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UNITED STATES ATOMIC ENERGY COMMISSION

METALLURGY DIVISION: SEMIANNUAL PROGRESS REPORT

for Period Ending April 10, 1954

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Edited by W. H. Bridges

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ORNL-754	Period Ending April 30, 1950
ORNL-827	Period Ending July 31, 1950
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ORNL-1267	Period Ending January 31, 1952
ORNL-1302	Period Ending April 30, 1952
ORNL-1366	Period Ending July 31, 1952
ORNL-1437	Period Ending October 31, 1952
ORNL-1503	Period Ending January 31, 1953
ORNL-1551	Period Ending April 10, 1953
ORNL-1625	Period Ending October 10, 1953

CONTENTS

PUBLICATIONS	viii
SUMMARY	ix
PHYSICAL METALLURGY OF REACTOR MATERIALS	1
Transformation Kinetics of Zirconium-Base Alloys	1
Mechanical Properties of Thorium	2
Metallurgical Processing of Spent Fuel Elements	3
Carburizing of stainless steel fuel elements	3
Slagging experiments on stainless steel fuel elements	5
Reduction of UO_2F_2 with Aluminum	6
HRP METALLURGY	9
Physical Metallurgy of Titanium and of Zirconium Alloys	9
Commercial titanium	9
Zirconium alloys	9
Welding of Stainless Steels	11
Dynamic Corrosion of Welded Stainless Steel Specimens	13
Metallographic studies	13
Effects of heat treatment and composition	17
Stress-Corrosion Cracking of Austenitic Stainless Steels	20
Selective Oxidation of Austenitic Stainless Steels	23
ANP METALLURGY	25
Static Corrosion	25
Fluoride corrosion	25
Static tests of brazing alloys in fluorides and sodium	25
Dissimilar metals in fluoride 30	29
Thorium oxide-sodium static tests	30
Inconel X-sodium tests	31
"Chromalloyed" steels in liquid metals	33
Miscellaneous tests	35
Vacuum dry box	37
Dynamic Corrosion	40
Operating time	40
Fluoride batch purity	41
Loop temperature	42
ARE fluoride batch 31	42
High-uranium fluoride mixture 44	42
Variations in uranium percentage	43
Inconel loop variations	44
Additional container materials	44
Dissimilar-metal mass transfer	46
Inconel forced-circulation loop	46
Physical Chemistry	47
Mass transfer in liquid lead	47
Mass transfer in fused hydroxides	52
Sodium-alloy flammability	53

Interfacial equilibria in the Cu-Bi system	53
Products of hydroxide-metal reactions	54
Dehydration of sodium hydroxide	56
Color changes in fused hydroxides	57
Electrical conductivity of fused sodium hydroxide	58
Oxidation of solid sodium	59
Welding and Brazing	59
High-temperature brazing alloy development program	59
Brazing of high-conductivity radiator fins	62
Sodium-to-air radiator fabrication	64
Inert-arc plug-welding of solid fuel elements	66
Fabrication	67
ANP radiator	67
Special alloys fabrication	71
Tubular fuel elements	71
Mechanical Testing	73
PACKAGE POWER REACTOR PROGRAM	80
Preparation of UO_2 -Stainless Steel- B_4C Powder Cores	80
Fabrication of Stainless-Steel-Clad Fuel Plate	80
Component Assembly by Brazing	81
Corrosion Studies	83
Control-Rod Development	83
CERAMICS RESEARCH	85
Petrographic Examination of Fluoride Fuels	85
Glass-Type Pump Seals	85
Ceramic Bearings	85
Ceramic Container for Fuel Studies	85
Rare-Earth Ceramics	86
Al- UO_2 Cermets	86
ThO_2 Investigations	86
Ceramic Coatings	86
High-Density Graphite	86
High-Density K_3CrF_6 Rods	87
FUNDAMENTAL PHYSIOMETALLURGICAL RESEARCH	97
Methods of Representing Preferred Orientation Data	97
Fundamental Studies of Alloying	104
Factors affecting the α/β boundaries	104
Experimental Investigation of Pure Zirconium	108
The $\alpha \rightarrow \beta$ transition temperature	108
Annealing of pure zirconium	111
Arc-melting of zirconium	117
Experimental Investigation of Alloys	120
The Ag-Zr system	120
The In-Zr system	131
The Pb-Zr system	134
The Sb-Zr system	135

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SUMMARY

PHYSICAL METALLURGY OF REACTOR MATERIALS

Transformation-kinetics studies have been started on Ag-Zr alloys. Experimental equipment has been assembled to allow automatic isothermal heat treatments to be made in a protective atmosphere. The microstructures associated with isothermal transformation of a 3.5 wt % Ag-Zr alloy have been identified.

The tensile properties of Ames thorium alloys with additions of 2 and 4% titanium and varying carbon content have been determined. In other tests on Ames thorium, the suspected precipitation hardening associated with low creep rates was not confirmed in tests on homogenized and aged tensile specimens.

Preliminary experiments aimed at the development of metallurgical techniques for improvement of uranium recovery from spent fuel elements have shown that carburization and sensitization of stainless steel elements prior to chemical treatment offer considerable merit. The use of a second approach, that is, removal of UO_2 from melted stainless steel fuel elements, has been demonstrated with a treatment involving the use of a calcium fluoride-iron fluoride slag.

The production of U-Al alloys by reduction of UO_2F_2 in a cryolite slag has been demonstrated. As a result, elimination of several processing steps in the recovery of enriched uranium from aluminum fuel elements may be possible.

HRP METALLURGY

In the dynamic-corrosion experiments, impact tests on commercial-purity titanium samples exposed to oxygen-pressurized UO_2SO_4 containing 5 g of uranium per liter for periods in excess of 500 hr indicated that there was no environmental effect on the impact behavior. Similar tests on Zircaloy 2 showed that there was no effect of corrosion environment on the impact behavior.

Investigations of crack-sensitivity of root-pass heliarc welds in type 347 stainless steel plates indicated that a minimum of 2½% ferrite, as measured by the Magne-gage, was required to prevent root-bead cracking under the specific welding conditions employed in the tests.

Design and fabrication of a jig for preforming stress-corrosion specimens were completed during

this period in anticipation of an extensive stress-corrosion investigation of a number of transgranular failures which have occurred in type 347 stainless steel tubing.

Additional information has been obtained on the crystal structure, composition, and dynamic-corrosion test behavior of moist-hydrogen-pretreated austenitic stainless steel films.

Corrosion tests, in oxygen-pressurized UO_2SO_4 containing 40 g of uranium per liter, on austenitic stainless steel weld specimens, heat-treated to simulate the annealing and stress-relieving treatments to which fabricated components containing such welds might be subjected, indicated a generally superior corrosion resistance of welds that had been heated to 1000°F for 6 hr, as compared with as-welded specimens or those which received other higher-temperature heat treatments.

ANP METALLURGY

Minute additions of oil and trichloroethylene to molten fluorides seem to have a negligible effect on corrosion. Additions of molybdenum disulfide appreciably increase corrosion. Of a series of brazing alloys tested, only Ni-P or Ni-P-Cr exhibited good corrosion resistance in molten fluorides and sodium. Various materials suitable for bearings and hard-facing have been tested in molten fluorides. Hastelloys B, C, and D and Stellite Nos. 21, 25, and 40 have good corrosion resistance. Titanium carbide plus 20 and 30% nickel binder and tungsten carbide plus 2½% cobalt binder had the best resistance of the several cermets tested.

