steel and other austenitic stainless steels which contain little or no molybdenum. Also, types 317 and 318 stainless steels which contain more molybdenum than type 316 stain-

less steel will be tested. The ferritic stainless steel test results are not encouraging, especially type 446 stainless steel, which suffers very deep intergranular attack due to preferential attack of the grain boundary carbides. Further tests are planned on type 430 stainless steel. The superior corrosion resistance of type 430 stainless steel over type 446 stainless steel is attributed to the lower carbon content of type 430 stainless steel (0.12 carbon maximum; type 446 steel - 0.35 carbon maximum).

It is interesting to note that in the two type 446 stainless steel loops which exhibited very large amounts of mass transfer as compared to the type 430 stainless steel test, there was evidence of complete intergranular penetration of the container wall at some location around the loop. Contamination of the lithium by lithium nitride and/or lithium oxide may lead to rapid increases in the rate of mass transfer and account for the large amount of crystals found in these loops, while in the other iron-base alloy loops listed in Table I as little as 0.7 to 1.5 grams of crystals was sufficient to cause plugging. The large increase in the mass transfer rate following contamination by lithium nitride might be explained to some extent by Figure 2. This photomicrograph shows that additions of lithium nitride to lithium leads to the exposure of an extremely large surface area of container metal to the corrosive action of the lithium metal. This effect would be in addition to any direct chemical effects which the nitride itself might have in the mass transfer mechanism. Many tests remain to be performed in order to explain the results observed in these investigations.

Figure 17 summarizes the data obtained to date and shows that none of the materials tested are satisfactory to contain lithium at hot leg temperatures of approximately 1500°F in flowing systems. Tests are presently being conducted on niobium in dynamic systems and it is believed that it and several of the other refractory metals -- especially molybdenum -- will withstand the corrosive action of lithium under these conditions, but as yet this has not been demonstrated. The effect of various amounts of nitride contamination on the amount of mass transfer will be studied further. Experiments will be conducted in order to determine the maximum temperature (in the range from 1000 to 1300°F) at which a stainless steel-dynamic lithium system may be operated since these alloys at present seem to be satisfactory at 1000°F and generally unsatisfactory at 1300°F.

BIBLIOGRAPHY

1. Lyon, R. N., Editor: Liquid Metals Handbook: NAVEXOS-P-733 (Rev.), U. S. Government Printing Office, Washington, D. C., 1954, p. 5.
2. Jackson, C. B. Editor: Liquid Metals Handbook, Sodium-NaK Supplement: Atomic Energy Commission -- Department of Navy, Washington, D. C., 1955.
3. Chart of the Nuclides. Knolls Atomic Power Laboratory, Fourth Edition, Revised to Nov., 1952.

4. Hoffman, E. E., W. D. Manly, and D. C. Vreeland: Corrosion Tests for Liquid Metals, Fused Salts at High Temperatures. Nucleonics, Vol. 11, No. 11, November, 1953, p. 36-39.
5. Manly, W. D.: Fundamentals of Liquid-Metal Corrosion. To be published in Corrosion.

ACKNOWLEDGEMENT

The authors would like to acknowledge the assistance of other personnel of the Oak Ridge National Laboratory in obtaining the information included in this paper. The metallographic work was performed by a group under the direction of Mr. R. J. Gray, of the Metallurgy Division.

256

TABLE I
LITHIUM THERMAL CONVECTION LOOP TESTS^a

Material	Temperature			Time (hr)	Results	
	Hot Leg °F	Cold Leg °F	Differential °F		Hot Leg	Cold Leg
Inconel	1300	1200	100	1000	16 mils attack	15.1 gm of crystals
316 S.S.	1500	1292	208	500	13 mils attack	0.5 gm of crystals
316 S.S.	1490	1220	270	1000	1.5 mil attack	0.1 gm of crystals
316 S.S.	1472	1335	117	1000	3 mils attack	0.01 gm of crystals
316 S.S.	1400	1130	270	2150 ^b	23 mils attack	4.7 gm of crystals
316 S.S.	1310	1058	252	290 ^b	2 mils attack	0.8 gm of crystals
316 S.S.	1292	1094	198	1000	15 mils attack	0.25 gm of crystals
321 S.S.	1500	1220	280	204 ^b	0.5 mils attack	1.0 gm of crystals
321 S.S.	1310	980	330	1230 ^b	3.0 mils attack	0.7 gm of crystals
347 S.S.	1500	1112	388	280 ^b	2 mils attack	1.5 gm of crystals
347 S.S.	1310	1060	250	1000	3.0 mils attack	1.3 gm of crystals
347 S.S.	1000	618	382	1000	1 mil attack	crystals 0.2 mils thick
347 S.S.	1000	618	382	3000	1.5 mils attack	crystals 0.3 mils thick
430 S.S.	1500	1220	280	1500	4.0 mils attack	1.0 gm of crystals
446 S.S.	1500	1166	334	864 ^b	1.0 mils attack	9 gm of crystals (84 mils attack)
446 S.S.	1500	1200	300	700 ^b	16 mils attack	6.8 gm of crystals (84 mils attack)
446 S.S.	1292	1058	234	1500	25 mils attack	0.23 gm of crystals (65 mils attack)