It has been confirmed that the depth of attack increases with increasing operating time of thermal convection loops in molten fluorides. The rate of attack is not so great in the later hours as in the earlier hours. The mass transfer of chromium metal is responsible for the continuing attack. While the mass transfer mechanism is not completely understood, it takes place at a very low chromium concentration which does not change with time. Mass transfer occurs both in fluorides which contain uranium and those which do not. Increasing the purity of the fluoride by lengthening the gas-purging time during production reduces the

corrosive attack on Inconel. Very little change in maximum penetration was found after the temperature of operation of a series of thermal convection loops was lowered. The depth of attack on Inconel was found to be inversely proportional to the surface-to-volume ratio of the loops and to be proportional to the uranium content.

Studies of mass transfer and corrosion of container materials in contact with liquid lead have continued with the use of small, quartz, thermal convection loops in which the test specimens were positioned in the hot and cold leg. Materials tested during this report period include a 25% Mo-75% Ni alloy, a 2% Si-14% Cr-84% Fe alloy, Hastelloy B (64% Ni-5% Fe-28% Mo), titanium, cobalt, beryllium, and a 13% Cr-87% Fe alloy. In addition, an investigation has been started to determine the influence on mass transfer of pre-oxidizing the stainless steel specimens.

Studies on the flammability of jets of sodium alloys in moist and dry air at temperatures up to 800°C have continued. The only alloys studied which did not burn were Na-Hg alloys containing less than 34 mole % sodium and Na-Bi alloys containing less than 40 mole % sodium. Other additions that were studied include indium, lead, silver, zinc, calcium, copper, magnesium, and potassium.

A new device has been built and has been carefully tested for use in determining the mass transfer characteristics of various structural metals when in contact with the fused hydroxides. Studies are being made to identify and determine the properties of compounds produced by the hydroxide-metal reaction. Previous studies in this series were concerned with the action of LiOH and NaOH on nickel in the presence of oxidizing agents. Current research is concerned with the reaction which occurs between NaOH and nickel when hydrogen is allowed to escape from the system. In the process of studying reactions between NaOH and nickel, it was possible to measure the evolution of water during the course of dehydration of the NaOH. It was found that virtually all the water evolution occurred near the melting points of sodium hydroxide monohydrate and NaOH. This result is not too surprising because of the enhanced diffusion rates in the liquid as compared with the solid, but the quantitative extent of this effect was greater than might have been predicted. Color changes observed in fused hydroxides indicate the existence of species in thermal equilibrium

other than the expected cations and hydroxyl ions. Various simple atmospheres, such as hydrogen, oxygen, and water vapor, can react with the fused alkaline hydroxides to produce different chemical species which can be characterized to a limited extent by their color. These interactions do not seem to be greatly altered by progressively changing the cation from sodium to cesium; hence they seem to be associated with the anion. The extent of interaction is rapidly established and thereafter seems only to change with time at temperature. The extent of interaction seems to increase markedly with increasing temperature.

Preliminary rate measurements of the oxidation of sodium at room temperature seem to indicate that sodium does not obey linear rate laws. The oxidation was characterized by the rapid formation of a thin oxide film, followed by a sharp decrease in the oxidation rate. In this respect the oxidation of sodium is similar to that experienced with aluminum and copper.

Studies pertaining to the evaluation of materials for brazing alloys have been continued on the Ni-P eutectic. The Ni-P brazing alloys have been made by preplating parts to be brazed by the "electroless" method of plating and through the use of Ni-P brazing alloy powder formed by the cataclysmic precipitation from an "electroless" plating bath. The third method used was to produce a Ni-P coating by reducing a slurry of nickel or nickelous oxide and dibasic ammonium phosphate with hydrogen at 930°C. Brazing alloys based on the Ni-Ge eutectic have been studied, and the role of germanium additions in lowering the melting point of existing Ni-Cr base brazing alloys has been effectively demonstrated. The oxidation resistance of the various brazing alloys on Inconel T-joints has been determined for 200- and 500-hr exposures at 1500°F in static air. Additional studies have shown that high-conductivity fin materials can be joined to such high-strength alloys as type 316 stainless steel and Inconel by the use of Ni-P, Ni-P-Cr, and Coast Metals No. 52 brazing alloys. A sodium-to-air radiator has been fabricated by brazing the tube-to-fin joints and heliarc-welding the tube-to-header and manifold joints which are backed up by brazing. This method of fabrication was found to be the most reliable one to follow in obtaining a pressure-tight system with one brazing operation.

An inert-arc plug-welding technique was applied to the problem of the assembly of stainless-steel-clad fuel plates into fuel elements of the size and the configuration of interest to the Package Reactor. In the high-conductivity fin problem for the ANP radiator, the work has centered on finding diffusion barriers for Inconel clad on copper. Small quantities of the various clad metals have been prepared for heat-exchanger applications.

The stress-rupture properties of sheet Inconel specimens have been determined in molten fluoride salts and argon at temperatures of 1300, 1500, and 1650°F. These data are presented in the text. Previously, the sensitivity of Inconel to both its test environment and annealing temperature has been shown by comparing the time-to-rupture for various test conditions. It is emphasized that the selection of the best annealing time or the effect of environment on the load-carrying ability of the material cannot necessarily be set on the rupture strength alone but must also be on such important criteria as a 1% total strain or the secondary creep rate.

PACKAGE POWER REACTOR PROGRAM

An experimental program was initiated to develop and produce cheap, reliable stainless steel fuel and control-rod components for long-time service in a 10-Mw package power reactor plant.

Sintered fuel-core compacts containing the desired composition of 34 wt % UO_2 , 65.5% stainless steel, and 0.5% B_4C can be successfully prepared by powder-metallurgy techniques. Complete encasement and bonding of the sintered core mixture with 304 grade stainless steel can be accomplished by hot-rolling the composite from a hydrogen muffle furnace at a temperature of 1225°C. The rolling schedule developed and adopted consists essentially of hot-rolling in eight passes to effect a total reduction in thickness of approximately 90% and of finishing to size with 30% cold reduction after descaling in an acid pickling bath. Preliminary inspection of fuel plates fabricated in this manner indicates that no difficulty should be encountered in meeting the dimensional specifications for composite plates of roughly 3 in. in width by 23 in. in length with a clad-core-clad thickness in mils of 5-20-5.

Initial tests to determine the feasibility of joining the fuel plates into a mechanically sound flat-plate-type assembly by brazing were extremely encouraging. Coating the graphite brazing jig with a mixture of alumina and an organic lacquer was found to serve as an excellent protective coating for preventing carburization of the stainless steel during the high-temperature brazing cycle. Sound joints between type 304 stainless steel dummy fuel and side plates were obtained by brazing in a dry hydrogen atmosphere at 1180°C with Nicrobraz.

The 60 wt % Pd-40 Ni and the 60 Pd-37 Ni-3 Si brazing alloys show essentially no attack, while the 60 Ni-20 Cr-11 Si alloy, although attacked, shows a negligible weight change when exposed to 295°C distilled water at a pressure of 1200 psi in the autoclave.

Although developmental work on this program is far from complete, sufficient metallurgical data have already been obtained to indicate, conclusively, that construction of the stainless steel fuel components proposed for service in the Package Power Reactor is certainly feasible.

CERAMICS RESEARCH

Petrographic investigations in support of the ANP fuel program continue. Developmental work is in progress on glass-type pump seals for the ANP. Bearing shapes prepared from BeO and high-density graphite (1.92 density) have been supplied to the ANP Project. Work continues on the fabrication of a ceramic container for use in electrical-conductivity studies of fluoride fuels for ANP.

A near-theoretical-dense (96% of theoretical) rod of K_3CrF_6 was prepared by isostatic pressing. This rod is intended for use in conductivity measurements by ANP.

A study of the ceramic properties of Sm_2O_3 and Gd_2O_3 was carried out. A specimen of $Al-UO_2$ cermet was fabricated in connection with "J" slug development. Thoria pellets (95% of theoretical density) in the form of a cylinder $\frac{1}{8}$ in. in diameter $\times$ $\frac{1}{2}$ in. in length have been fabricated for the HRE. A rod of thoria (95% of theoretical density) has been prepared, by isostatic pressing and sintering, for radiation-damage experiments. A high-boron-containing ceramic coating has been applied to a large plate for shielding tests. A model of a core design for the Reflector-Moderated Reactor, suggested by Fraas of the ANP, has been fabricated in a high-density graphite for the Ceramics Laboratory.

FUNDAMENTAL PHYSIOMETALLURGICAL RESEARCH

The proposed relationship between the fiber axis distribution and the pole distribution for fiber textures has now been confirmed experimentally. In order to obtain a specimen having a homogeneous and ideal fiber texture, a spherical specimen was machined from the center of an extruded aluminum rod. An analysis of the x-ray diffraction data obtained in the usual manner indicated that the preferred directions of the fiber axes were $\langle 111 \rangle$ and $\langle 100 \rangle$, that the axis distribution fell off rapidly from these positions but never reached zero along the $[110]$ zone, and that the ratio $\langle 111 \rangle$: $\langle 100 \rangle$ was 9:10. This fiber axis distribution was shown to reproduce the observed pole distribution for all diffracting planes to within a few per cent.

In order to obtain quantitative preferred orientation data for rolled sheets and plates, it has been proposed to study the axis distribution by using the rolling, transverse, and normal directions as "fiber axes." Axis distribution data were obtained for a spherical diffraction specimen of laminated brass sheet. Preliminary analyses of these data indicate that the proposed method gives quantitatively the information given only qualitatively by the pole-figure method.

In the study of the alloying of Group IVA elements, new phase diagrams are reported for the systems Ag-Zr, In-Zr, Pb-Zr, and Sb-Zr. The observation that the α/β boundaries of these systems and others from the literature may depend upon electron concentration leads to an approximate calculation of the density of states in body-centered-cubic zirconium of 0.59 levels/atom/ev. This is relative to the experimental density of states in the close-packed hexagonal form of 0.61 levels/atom/ev from low-temperature specific heats and shows that only small $N(E)$ differences are needed to account for the type of dependence on electron concentration observed.

In pure zirconium, the results of a new determination indicate the $\alpha \rightarrow \beta$ transition temperature to be $870 \pm 3^\circ\text{C}$. Several other results in connection with phase-diagram technique are reported. First, pure zirconium specimens undergo hardening effects when rapidly cooled through the $\alpha \rightarrow \beta$ transition, and this effect must be considered in the use of such specimens to indicate gas contamination; second, zirconium specimens can be annealed in silica capsules for three days at 1200°C without hardness increases when a tantalum or molybdenum foil is used to prevent the zirconium-silica reaction.

METALLURGY DIVISION SEMIANNUAL PROGRESS REPORT

PHYSICAL METALLURGY OF REACTOR MATERIALS

E. J. Boyle

TRANSFORMATION KINETICS OF ZIRCONIUM-BASE ALLOYS

E. E. Stansbury

M. L. Picklesimer

Phase-diagram studies have shown the presence of a eutectoidal transformation in the Ag-Zr alloy system. Transformation-kinetics studies have been initiated on these alloys in an effort to determine whether improved mechanical properties may be derived from isothermal transformation of zirconium-base alloys of this type.

A 3.5 wt % silver alloy was prepared by consumable-electrode arc-melting. The electrode consisted of a zirconium crystal bar on which was placed a 0.032-in. silver wire wound into a spiral groove. Melting was carried out in an argon atmosphere at 22 psia. Following a beta-heat treatment, the cast alloy could be cold-rolled 85%.

In contrast to the mixed microstructure of the as-cast ingot, the microstructure of a section of the ingot after annealing for two days at 800°C, which is just under the eutectoid transformation, was very uniform throughout. This structure consisted of small particles of secondary phase, presumably an intermetallic compound, in a matrix of alpha. The annealed structure had a Vicker's hardness of 120 as compared with 70 to 80 for the as-cast ingot.

A larger casting, made by melting three electrodes successively, fractured during rolling and swaging because of the cold shuts formed when the melting of the new electrode was started on the old ingot. Specimens of the broken ingot have been used to determine the required heat treatment for homogenization of the ingot.

An automatic feed mechanism for the consumable-electrode arc furnace has been designed to permit the casting of a larger ingot in one operation. The electrode position and the feed rate will be automatically controlled to maintain a preset arc voltage for stable melting conditions. The drawings have been completed and the shop work is scheduled.

Automatic isothermal transformation equipment has been designed and built that permits the determination of the transformation kinetics of specimens with very close control of times and temperatures. The equipment consists of a high-temperature lead pot, a lower-temperature stirred lead pot for isothermal transformation of the specimen, and a water-cooled mercury quench pot, all enclosed in an inert atmosphere. The transfer of the specimen from one pot to another is controlled automatically, as is the time in the isothermal bath. Transformation times may vary from 2.5 sec to 20 min with fully automatic control. Longer times of transformation will require some manual operation. The equipment has been assembled and tested. Unfortunately, a furnace element burned out during testing and so no test specimens could be run. The furnace element has been redesigned for easier replacement and is now being constructed.

In the interim, specimens have been sealed in argon-filled quartz capsules and isothermally transformed from the beta phase at 750 and 800°C for several different time periods. The microstructure of the 750°C specimens showed a small amount of a bainitic type of transformation in the grain boundaries, with the transformation completed by an irresolvable structure. This latter transformation probably occurred during the water quench. The quartz capsule was broken mechanically in the water quench, thus providing a relatively slow quench. The microstructure of the 800°C specimens revealed grain boundary and Widmanstätten-type alpha plates in a matrix of beta at 800°C. The matrix of beta did not transform to the basket-weave martensitic structure typical of the specimens water-quenched from 1000°C nor to the irresolvable structure occurring in the 750°C specimens. X-ray examination of the specimen showed that there were two forms of alpha (close-packed hexagonal) present with two different lattice spacings. Therefore, the beta was not retained at room temperature, as might have been inferred from the microstructure.

METALLURGY PROGRESS REPORT

A new etching procedure was developed for examination of the Ag-Zr alloys. This etching technique will not produce the undesirable pitting associated with all other solutions tried. It consists of a stock solution of iodine and potassium iodide dissolved in methyl alcohol and an etching solution of nitric acid, hydrofluoric acid or ammonium fluoride, alcohol, glycerine, and water. Just prior to etching, the two solutions are mixed and applied by swabbing for time periods from 20 sec to 5 min. The hydrofluoric acid or ammonium fluoride content is critical and controls the amount of initial staining which can be removed by any further swabbing.

MECHANICAL PROPERTIES OF THORIUM

R. B. Oliver

The creep-rupture properties of several billets of thorium have been investigated at 300°C. One of the significant facts revealed by these tests is that although considerable plastic deformation occurs during loading there is no significant creep unless the load applied is sufficient to produce strains of from 4 to 6%. These elongations are not usually reached until a specimen is stressed to within 2000 psi of the ultimate strength. In consideration of this fact, it was thought that tensile tests would provide more data in a shorter time than were possible with a creep test.

One problem, which is currently being investigated by means of hot-tensile tests, is the effect of various additions of titanium and carbon. Three billets with varying carbon and titanium contents were extruded and tested. The results for tests at 300°C are shown in Table 1. Other investigators have indicated that there is a critical titanium-to-carbon ratio for high strength. Although the above

data are insufficient for drawing definite conclusions, they do show that alloys 2 and 4, with about a 30 to 1 titanium-to-carbon ratio, are superior in strength and ductility to alloy 3, having a 15 to 1 ratio.