a. All loops constructed of 1/2" Schedule 40 pipe (0.84" OD x 0.622" ID)

b. Loop plugged with crystals

Y-17304

SOME IMPORTANT PROPERTIES OF HEAT TRANSFER FLUIDS
FOR REACTOR APPLICATIONS

	MELTING POINT, (°F)	BOILING POINT, (°F)	DENSITY AT M.P. (g/cm ³)	HEAT CAPACITY AT M.P. (cal/g-°C)	THERMAL CONDUCTIVITY AT M.P. (cal/sec-cm-°C)	ABSORPTION CROSS SECTION BARNs (10 ⁻²⁴ cm ²)
H ₂ O	32	<u>212</u>	1.0	1.0	<u>0.001</u>	0.6
Na	208	1616	0.92	0.33	0.21	0.45
Na(56%) K(44%)	66	1518	0.87	0.26	0.06	1.1
Pb	<u>622</u>	3170	<u>10.4</u>	0.04	0.04	0.2
Li	367	2403	0.50	1.0	0.09	<u>65</u>
Hg	-37	<u>675</u>	<u>13.6</u>	0.03	0.02	<u>430</u>

UNDESIRABLE PROPERTIES ARE UNDERLINED

Figure 1

Figure 2

Type 316 stainless steel tube after a 100-hour exposure to lithium (plus 0.1% Li_3N) at 1600°F.

Figure 3

Phase change (austenite to ferrite) on exposed surface of Type 304 stainless steel specimens caused by preferential leaching of nickel. Note very heavy attack on the specimen on the right; this attack was encountered when an iron container was used. Etched with glyceria regia.

Figure 4

Edge of molybdenum specimen following a 100-hour exposure to static lithium at 1500°F. Note absence of attack on surface of specimen. Etched with 50% hydrogen peroxide -50% ammonium hydroxide.

ORNL-LR-DWG 5643

TEMPERATURE GRADIENT MASS TRANSFER

Figure 5

Figure 6

Seesaw test furnace and instrumentation. Container tube partially filled with lithium is inside furnace which rocks up and down.

Y-10174

HOT ZONE - 871°C (1600°F) COLD ZONE - 593°C (1100°F)

SS-Li-96

LITHIUM - 500 HOURS (30,000 CYCLES)

316 S.S. (18" L. X 3/4" O.D. X 0.035" WALL)

Figure 7

Appearance of hot and cold zone following seesaw test. Note polished appearance due to solution of tube in hot zone and the crystal deposition which occurred in the cold zone.

Figure 8

Thermal convection test loop in operation. Bath metal is flowing in a clockwise direction due to the temperature differences in various sections of the loop.

316 STAINLESS STEEL-LITHIUM
THERMAL CONVECTION LOOP
1000 HOURS

Figure 9

Figure 10

Y-I

HOT ZONE - 710°C (1310°F)

COLD ZONE - 570°C (1060°F)

THERMAL CONVECTION LOOP NO. 16
316 STAINLESS STEEL - LITHIUM - 290 HOURS

Figure 11

262

Y-18624

HOT ZONE - 815°C (1500°F)

COLD ZONE - 660°C (1220°F)

THERMAL CONVECTION LOOP NO. 21
321 STAINLESS STEEL-LITHIUM-204 HOURS

Figure 12

263

Y-17897

HOT ZONE — 538°C (1000°F)

COLD ZONE — 325°C (618°F)

SECTIONS FROM TYPE 347 STAINLESS STEEL LOOP IN WHICH
LITHIUM WAS CIRCULATED FOR 3000 HOURS

263

Figure 13

Y-18087

HOT ZONE - 816°C (1500°F)

COLD ZONE - 660°C (1220°F)