Thorium exhibits a number of unusual characteristics during stress-rupture testing which, at the present time, are not satisfactorily explained. For instance, the creep curve shows an asymptotically decreasing creep rate. Also, specimens which are put in test and allowed to creep for several hundred hours and then loaded to rupture have increased yield and tensile values.¹ Calculations indicate that this increase is not explained by the amount of mechanical working involved. Some specimens from billets which were extruded at rates of 600 fpm and water-quenched at the extrusion die show unusually high yield and rupture strengths.² It was thought that a precipitation-hardening reaction might account for these various phenomena. Other work³ has indicated that precipitation hardening occurs in specimens with a carbon content somewhat higher than that of the billets currently being tested. An investigation of this possibility was made by heat-treating a number of specimens from a billet which had been extruded at 32 fpm. Results are given in Table 2 of the specimens that were tested in vacuum at 300°C in the tensile machine. The data given in Table 2 would indicate that heat-treating does not improve the mechanical properties of the extruded billet. There is no evidence of a precipitation or age-hardening reaction with the

¹R. B. Oliver, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p 5.

²R. B. Oliver, *Met. Semiann. Prog. Rep.* April 10, 1953, ORNL-1551, p 5.

³R. M. Goldhoff, H. R. Ogden, and R. I. Jaffee, *Thorium-Carbon Alloys*, BMI-844 (June 19, 1953).

TABLE 1. EFFECT OF CARBON AND TITANIUM ADDITIONS ON THORIUM AT 300°C

ALLOY NO.	COMPOSITION (%)		YIELD STRENGTH (psi)	TENSILE STRENGTH (psi)	ELONGATION (%)	EXTRUSION RATE (fpm)
	C	Ti				
1	0.07	0	11,000	22,000	>32	36
2	0.06	2	27,180	28,180	12.5	44
3	0.14	2	23,750	26,000	11.3	36
4	0.11	4	29,400	31,600	18.0	52

TABLE 2. EFFECT OF HEAT TREATMENT ON THORIUM TESTED AT 300°C

SPECIMEN NO.	HEAT TREATMENT	YIELD STRENGTH (psi)	TENSILE STRENGTH (psi)	ELONGATION (%)
1	As-extruded	16,000	24,700	28.5
2	850°C for 2 hr; quenched in oil	10,200	22,000	20.0
3	850°C for 2 hr; quenched in oil; heated at 350°C for 1 hr; furnace-cooled	9,400	21,100	31.0
4	850°C for 2 hr; furnace-cooled	7,200	16,600	31.0

treatments used. It is apparent that more investigation is required before this behavior of thorium can be explained.

METALLURGICAL PROCESSING OF SPENT FUEL ELEMENTS

The recovery of the unburned U^{235} in spent fuel elements has been done thus far by wet chemistry only. The fuel elements which have been processed have consisted of either the Hanford type, that is, uranium clad with aluminum, or the MTR type, that is, U^{235} -Al alloy clad with aluminum. Wet chemical methods are very satisfactory for these types of elements; however, since fuel elements of zirconium or stainless steel are being used or planned for use in the newer reactors, it is obvious that chemical dissolution of these very corrosion-resistant materials presents many difficulties and promises to be expensive.

The present work is aimed at development of a metallurgical processing which could be used prior to aqueous chemical processing and which would materially reduce costs. The objectives which have been outlined are concentration of the uranium in the fuel elements so that the amount of material which must be handled will be decreased and development of techniques which will result in a more easily dissolvable fuel element. The approach to these objectives has been by gaseous treatment of solid stainless steel fuel elements or by slagging treatment of melted stainless elements.

Carburizing of Stainless Steel Fuel Elements

R. E. Adams

Preliminary consideration of the gaseous treatment led to a consideration of the role of carbon in

the corrosion resistance of stainless steels. Since it is well known that stainless steels of high carbon content may be made susceptible to intergranular attack by heat treatments which precipitate chromium carbides at the grain boundaries, carburization appeared to be a promising technique. In fact, this technique is the subject of a patent⁴ dealing with a method for producing commercial stainless steel powders. The method consists in (1) carburizing stainless steel in a carbonaceous atmosphere, (2) heat-treating to produce carbide precipitation, and (3) exposing the steel to a solution of sulfuric acid and copper sulfate which produces intergranular attack and disintegration into powder.

Experiments were started to determine the feasibility of adapting this process to the treatment of the stainless steel fuel elements which are planned for use in the ORNL Package Reactor. These elements consist of an MTR-type assembly of plates having 0.020-in. cores of 34 wt % UO_2 -type 304 stainless steel clad with 0.005 in. of type 304 stainless steel. Specimens of these plates were carburized in a ceramic tube furnace in which an atmosphere of natural gas (about 97% methane) was used with tank nitrogen as a diluent. It is possible to obtain a carbon content of up to 2% in type 304 stainless steel with this atmosphere.

Figure 1 shows the kind of structures obtained in type 304 stainless steel after a carburizing treatment and after carburizing plus partial dissolution in a solution of 8% H_2SO_4 and 1.3% $CuSO_4$.⁵ Both specimens were carburized for 45 min at 930°C, homogenized at 1150°C, furnace-cooled to 700°C

⁴J. Wulff, *Method of Producing Metal Powder*, U.S. Pat. 2,361,443, Oct. 31, 1944.

⁵Dissolution tests carried out by Chemical Technology Division.

METALLURGY PROGRESS REPORT

Fig. 1. Carburized Type 304 Stainless Steel. Structure as carburized and heat-treated (right); polished cross section after 2-hr treatment in boiling solution containing 8% H_2SO_4 and 1.3% $CuSO_4$ (left). 100X

and held at this temperature for 2 hr. The sample on the left was treated for 2 hr in a boiling solution of H_2SO_4 - $CuSO_4$. The copper, which deposits on the stainless steel during this treatment, was removed by dissolution in HNO_3 . In some cases it has been possible to get complete dissolution of carburized stainless steel samples in the H_2SO_4 - $CuSO_4$ solution.

Preliminary experiments, similar to those listed above, have been carried out on samples of ORNL Package Reactor fuel plates. It was noted that only 0.3% of the uranium in the sample was dissolved in the H_2SO_4 - $CuSO_4$ solution and that treatment of the disintegrated powder with warm HNO_3 picked up 98.4% of the total uranium in the original sample.

In summary, the succession of treatments used in treating spent stainless steel fuel elements might be as follows:

1. Carburize with carbonaceous atmosphere.

2. Heat treat to homogenize and to obtain uniform carbon content throughout the fuel plate.

3. Sensitize by holding at temperature for several hours in carbide precipitation temperature range.

4. Dissolve carburized fuel element in slightly acidic $CuSO_4$ solution.

5. Discard sulfate solution, providing uranium concentration can be kept low, and treat with nitric acid to take UO_2 into solution.

6. Feed HNO_3 solution to standard solvent-extraction columns for uranium recovery and fission-product extraction.

On the basis of the preliminary experiments listed above, the technique of carburizing and sensitizing spent stainless steel fuel elements prior to chemical dissolution appears to offer the following advantages:

1. The container materials for the dissolver equipment can be conventional stainless steels

since there is no severe corrosion problem associated with handling slightly acidic CuSO_4 solutions.

2. The volume of the solution to be fed into the solvent-extraction columns is considerably less than that contemplated in existing processes.

3. The nitric acid content of the feed solution for the solvent-extraction columns is considerably less than that in the present processes.

Slagging Experiments on Stainless Steel Fuel Elements

J. A. Milko

A second approach to the problem of concentrating the uranium contained in solid fuel elements in a more easily dissolvable form has been to investigate the feasibility of melting such elements under a slag cover which would have a high solubility for UO_2 and which might remove quantitatively all the uranium present in the fuel element. Such slags might then be treated with conventional wet chemical means for uranium extraction and fission-product removal.