THERMAL CONVECTION LOOP NO. 14
430 STAINLESS STEEL - LITHIUM - 1500 HOURS

Figure 14

Y-18639

HOT ZONE - 815°C (1500°F)

COLD ZONE - 648°C (1200°F)

THERMAL CONVECTION LOOP NO. 24
446 STAINLESS STEEL-LITHIUM - 700 HOURS

Figure 15

Figure 16

Photomicrograph of cold-leg wall of type 446 stainless steel loop following exposure to lithium (See Fig. 15). Very hard phase (Vickers Hardness Number -- approximately 1100) is Cr_2C_6 , while soft crystal attached to it is a ferrite crystal of composition 90 Fe-6 Cr. Specimen was nickel plated (VHN-210) following test to preserve the edge and hold crystals in place. Etch: Glyceria Regia.

*BARS INDICATE APPROXIMATE TEMPERATURES BELOW WHICH A SYSTEM MIGHT BE OPERATED FOR 1000 HOURS WITH LESS THAN 0.005 in. OF ATTACK OR CONTAINER SURFACE REMOVAL.

CORROSION RESISTANCE OF VARIOUS METALS AND ALLOYS IN LITHIUM*

Figure 17

SILICONIZING OF METALS IN LIQUID NaK

by

E. S. Fisher, R. A. Noland, and C. Marzano

Argonne National Laboratory
Lemont, Illinois

Abstract

Surface diffusion layers consisting of base metal silicides have been produced on uranium, molybdenum and some steels by immersing the metal in liquid sodium-potassium alloy containing dissolved silicon. This method of siliconizing is advantageous in that the coatings can be produced at relatively low temperature and oxidation of the surface prior to the formation of the silicides can be minimized in the NaK medium. Consequently, it may be a favorable means for producing corrosion resistant surfaces on some reactive metals.

An apparatus and procedure used for producing adherent uranium silicide coatings is described. The amount of silicon added to the uranium can be easily controlled by this procedure. This method is used as part of the process for preparing alpha uranium single crystals.

INTRODUCTION

There is considerable interest today in the silicides of various metals because of the apparent ability of some of the compounds to resist the corrosive effects of various media. The disilicides of Mo¹ and W² for example have been shown to resist oxidation at 1500°C in air to a significantly greater degree than either metal. Similarly, the epsilon phase of the uranium silicon system, U₃Si, has been shown to resist corrosion in high temperature pressurized water to a much greater degree than uranium metal.³ Consequently these alloys may have utility where these properties are desirable. However, these alloys are somewhat difficult to fabricate and/or to prepare. It would

be advantageous to be able to form the parts from the base metal and subsequently process these parts so that the surfaces are covered by a diffusion layer of the base metal silicide which is resistant to corrosion.

Various methods of producing silicide diffusion layers have been investigated. Some of these methods depend on diffusion of silicon into the base metal from mechanically applied surface coatings.⁴ In other methods the silicides are produced through chemical reaction between the base metal and a surrounding atmosphere containing gaseous or liquid compounds of silicon.^{5,6} The Ames Laboratory has investigated still another principle in which the base metal is immersed in a bath of a lower melting liquid metal which contains dissolved silicon.⁷ Specifically, they applied this principle to the preparation of uranium silicide diffusion layers on uranium metal immersed in liquid magnesium. Because uranium is relatively immiscible in liquid magnesium the surface of the uranium reacts only with the dissolved constituents for which there is affinity. It is this latter principle which we have investigated using liquid NaK alloy of the eutectic composition, in place of magnesium. NaK has several advantages which are discussed below.

The primary problems in preparing silicide diffusion layers are uniformity and adherence. To provide the desired surface protection it is generally necessary that the base metal surface be completely covered and that the diffusion layer remain bonded to the base metal during service. If the siliconizing process permits other surface reactions to occur prior to the formation of the desired diffusion layer it is probable that the protective layer will be poorly adherent or completely absent in local areas. The problem of preventing such barrier layers is particularly serious with base metals such as uranium and molybdenum where there is a great affinity for oxygen at high temperatures. The method using immersion in liquid metals has the advantage over other methods in that oxide barrier layers are prevented if the liquid metal is free of dissolved oxygen or oxide particles, provided the metal surface is clean upon immersion. The use of NaK is particularly advantageous in this respect for the following reasons:

- (a) eutectic NaK melts at -12°C ; consequently, high temperatures are not necessary to retain the molten state.
- (b) NaK is relatively inert to many structural metals; consequently, ceramics are not necessary to contain the bath.