Initially, a series of experiments was carried out to determine the distribution of uranium between a stainless steel melt and a fluoride slag. These tests were made on alloys of 16% uranium-84% type 304 stainless steel prepared by melting the stainless steel and adding metallic uranium. All melting was done in air in graphite crucibles, and the melt was frozen in place in the crucible. Two initial melts, aimed at determining uranium distribution and recovery, were made in which no slag cover was employed. Analyses, taken from drillings at various positions along the ingot, indicated severe segregation from top to bottom and recoveries of only 22 to 40% of the added uranium. A third melt, prepared in a MgO crucible, was sectioned and analyzed very thoroughly as shown in Fig. 2. It is evident that there is considerable variation in uranium content and that a material balance is thus impossible. The fact that the natural slag formed on the surface of the melt showed a uranium content of 33% indicated that a major portion of the added uranium was oxidized during alloying.

The uranium-stainless steel melts described above were used for preliminary experiments aimed at determination of uranium distribution between slag and metal. The results, listed in Table 3, indicate that the removal of uranium from stainless steel melts with fluoride slags was not encouraging.

Fig. 2. Location of Samples and Distribution of Uranium in a Type 304 Stainless Steel Casting of 16% Uranium Nominal Composition.

The next series of experiments was carried out on samples from mockup fuel plates for the ORNL Package Reactor. The samples consisted of plates with a 0.020-in.-thick core of 34 wt % UO_2 -type 304 stainless steel clad on both sides with 0.005-in.-thick type 304 stainless steel. The external dimensions were: length, 22 in.; width, 2½ in.; thickness, 0.030 in. Based on the total weight, the uranium concentration in each plate was 16%.

Initially, attempts were made to melt coiled sections of fuel plate in a zirconia crucible. The results of heating a sample to 1725°C are shown in Fig. 3. It will be noted that the UO_2 -stainless steel cores remained almost intact and that no dispersion of UO_2 was obtained.

In a second melting experiment, a similar sample of fuel plate was melted in argon in a graphite crucible under a $3\text{NaF}\cdot\text{AlF}_3$, FeF_2 slag. Again, the UO_2 -stainless steel core material maintained partial integrity, as shown in Fig. 4.

METALLURGY PROGRESS REPORT

TABLE 3. DISTRIBUTION OF URANIUM (ORIGINAL CONTENT 3 TO 11%)
BETWEEN TYPE 304 STAINLESS STEEL AND SLAG^a

MELT NO.	SLAG COMPOSITION	FINAL URANIUM CONTENT (%)	
		Metal	Slag
1	3NaF·AlF ₃	2.4 ^b	0.07 - 4.4
2	3NaF·AlF ₃ + Fe ₂ O ₃	0.06 ^{b,c}	0.63 - 13.7
3	3NaF·AlF ₃ + Fe ₂ O ₃	3.5 ^b	10 ^b
4	3NaF·AlF ₃ + Fe ₂ O ₃	3.7 ^b	7.7 ^b

^aAll melts made in graphite crucible in air.

^bAverage values.

^cAnalyses made on surface drillings - probably not representative.

A third experiment was made under melting conditions identical with the second one except that a slag of CaF₂ + FeF₂ in the ratio of 2.5 to 1 was employed. The appearance of the resulting metal button and slag after freezing in the crucible is shown in Fig. 5. Analyses made on the stainless steel showed less than 0.001% uranium, while the slag contained 9% uranium. Although this single experiment is quite preliminary, the apparent complete removal of uranium from the stainless steel is very encouraging. It is planned to pursue this method of approach with further testing.

REDUCTION OF UO₂F₂ WITH ALUMINUM

J. A. Milko

In a contemplated process for recovery of U²³⁵ from aluminum fuel elements, such as the MTR elements, one stage in the process results in the formation of uranyl fluoride, UO₂F₂. If this material could be used for direct production of U-Al alloy, considerable cost savings could be effected by elimination of additional steps, such as the production of UF₄ and subsequent reduction to uranium metal.

In order to examine the feasibility of a direct reduction of UO₂F₂ in contact with aluminum, two

TABLE 4. REDUCTION OF UO₂F₂
WITH ALUMINUM

	RUN NO. 1	RUN NO. 2
Charge		
Weight of UO ₂ F ₂ , g	1400	1412
Uranium in UO ₂ F ₂ , %	76.728	76.728
Weight of uranium, g	1073.3	1082.5
Weight of aluminum, g	2000.0	2000.0
Weight of cryolite, g	2000.0	2000.0
Material recovered		
Weight of U-Al alloy, g	3038.0	3000.0
Uranium in U-Al alloy, %*	31.1	31.5
Uranium in slag, %**	<0.004	<0.004

*Average of 14 analyses on 7 samples - not accurate because of uranium segregation in alloy.

**Average of 10 analyses on 5 samples - all results reported were <0.004% uranium.

experiments were carried out. The charge in both cases consisted of UO₂F₂, cryolite, and 99.9% aluminum. The reduction was carried out at 1090 to 1110°C in a graphite crucible in air. After solidification in the crucible, the slag and metal were

Fig. 3. Appearance of a Stainless Steel-Uranium Oxide Melt. (a) Side view. (b) Bottom view. (c) Cross section; numbers indicate distribution of uranium in particular locations.

separated and analyzed for uranium content. The data in Table 4 show the results. It is apparent that uranium may be reduced practically quantitatively from UO_2F_2 by aluminum. However, in order to check more accurately the uranium recovery, it is proposed to repeat the experiments with a final U-Al alloy composition of 5 wt % in order to avoid the segregation difficulties associated with the higher uranium alloys.

Fig. 4. Appearance of Incompletely Melted Core of Stainless Steel-Uranium Oxide Mixture After Slag was Removed. (a) Top view. (b) Cross section; numbers represent uranium content in particular locations.

UNCLASSIFIED
Y-10858

(a)

UNCLASSIFIED
Y-11012

(b)

Fig. 5. Appearance of Stainless Steel, Uranium Oxide, and Slag Portions After Solidification in Crucible, (a) After sectioning of the crucible. (b) Cross section of stainless steel portion after treatment with calcium fluoride and ferrous fluoride slag.

HRP METALLURGY

E. C. Miller

PHYSICAL METALLURGY OF TITANIUM AND
OF ZIRCONIUM ALLOYS

W. J. Fretague

Commercial Titanium

In connection with the program of investigating the impact behavior of commercial titanium after exposure to various corrosive environments, two sets of four multiple-break impact specimens were exposed to flowing uranyl sulfate solutions for different lengths of time and temperatures (see Table 5). The results obtained on impact-testing a commercial titanium (Ti-75A, item 24, heat L782) bar in the temperature range from -195.6 to $+200^{\circ}\text{C}$ are presented in Fig. 6. The specimen was a 1-in.-dia bar swaged to about a $\frac{1}{4}$ -in. rod, vacuum-annealed at 500°C for 1 hr, furnace-cooled, machined to final size, and reannealed in vacuum at 600°C for 1 hr after machining.

A comparison of these data with those presented previously¹ for annealed titanium (Ti-75A, item 24, heat L782) shows that within the limits of experimental error there is no apparent environmental

effect on the impact properties of commercial titanium.

Zirconium Alloys

Zirconium-Tin-Iron-Chromium-Nickel (Zircaloy 2). A series of Zircaloy 2 impact specimens have been exposed to a variety of corrosive environments prior to impact testing to determine the effect of

Fig. 6. Impact-Testing Behavior of Commercial Titanium.

¹W. J. Fretague, A. R. Olsen, and R. G. Berggren, *Met. Semiann. Prog. Rep.* April 10, 1953, ORNL-1551, p 13-17 and Fig. 12.