There are 2 other properties of NaK which make it particularly suitable for use as a siliconizing bath:

- (c) NaK is relatively inert to uranium and other base metals of interest to reactor design,
- (d) silicon is apparently rapidly dissolved in NaK at temperatures as low as 450°C .

Our investigation was conducted primarily to determine the feasibility of using NaK as a siliconizing medium for producing silicide diffusion coatings on uranium and other metals of possible use as reactor materials. It was found that the method is applicable to uranium, molybdenum, and various steels. There are indications that thorium silicide layers can be produced by this means; however, positive identification of the diffusion layers has not been attained. Attempts to siliconize zirconium and titanium were unsuccessful.

During this investigation some of the factors influencing the rates of diffusion layer growth were observed. Where possible the identification of the diffusion layers from available literature data was made. The adherence and corrosion properties of some of the layers were surveyed.

Subsequently the process was adopted for use in the preparation of alpha uranium single crystals by the grain coarsening method.⁸ In this method it is desired to have fine grained uranium rods of circular cross section in which the grain growth inhibiting inclusions are dispersed in a concentration gradient increasing from the center of the rod to the cylindrical surface. When such rods are annealed for prolonged periods at 650°C large grains begin to grow from the center to the surface of a cross section. However, in order for the method to be successful it is necessary that the concentrations of inhibiting inclusions be very small and that the gradient of inclusions be of optimum character, i.e., neither too shallow nor too steep. To attain such conditions a system for siliconizing was developed whereby the amount of silicon added to the uranium surfaces could be carefully controlled to within 1 mg. without too much difficulty. The equipment and process used for maintaining this degree of control is described in this paper.

At present, diffusion layers capable of preventing oxidation of uranium and molybdenum at high temperatures are not attainable by this method. The utility of the diffusion layers depends on which of the silicide compounds is present at the temperature of test, the uniformity of the layer and the spalling tendency. Further work is necessary to find the siliconizing conditions which will yield protective surface layers with good precision. The observations described in this report indicate that the NaK siliconizing method is a promising approach to the problem.

INITIAL PROCEDURE

The experiments were carried out by a batch process. The material to be siliconized was machined to cylinders in the order of 3/8 inch diameter by 1 inch long. The surfaces were cleaned by electrolytic polishing in an aqueous solution containing 45% concentrated sulfuric acid and 9% glycerine. The samples were then supported in a stainless steel rack which was placed in a stainless steel (AISI Type 347) flanged container 3 inches I.D. x 14 inches long. The silicon in form of small pellets was placed in the bomb beside the rack in quantities of 0.1 to 10 grams. The container was then sealed vacuum tight using

metal "O" ring flanges and steel bolts. After evacuation, the NaK was siphoned into the bomb in volumes of 300 to 500 cc. The system was then pressurized with argon and the inlet pipes were sealed by valves. The bomb was then heated at different temperatures varying from 400°C to 800°C for various periods of time. Upon removal from the furnace the NaK was discarded and the specimens were cleaned of residual NaK by immersion in butyl alcohol.

A series of tests were conducted: 1) to determine the feasibility of siliconizing various materials, 2) to observe the effects of siliconizing temperature, time, and silicon concentration in the NaK on the rates of siliconizing and the quality of the diffusion layers. Approximately 15 tests were carried out with this procedure. In half of the tests only uranium samples were involved. In the other tests specimens of uranium, molybdenum, thorium, steel, zirconium and titanium in various combinations were simultaneously exposed.

This system had a number of disadvantages. Because the system was loaded at room temperature and then heated to high temperatures there was a tendency for the sample surfaces to oxidize before the silicon dissolved in the NaK and the siliconizing reaction could proceed. Secondly, it was difficult to control the quantity of silicon weight gain by the methods used because some siliconizing undoubtedly occurred during heating to the temperature of test. Finally, the process was quite inefficient with respect to the use of NaK and to the preparation time.