TABLE 5. LOOP HISTORY OF TITANIUM IMPACT SPECIMENS

RUN NO.	SPECIMEN NO.	SOLUTION	REMARKS
A-62	67 and 68	5 g of U per liter of UO_2SO_4 plus 0.005 M H_2SO_4 at 320°C for 682 hr	The solution contained 900 to 1500 ppm O_2 and flowed past the specimens at 3 to 5 fps
	71 and 72	Same as above	Same as above except specimens were abraded with 400-mesh emery paper prior to loading
G-6	69 and 70	5 g of U per liter of UO_2SO_4 plus 0.010 M H_2SO_4 at 300°C for 529 hr	The solution contained ~ 1000 ppm O_2 ; during the run the specimens came loose from their holder and were badly battered
	73 and 74	Same as above	Same as above except specimens were abraded with 400-mesh emery paper prior to loading

METALLURGY PROGRESS REPORT

simulated operating conditions on the impact properties of Zircaloy 2. The specimens were $\frac{3}{8}$ -in.-dia rods swaged to 0.217 in., sand-blasted, pickled, vacuum-annealed at 750°C for 2 hr, furnace-cooled, and machined to final size. Table 6 lists the corrosive environments employed. The impact-test data are plotted in Figs. 7, 8, 9, and 10. A comparison based on the results from a single annealed specimen (Z 2-16, Fig. 8) shows no effect from the environment on impact behavior.

Tests on Zircaloy 2 impact specimens swaged from a $\frac{3}{8}$ -in. dia to a 0.225-in. dia and vacuum-annealed at 750°C for 2 hr are in progress. When these tests are completed, a comparison can be made between the impact properties of the annealed Zircaloy 2 material and the impact behavior of

Zircaloy exposed to various corrosive environments.

Material for in-pile loop specimens (Zircaloy 2) was fabricated, annealed, and machined to final specimen dimensions.

Approximately 100 ft of $\frac{3}{64}$ -in.-dia Zircaloy 2 wire was swaged for use in a consumable-electrode welding test by the fabricator of the Zircaloy 2 core tank.

Fig. 7. Impact-Testing Behavior of Zircaloy 2, Run A-62 (See Table 6).

Fig. 8. Impact-Testing Behavior of Zircaloy 2, Run G-4.

TABLE 6. LOOP HISTORY OF ZIRCALOY IMPACT SPECIMENS

RUN NO.	SPECIMEN NO.	SOLUTION	REMARKS
A-62	Z 2-1, -4, -10, and -11	5 g of U per liter of UO_2SO_4 plus 0.005 M H_2SO_4 at 320°C for 682 hr	The solution contained 900 to 1500 ppm O_2 and flowed past the specimens at 3 to 5 fps
G-4	Z 2-3, -7, -8, and -13	5 g of U per liter of UO_2SO_4 plus 25 mole % H_2SO_4 at 250°C for 1010 hr	The solution contained 200 psi O_2 and was run in an all-titanium loop
G-5	Z 2-2, -5, -6, and -17	5 g of U per liter of UO_2SO_4 plus 0.005 M H_2SO_4 at 300°C for 693 hr	
A-57	Z 2-9, -12, -14, and -15	40 g of U per liter of UO_2SO_4 at 300°C for 400 hr	100 psi O_2 overpressure in loop

Fig. 9. Impact-Testing Behavior of Zircaloy 2, Run G-5.

WELDING OF STAINLESS STEELS

W. J. Leonard

Samples of type 347 stainless steel of selected compositions (Table 7) were melted and prepared for metallographic examination.² Samples 1 and 2 are commercial heats of type 347 stainless steel and are on the low side and high side, respectively, of the permissible silicon range allowed in the AISI specifications for the steel. Sample 3 is Oxweld 60 bare welding wire, the material used in HRE and HRP heliarc welding. The microsections gave no indication of abnormal ferrite segregation in the area of the pipe of the cast button. Some normal carbide segregation was observed. Metallo-

²W. J. Leonard, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p 14.

TABLE 7. CHEMICAL COMPOSITION OF TYPE 347 STAINLESS STEEL USED FOR ARC-MELTED BUTTONS

SAMPLE	COMPOSITION (%)								
	C	Mn	P	S	Si	Ni	Cr	Cu	Cb
1	0.05	1.53	0.020	0.014	0.39	11.02	17.76	0.24	0.62
2	0.07	1.57	0.013	0.007	0.97	11.48	18.08	0.21	0.98
3	0.06	1.74	0.011	0.015	0.48	9.58	18.05		0.74

Fig. 10. Impact-Testing Behavior of Zircaloy 2, Run A-57.

graphic and Magne-gage examinations of the buttons showed ferrite contents of approximately 2% in sample 1, 3% in sample 2, and 8 to 9% in sample 3. Figures 11, 12, and 13 are photomicrographs of the area near the pipe.

Because some welds of relatively high ferrite content, when tested in certain corrosive media under dynamic test conditions, suffer more corrosion compared with fully austenitic base metal, several experimental heliarc welds were made in order to study the feasibility of producing suitable welds with a minimum ferrite content.

Welds were made in $\frac{1}{4}$ -in. type 347 fully austenitic base plate; a 45-deg level and a small root face (<0.015 in.) were used. No filler metal was added; one fusion pass was made at a current of 150 to 200 amp at a relatively rapid speed of travel. About one out of three of these weld beads contained cracks. Magne-gage readings indicated about 1.5% ferrite average in the fused zone.

UNCLASSIFIED
Y-10203

Fig. 11. Melted, Low-Silicon Type 347 Stainless Steel Base Metal. Etchant: glyceria regia. 200X

UNCLASSIFIED
Y-10204

Fig. 12. Melted, High-Silicon Type 347 Stainless Steel Base Metal. Etchant: glyceria regia. 200X

Fig. 13. Melted Oxweld 60 Type 347 Stainless Steel Welding Wire. Etchant: glyceria regia. 200X

Figure 14 reveals the microstructure at this position.

Some sound welds, as shown in Fig. 14, were completed by heliarc welding and the use of a commercial filler wire (Oxweld 28), which is fully austenitic type 347 stainless steel annealed wire. Figure 15 illustrates this type of weld; all welds were sound.

Figure 16 illustrates welds that were made to the same design, except that a filler rod was used in the root pass as well as in the two filler passes. All welds were sound.

The effect of excessive dilution in lowering the ferrite in the root pass is illustrated by Fig. 15; in this case the amount of ferrite is $2\frac{1}{4}\%$; in Fig. 16 the ferrite was about $3\frac{1}{2}\%$, and less dilution of the base metal resulted. A minimum of $2\frac{1}{4}\%$ ferrite in the root is indicated to secure a sound crack-free weld at the root position. Specimens were taken from this weldment for comparison with similar weldments made with Oxweld 60 welding wire (6 to 10% ferrite) to assess the role of ferrite content of welds as related to corrosion resistance.

DYNAMIC CORROSION OF WELDED STAINLESS STEEL SPECIMENS

W. O. Harms

W. J. Leonard

Metallographic Studies

Representative samples of 126 pin-type specimens of welded austenitic stainless steels (dynamic-corrosion weight-loss data reported and summarized previously³) were examined metallographically to determine whether differences in corrosion behavior in the various combinations in uranyl sulfate solutions could be attributed to abnormal structures within the base or weld metals.

Results of this study indicated that, in general, the corrosion attack was uniform on both base metals and welds and that no appreciable preferential attack had occurred on particular microconstituents. However, on specimens which had been

³W. O. Harms and W. J. Leonard, HRP Quar. Prog. Rep. July 31, 1953, ORNL-1605, p 112; Met. Semiann. Prog. Rep. Oct. 10, 1953, ORNL-1625, p 14.