PRESENT PROCEDURE

A schematic view of the apparatus presently used for siliconizing is shown in Figure 1. The system is designed so that the bath of NaK containing silicon can be heated to the siliconizing temperature before the specimens are immersed. In addition, the same bath of NaK can be used continuously for a number of successive runs. The NaK is contained in a zirconium tube, 2 inches in diameter x 15 inches long, at the bottom of a 2 inch diameter x 30 inches long stainless steel tube which is capped by a 2 inch stainless steel gate valve. The lower two-thirds of the tube is heated externally and the top end is water cooled through attached copper tubing. This part of the system is constantly under a positive pressure of purified argon gas. The silicon, in form of high purity silicon powder, is placed in a tray to which is attached a long rod. To immerse the silicon in the NaK, the tray is placed first in the loading chamber above the valve with the rod extending out through a neoprene packing gland. This chamber is carefully evacuated and flushed with purified argon before opening the gate valve to the lower system. The tray is then lowered into the hot NaK by manipulating the attached rod. The tray is generally left in the NaK for 2 to 4 hours to insure dissolution of the silicon and is then removed by pulling it up into loading chamber. The valve is then closed.

The process for immersing the specimens is the same. The specimens are clamped in a rack to which is attached a long rod. After siliconizing the NaK adhering to the specimens and rack is removed by spraying the rack with cold water. Although the reaction is quite violent the heat evolved is quickly dissipated by the water flow so that no apparent oxidation of the specimen surface occurs due to this phase of processing.

This system is used primarily for adding small controlled quantities of silicon to high purity uranium for the preparation of single crystals. To attain the precision necessary in working with such small quantities of silicon, a mass balance method of controlling the quantity of silicon added to the specimens is used. Generally the amount of silicon desired varies from 10 to 15 mgs. per specimen depending on the specimen weight. Three specimens of similar weights are generally siliconized at one time. Before immersing the specimens we add to the NaK just that total weight of silicon which we would like to add to the uranium. The specimens surfaces are carefully electropolished to a high luster and weighed to the nearest 0.1 mg. before immersion. To prevent loss of silicon to the container, the silicon tray and the specimen rack, these parts are made entirely from zirconium, which has been shown not to react with silicon at the temperatures used. With this method it is not necessary to rely on reproducing the kinetics of the reaction. The NaK temperature varies from 475°C to 485°C. The specimens are generally left immersed in the NaK overnight.

RESULTS WITH URANIUM

Weight Gains and Surface Appearance in Uranium Specimens

The success of the mass balance method of controlling the quantity of silicon added to the uranium rods depends primarily on the cleanliness of the atmosphere above the NaK. If the loading chamber has been well depleted of air by pumping and flushing, the method is very successful. Generally the total weight gains of the specimens is 1 mg. less than the quantity of silicon added to the NaK prior to immersion of the specimens. The total weight gain has never been greater than the quantity of silicon added. The surfaces of the siliconized specimens have a uniform dull silvery appearance. Periodic checks have been made to determine whether the specimen weight gains are due primarily to the addition of silicon. Uranium specimens were immersed into NaK into which no silicon had been added since the prior specimen immersion. These specimens generally show weight gains which are less than 1 mg. and which could be attributed to a very thin uniformly coherent oxide film. The surfaces appear lustrous but slightly darker than the original electropolished appearance.

When significant oxidation occurs during the siliconizing immersion the effects on the weight gains and appearance are quite marked. The surfaces have a non-uniform distribution of interference colors due to variations in thickness of the coatings. After removal of the

NaK by water spray the specimens generally show a significant loss in weight, compared to the weight before immersion. It appears that when significant oxidation occurs the siliconized surface layer is not strongly bonded to the base metal and, consequently, spalls during the specimen cleaning process.

Effect of Temperature on Siliconizing Rates

During the experiments using the batch process some observations were made concerning the rates of specimen weight gains at different siliconizing temperatures. The very first experiments were made using 10 grams of silicon in 300 cc of NaK. These tests indicated that the rate of siliconizing increases quite abruptly between 400°C and 600°C. At 475°C very significant weight gains were observed after 1 hour. After 2-1/2 hours at 400°C no evidence of siliconizing was apparent.

Adherence of Diffusion Layer

As stated above, the adherence to the base metal of the compound formed by the surface reaction is affected primarily by the presence of an oxide layer on the base metal surface. This fact is indicated in the correlation between appearance of the surface and weighing data of the specimens siliconized by the present procedure. Further evidence of the oxidation effect was observed among the specimens which were siliconized by the batch process. The NaK adhering to these specimens was removed by the relatively slow reaction between butyl alcohol and NaK. Consequently the less tenacious layers remained on the specimen even after the cleaning. However, spalling was frequently observed during subsequent handling of these specimens. Most of the spalling was apparently caused by oxidation of the uranium prior to and during siliconizing, as indicated by the dark films and non-uniform surface appearance. Some spalling, however, was observed on specimens which appeared silvery; this spalling may have been due to the relatively thick diffusion layers which were present on the surfaces of these specimens.

Diffusion layers formed where oxidation is not significant appear to be quite tenacious. These diffusion layers show no tendency to spall due to mechanical stresses or to stresses induced during heating of the specimens to temperatures as high as 975°C. A typical cross section of a siliconized rod is shown in Figure 2. This area was photographed at 250 magnification. The specimen was mechanically polished through 1 micron diamond paste and then electropolished in a phosphoric acid electrolyte normally used for preparing uranium surfaces. Because the diffusion layer is not dissolved in the electrolysis the diffusion layer and the uranium are not in the same plane. Consequently, the boundary between the uranium (lower portion of Figure) and the diffusion layer appears as a dark line. The specimen was approximately 1/2 inch in diameter. The diffusion layer covered the surface of the specimen but varied in thickness from 0.0003 inch to 0.001 inch. When properly siliconized specimens are heated to

975°C in evacuated glass capsules the silicon apparently diffuses rapidly into the uranium. However no spalled pieces of the layer are found in the capsule.

Identification of Diffusion Layer Structure

Under microscopic inspection only one phase appears to form as a result of the siliconizing process (Figure 2), although 6 intermediate compounds of uranium and silicon have been reported. X-ray diffraction data from a number of different samples shows the compound beta $U Si_2$ to be generally present at the surface of the specimens. In some cases diffraction patterns corresponding to the $U Si$ and U_3Si structure have been identified.

Mechanical Properties of Diffusion Layer

Figure 3 shows a cross section through a diffusion layer which has fractured during mechanical grinding and polishing for metallographic inspection. These fractured regions were observed where the diffusion layer was greater than average in thickness. These layers are apparently quite hard and deform primarily by brittle fracture.

Corrosion in Boiling Water

A number of siliconized samples have been corrosion tested in boiling distilled water. In general the corrosion resistance of the tenacious layers is significantly better than that of uranium. Whereas black uranium oxide powder begins to appear on uranium surfaces after a few hours in this test, the siliconized surfaces were corroded only at local areas where pinholes appeared to have formed and grown. After 1 week these pinholes were in order of 1 mm. diameter and widely dispersed. Further study is necessary to determine the source of these pinholes and to obtain quantitative data regarding the rates of oxidation of this diffusion layer.

Diffusion of Silicon during Subsequent Heating

In application to the preparation of single crystals the uranium specimens are heated at 975°C, subsequent to siliconizing at 475°C, for diffusion penetration of the silicon. The silicon from a diffusion layer in the order of 0.001 inch thickness penetrates in the order of 0.100 inch from the surface in 48 hours and 0.150 inch from the surface in 96 hours. When the as diffused high purity rods are rolled and annealed in the alpha phase the effect of the diffusion on alpha grain growth is very apparent, as shown in Figure 4, because of the grain coarsening phenomenon. Whereas large grains appear at the cross sectional centers of the rods after prolonged annealing at temperatures above 600°C, the peripheral area which contains the higher silicon concentration remains fine grained. The fine inclusions formed by the alpha phase precipitation of uranium silicides are apparently quite

effective grain growth inhibitors.

Diffusion heat treatment of siliconized rods may also be a means for increasing the utility of the siliconizing process. Although the beta $U Si_2$ phase which is the predominant diffusion layer after siliconizing at $475^\circ C$ may not be sufficiently oxidation resistant to be useful, it may be possible to form sufficiently thick layers of the U_3Si phase by manipulation of diffusion temperature and time. At present it is known that a 0.001 inch thick diffusion layer formed at $475^\circ C$ by siliconizing disappears after 6 hours diffusion at $975^\circ C$.

RESULTS WITH MOLYBDENUM

Six tests have been carried out in which molybdenum rods of 1/4 inch to 1/2 inch diameter have been immersed in NaK baths of different silicon concentrations. The results show that diffusion layers of molybdenum silicide compounds can be prepared by this method. The rates of formation of these layers are apparently significantly smaller than those involved in siliconizing of uranium. The tenacity and appearance of these layers is affected by the oxygen content of the siliconizing system. The diffusion layers formed at temperatures above $600^\circ C$ were primarily the compound $MoSi_2$, whereas, a different structure is formed at $600^\circ C$ in smaller concentrations of silicon.