METALLURGY PROGRESS REPORT

exposed, at moderate flow rates, to concentrated solutions containing 300 g of uranium per liter at the relatively low temperatures of 150 and 175°C, the following observations were made:

1. Type 304 stainless steel base plate, welded with type 347 stainless steel rod by the heliarc process, was attacked intergranularly, and there

was an accelerated corrosion in the heat-affected zone under loop conditions of 150°C for 997 hr (see Fig. 17).

2. Type 304L stainless steel base plate heliarc-welded with type 347 stainless steel rod showed no intergranular corrosion under similar test conditions, the defilmed weight loss being less than that

Fig. 14. Fusion Root Pass in Type 347 Stainless Steel Made by Using Heliarc Process with No Filler Wire. Etchant: glyceria regia. 200X

PERIOD ENDING APRIL 10, 1954

Fig. 15. Heliarc Weld in Type 347 Stainless Steel Made by Using One Fusion Root Pass Plus Two Filler Passes of Oxweld 28. Etchant: glyceria regia. 200X. Reduced 23%.

Fig. 16: Heliarc Weld Made by Using Oxweld 28 Filler Wire for All Passes on Type 347 Stainless Steel Base Plate. Etchant: glyceric regia. 200X. Reduced 23%.

Fig. 17. Intergranular Attack in Type 304 Stainless Steel Base Metal of Welded Loop Pin Exposed to Uranyl Sulfate Solution Containing 300 g of Uranium per Liter for 997 hr at 150°C and 16 fps. Etchant: glyceria regia. 500X

of specimens involving type 304 by a factor of about 10.

3. Type 321 stainless steel base plate welded with type 347 stainless steel rod and tested at 175°C for 308 hr showed selective attack on elongated stringers of ferrite (see Fig. 18), the positive identification of which has been reported elsewhere.⁴ This last observation could account for the generally inferior corrosion resistance of welds involving this stock item of type 321 base material at lower temperatures. It is interesting to note that the composition of this slightly magnetic material is such that, by use of a Schaeffler-type constitution diagram for wrought metal,⁵ a two-phase alloy, at room temperature, containing approximately 5% ferrite could be predicted.

⁴R. J. Gray, T. M. Kegley, Jr., R. S. Crouse, and T. K. Roche, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p 72.

⁵See, for example, L. K. Poole, *The Incidence of Cracking in the Welding of Type 347 Steels*, NYO-3494 (May 22, 1952), p 25, Fig. 1.

Microscopic study of types 304L and 347 stainless steel base plates, welded with type 347 rod, showed that they had almost identical corrosion resistance under varying corrosion conditions; both were superior to types 304 and 321. Figure 19 shows the effect of temperature on corrosion of welded austenitic stainless steel pins in solutions containing 300 g of uranium per liter; test data are shown in Table 8. These pins were machined from welds on base materials of types 304, 304L, and 321 stainless steel welded with type 347 rod by the heliarc process. Practically the same direct relation between corrosion attack and temperature was observed on pins machined from welds on type 347 base metal.

Effects of Heat Treatment and Composition

A proposed study, under closely controlled conditions, of the effects of composition and heat treatment on the dynamic-corrosion resistance of austenitic stainless steel welds was discussed

METALLURGY PROGRESS REPORT

in the previous semiannual report.⁶ One hundred seventy-nine pin-type specimens were machined from weldments of known composition and metallurgical histories used in a development program involving single U-groove welds in 1- and 1¼-in. base plates. The various alloy combinations and

⁶W. O. Harms and W. J. Leonard, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p 14.

ferrite contents of welds, as determined by Magne-gage measurements, are given in Table 9. Root passes, in welds involving coated electrode filler-rod passes of composition "H" (an experimental, fully austenitic, columbium-stabilized alloy with nominal composition of 18% Cr, 13% Ni, and 5% Mn), were made with type 347 stainless steel rod, since no bare composition "H" was available for

Fig. 18. Preferential Attack Along Ferrite Stringers in Type 321 Stainless Steel Base Metal of Welded Loop Pin Exposed to Uranyl Sulfate Solution Containing 300 g of Uranium per Liter for 308 hr at 175°C and 21 fps. Etchant: glyceria regia. 500X

TABLE 8. EFFECT OF TEMPERATURE ON CORROSION OF WELDED AUSTENITIC PINS IN SOLUTIONS CONTAINING 300 g OF URANIUM PER LITER

SPECIMEN	BASE MATERIAL, AISI TYPE	TEMPERATURE (°C)	TIME (hr)	FLOW (fps)	DEFILMED WEIGHT LOSS (mg)
A	304	150	997	16	22
B	321	175	308	21	47
C	304L	250	117	12	94
D	304	250	117	12	176

this purpose. Type 308L is a nominal 20% Cr-10% Ni alloy containing less than 0.04% carbon as deposited.

The machined pins were subjected to various heat treatments, as listed in Table 10, in a hydrogen atmosphere. All specimens were electropolished prior to corrosion-testing to eliminate surface effects due to heat treatments and machining. The corrosion tests were performed in a solution containing 40 g of uranium per liter for 400 hr at 250°C and 23 to 26 fps.

Results of the corrosion tests are summarized in Table 10. Gross inconsistencies in weight-loss

data were attributed to flow rates being used that were in the transition zone for the test conditions employed. By transition zone is meant that range of flow rates below which the protective oxide film on a given specimen is stable and above which the specimen undergoes essentially bare-metal corrosion. The flow rates used in this experiment, then, served to evaluate rather critically the weld combinations and heat treatments under investigation. In this connection, it is seen in Table 10 that film integrity was maintained on all specimens which had received the 1000°F stress relief anneal (heat treatments designated as B and E in the table), while all but two of the 27 specimens which had received a solution anneal at 1950°F (heat treatments F and G) showed bare-metal attack and high weight losses. Other treatments appeared to decrease, or at best failed to improve, the corrosion resistance relative to the as-welded condition except in the case of type 308L, where the as-welded condition showed very poor resistance to attack. The reasons for the observed behavior are not clear; the role of microstructure is being investigated by an intensive metallographic study of the test specimens.

Special, flat-plate type of corrosion specimens (see Fig. 20) were machined from each of the nine welded plates listed in Table 9 and were prepared, along with nine standards, for loop testing.

Fig. 19. Pin-Type Specimens of Austenitic Stainless Steels Welded with Type 347 Rod by the Heliarc Process and Subjected to Dynamic Corrosion Tests in Uranyl Sulfate Solutions Containing 300 g of Uranium per Liter. The pins were photographed after cathodic defilming treatment in inhibited 5% sulfuric acid.

Fig. 20. Flat-Plate-Type Welded Specimen of Types 304L and 347 Stainless Steel Welded with Type 347 Rod. Tested in uranyl sulfate solution containing 40 g of uranium per liter for 200 hr at 250°C and 20 fps; scrubbed but not defilmed. Note adherent subscale on type 304L base plate at right.

METALLURGY PROGRESS REPORT

TABLE 9. DESCRIPTION OF WELDS USED IN STUDY OF EFFECTS OF COMPOSITION AND HEAT TREATMENT ON THE DYNAMIC-CORROSION RESISTANCE IN URANYL SULFATE SOLUTIONS

DESIGNATION	BASE METAL, AISI TYPE	WELD METAL, AISI TYPE*		ORIGINAL PLATE THICKNESS (in.)	FERRITE IN WELD** (%)
		Initial Heliarc Pass	Coated Electrode		
1	347	347	347	1 1/4	8
2	347	308L	308L	1 1/4	9 to 11
3	347	347	Comp H	1 1/4	0
4	304L	308L	308L	1	9 to 11
5	304L	347	347	1	8
6	304L	347	Comp H	1	0
7	304L/347	347	347	1	8
8	304L/347	308L	308L	1	9 to 11
9	304L/347	347	Comp H	1	0

*Composition "H" is an experimental, fully austenitic columbium-stabilized rod with nominal composition of 18% Cr, 13% Ni, 5% Mn.