The first 4 tests were made with the batch process procedure, described above. The siliconizing temperatures varied from $700^\circ C$ to $800^\circ C$, with silicon concentrations of 5 to 9 grams in 500 cc of NaK. The time of immersion varied from 6 to 20 hours. The diffusion layers formed in these experiments were relatively thick and varied in color from dark blue to light blue. The surface layers formed at $750^\circ C$ and $800^\circ C$ contained macroscopically visible grooves, providing a checked appearance. The specimens which were immersed for the longer time periods weighed less after test than the initial weight, indicating that some spalling of the diffusion layer had occurred during processing. X-ray diffraction patterns from surface layers and the spalled pieces corresponded to that of $MoSi_2$.

Two molybdenum specimens were treated in the continuous siliconizing apparatus. One of these specimens was immersed simultaneously with 2 uranium rods at $475^\circ C$ for 20 hours. All of the silicon added to the NaK before the immersion of the specimens was picked up by the uranium, the molybdenum specimen showing no change in weight. In the second test a molybdenum specimen was immersed singly in NaK which contained 48 mgs. of silicon at $600^\circ C$. After 20 hours this specimen had gained 35 mgs. of weight and appeared light blue in color. A cross section of the siliconized specimen is shown in Figure 5. The mechanically polished surface was immersion etched in an aqueous solution containing 5% HF and 10% HNO_3 . The molybdenum was not attacked by this solution but the diffusion layer became brown in color and columnar grain boundaries within this single phase layer became apparent. The layer was in the order of 0.0007 inch in thickness. The X-ray diffraction patterns from the surface of the specimen and from filings of the surface layer do not correspond to any of the reported structures of

Mo-Si compounds, Mo_3Si , Mo_3Si_2 nor MoSi_2 .¹ A qualitative chemical analysis of the layer by spectrographic detection showed that only molybdenum and silicon were present in significant quantities.

Two siliconized molybdenum specimens were subjected to oxidation tests at 1000°C in air. In both cases only the cylindrical surfaces were covered by silicide layers. After 20 hours of test the specimens were hollow shells, indicating that the molybdenum had oxidized and evaporated, whereas, the silicide was relatively stable. The diffusion layer on one specimen was MoSi_2 produced by siliconizing at 700°C. The other specimen contained the unidentified diffusion layer formed at 600°C.

RESULTS WITH STEEL

Evidence of the ability to siliconize steels have been obtained from batch siliconizing tests with SAE 1020 steel and AISI type 347 stainless steel cylinders and from the appearance of 347 stainless steel racks used for supporting other materials during siliconizing. On both types of steels surface diffusion layers containing the compound FeSi have been identified. The reaction rates for the siliconizing of 347 stainless steel are apparently much lower than those of uranium at temperatures of 475°C and 500°C. The siliconized surface appear dark gray to black. At temperatures of 700°C and 800°C plain carbon steels appear to react faster than stainless steel with the silicon in the NaK. However, the diffusion layers formed on the plain carbon steel were significantly less tenacious.

RESULTS WITH THORIUM

Thorium specimens were tested by the batch siliconizing process at 475°C. Of three specimens, two gained weight due to immersion in the bath, whereas one lost weight, indicating a spalling of a diffusion layer. All 3 specimens appeared dark gray after immersion whereas they were originally bright. The structure of the surface layer has not been identified.

RESULTS WITH ZIRCONIUM AND TITANIUM

Attempts were made to siliconize zirconium and titanium samples by the batch process at temperatures of 700°C, 750°C, and 800°C. All of the specimens tested showed a gain in weight due to the processing. The dark surface layers produced were, however, identified as ZrC and TiC by X-ray diffraction. Further evidence that zirconium silicides are difficult to prepare by this process is shown in the continuous siliconizing apparatus; the zirconium cup used for containing the NaK does not interfere with the weight balance method for controlling the quantity of silicon added to the samples immersed in the NaK.

SUMMARY

Surface diffusion layers consisting of the silicides of the base metal have been produced in uranium, molybdenum, plain carbon steel and AISI type 347 stainless steel by immersing these metals in liquid NaK containing dissolved silicon. The silicon reacts with the immersed metal surface to form a single diffusion layer. The kinetics of the reactions with uranium and molybdenum and the conditions for producing diffusion layers which adhere to the base metal upon subsequent handling and heating have been qualitatively observed.

In general the rates of the siliconizing reaction increase with temperature, as is to be expected. However, the rates appear to depend significantly on the base metal. Of the 4 materials mentioned above, uranium appears to react most rapidly. Below 400°C the reaction with uranium is extremely slow; whereas at 475°C significant siliconizing occurs within 1 hour. Molybdenum apparently reacts slowly at temperatures below 600°C. There are indications that the rates of reaction also depend on the concentration of silicon in the NaK and on the surface area of the immersed metal. Systematic studies of these effects have not been carried out.

The adherence of the diffusion layer to the base metal is adversely affected by any oxidation which occurs on the base metal prior to or during the siliconizing reaction. An apparatus and procedure have been developed to permit siliconizing with a minimum amount of oxidation.

The structure and composition of the diffusion layer formed could conceivably vary depending on the temperature of siliconizing, the quantity of silicon in the NaK, the surface area of the specimen, and the rate of diffusion of silicon in the metal at the temperature of siliconizing. With uranium the quantity of silicon and the surface area apparently have little effect on which silicide is formed at temperatures between 475°C and 600°C. The beta $U Si_2$ phase is generally found to be predominant in X-ray diffraction patterns. With molybdenum the $Mo Si_2$ phase is formed at temperatures above 700°C in the presence of large quantities of silicon. At 600°C an unidentified Mo - Si phase is formed with small quantities of silicon in the NaK.

The uranium and molybdenum silicide diffusion layers are hard and brittle. When the diffusion layer is formed under optimum conditions the surface of the uranium specimens shows a markedly lower corrosion rate in boiling water than that of the base metal. The diffusion layers on molybdenum are significantly more resistant to oxidation at 1000°C than molybdenum.

At present the continuous siliconizing process is used as a means for producing diffusion gradients of silicon in uranium rods, as part of the process for preparing single crystals. This siliconizing method is very satisfactory for controlling the quantities of silicon added to the uranium within 1 mg. precision.

The process may be useful for producing protective coatings on metals which are too exposed to oxidizing conditions. For uranium this would presumably require that the surface layer be the U_3Si phase. Further investigation is necessary to determine the conditions for preparing U_3Si diffusion layers.

REFERENCES

1. Kieffer, R. and E. Cerwenka; Beitrag zum System Molybdan - Silizium, Z. Metallkunde. 43, 1953, 101.
2. Kieffer, R., F. Benesovsky and E. Gallistl: Beitrag zum System Wolfram - Silizium und uber die Zunderstand Keit einiger Silizide. Z. Metallkunde. 43, 1952, 284.
3. Bitsianes, G.: Alloys of Uranium and Silicon - The Epsilon Phase. CT-3309, MIT, June 1945, (classified).
4. Kluz, S., C. Kalinowsky and R. Wehrman: Program Report on Siliconizing of Titanium. Fansteel Met. Corp., N. P. 4347, Dec. 31, 1952.
5. Powell, C., and R. P. Jones: Protective Coatings for Molybdenum. BMI-810, Feb. 17, 1953.
6. Blanchard, J. R.: Oxidation-Resistant Coatings for Molybdenum. WADC-TR-54-492, Dec. 1954.
7. Ames Laboratory: Quarterly Summary Research Report, Oct., Nov., Dec., 1953. ISC - 453, May 25, 1954.
8. Fisher, E. S.: Preparation of Alpha Uranium Single Crystals - Part III. ANL-5021, August 1954.

ACKNOWLEDGEMENTS

The initial studies were carried out by Messrs. C. Marzano, E. Moretti and D. Walker.

The authors are grateful to Dr. M. Mueller and Mr. H. Knott for X-ray diffraction studies and to Mr. W. Ruther for corrosion testing.

Figure 1. Schematic Sketch of Continuous Siliconizing System

250X Electropolished 19,387

Figure 2. Diffusion layer on surface of 1/2" diameter x 1" long uranium rod, siliconized at 475°C, gained 185 ppm silicon.

250X

19,388

Figure 3. Same specimen as Fig. 2, showing portion of diffusion layer fractured in metallographic preparation.

8X Macro-etched

16,902

Figure 4. The effect siliconizing and diffusion on grain growth in alpha uranium. Sample treated as follows:

- (a) 9/16" diameter rod siliconized (gained 180 ppm silicon)
- (b) diffusion treated 48 hours 975°C.
- (c) swaged to 1/4" at 300°C.
- (d) annealed 24 hours at 650°C.

Fine grained periphery is due to silicide inclusions. Large grains are result of grain coarsening.

—Copper Plate

—Molybdenum Silicide

—Molybdenum

500X

19,593

Figure 5. Diffusion layer on molybdenum sample, 3/8" diameter x 1" long, siliconized at 600°C, gained 0.17% silicon.