**Percentage of ferrite was determined by Magne-gage measurements and is representative of the center portion of the weld. Actual ferrite contents in the root vary due to dilution by the base metal and are not precisely known. Based on other data for 347 and 308L heliarc welds, the maximum ferrite content of the root passes is probably about 11%.

The standards were annealed, wrought specimens of types 304, 304L, 310, 309SCb, and 347 stainless steel. These specimens were loop-tested in straight-bore specimen holders under the conditions to which the pins were exposed, except that the flow rate was at a subcritical 20 fps and the length of the run was 200 hr. The raised face possessed by the flat-plate type of specimen used in this study made larger flat areas available for surface study by metallographic examination; in addition, the specimens can be used, with intermittent heat treatments, if desired, for several corrosion tests. The results of the initial corrosion test failed to show any significant differences among the welds. It was noted, however, that wrought type 304L, whether alone or as base plate in a weld, exhibited the best corrosion resistance. This could be attributed to an adherent brown subscale, which by x-ray diffraction analysis was found to contain approximately 25% Cr_2O_3 and 75% $\alpha\text{-Fe}_2\text{O}_3$, found only on type 304L. The same oxide components were found in the scale on type 347, but Cr_2O_3 was present to the extent of only about 10%. The

specimens have been reprepared and are being tested in a 400-hr run.

STRESS-CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS

W. O. Harms

E. C. Miller

Recent transgranular failures of type 347 stainless steel tubing in right-angle and U-bend sections of dynamic-corrosion test loops, plus the results of preliminary experiments described in the previous semiannual report,⁷ have prompted a more controlled experimental study of the effects of elastic and residual stresses and composition on the susceptibility of austenitic stainless steels to transgranular stress-corrosion cracking.

Design and fabrication of a jig for preforming stress-corrosion specimens were completed during this period. The type of specimen adopted for this investigation is a modification of one intro-

⁷E. C. Miller and W. O. Harms, Met. Semiann. Prog. Rep. Oct. 10, 1953, ORNL-1625, p 15.

PERIOD ENDING APRIL 10, 1954

TABLE 10. RESULTS OF DYNAMIC-CORROSION TESTS OF HEAT-TREATED, WELDED AUSTENITIC STAINLESS STEEL SPECIMENS IN URANYL SULFATE SOLUTION CONTAINING 40 g OF URANIUM PER LITER FOR 400 hr AT 250°C AND 23 TO 26 fps

TYPE OF HEAT TREATMENT*	NO. OF SPECIMENS TESTED	NO. OF SPECIMENS SHOWING REMOVAL OF OXIDE FILM AND UNDERLYING METAL DURING TEST	AVERAGE DEFILMED WEIGHT LOSS (mg)
Type 347 Stainless Steel, All-Coated Electrode Weld			
A	4	0	56
B	3	0	35
C	5	1	49
D	4	1	83
E	5	1	52
F	4	4	170
G	3	0	61
Type 347 Stainless Steel, Coated Electrode and Base Metal			
A	3	0	52
B	3	0	36
C	4	2	104
D	2	2	210
E	1	0	25
F	3	2	131
G	2	0	46
Type 347 Stainless Steel, Heliarc Root Pass and Base Metal			
A	3	0	52
B	3	0	55
C	2	1	94
D	3	2	132
E	1	0	29
F	2	2	140
G	3	0	59
Type 308L Stainless Steel, All-Coated Electrode Weld			
A	4	3	146
B	4	0	26
C	4	2	119
D	3	1	102
E	2	0	48
F	2	2	226
G	3	1	73
Type 308L Stainless Steel, Coated Electrode and Base Metal			
A	2	2	277
B	2	0	28
C	1	1	146
D	3	1	117
E	2	0	36
F	4	4	134
G	2	1	129
Type 308L Stainless Steel, Heliarc Root Pass and Base Metal			
A	3	2	86
B	3	0	32
C	2	1	94
D	3	1	76
E	2	0	63
F	3	3	135
G	2	2	128

METALLURGY PROGRESS REPORT

TABLE 10. (continued)

TYPE OF HEAT TREATMENT*	NO. OF SPECIMENS TESTED	NO. OF SPECIMENS SHOWING REMOVAL OF OXIDE FILM AND UNDERLYING METAL DURING TEST	AVERAGE DEFILMED WEIGHT LOSS (mg)
Composition "H", All-Coated Electrode Weld			
A	6	0	33
B	4	0	31
C	3	1	93
D	4	1	121
E	2	0	110
F	3	3	150
G	3	2	135
Composition "H", Coated Electrode and Base Metal			
A	2	0	30
B	3	0	46
C	4	2	90
D	3	1	91
E	2	1	114
F	3	2	110
G	3	2	122
Type 347 Stainless Steel Heliarc Root Pass, Diluted by Composition "H", and Base Metal			
A	2	0	40
B	2	0	34
C	2	1	99
D	2	1	103
E	2	1	125
F	3	2	111
G	2	0	52

*A: As welded.

B: 1000°F for 6 hr, air-cooled.

C: 1625°F for 2 hr, furnace-cooled.

D: 1625°F for 2 hr, water-quenched.

E: 1625°F for 2 hr, water-quenched and 1000°F for 6 hr, air-cooled.

F: 1950°F for ½ hr, water-quenched.

G: 1950°F for ½ hr, furnace-cooled.

duced by Waber and McDonald⁸ and is shown in Fig. 21. This specimen is so designed that, when a load is applied by means of the stud-and-nut arrangement, the bending moment, and thus the stress distribution at any point along the large, flat (horizontal) portion, should remain essentially constant. This was shown to be the case on both annealed and as-formed specimens in outer-fiber stress evaluations by means of resistance-type strain-gage measurements.

Initial corrosion tests are being made in boiling 42% magnesium chloride solutions; the specimen geometry is such that further testing can be carried

Fig. 21. Stress-Corrosion Specimen.

⁸J. T. Waber and H. J. McDonald, *Corrosion and Material Protect.* 3, 13 (1946).

out in oxygen-pressurized uranyl sulfate solutions at elevated temperatures (200 to 300°C) in existing autoclaves. It is planned to study the effects of varying the following conditions: (1) elastic stress, (2) residual stress, (3) combined residual and elastic stresses, and (4) chemical composition as it is related to the tendency for austenitic stainless steel to transform to the more stable ferritic structure when strained during or prior to testing.

SELECTIVE OXIDATION OF AUSTENITIC STAINLESS STEELS

W. O. Harms

E. C. Miller

The examination of the results of earlier dynamic-corrosion tests and the film studies on moist-hydrogen-pretreated austenitic stainless steel specimens were continued during this period. The indication by previous studies⁹ that preoxidation treatments of this type improve corrosion resistance in uranyl sulfate solutions prompted a more systematic study to determine optimum conditions of time, temperature, moisture content, and alloy composition. With a consideration toward possible practical application of this type of pretreatment, the times in initial experiments were held to $\frac{1}{2}$ to 1 hr, but the other variables were studied between rather wide limits.

Specimens of type 304L stainless steel were pretreated for 1 hr at temperatures of 700, 1300, and 1900°F and at moisture contents of about 0.2, 0.5, and 5 to 9 vol % at each temperature. Also, pins of types 304L, 347, 321, and 309SCb were pretreated at 1850°F for $\frac{1}{2}$ hr in hydrogen containing 0.5, 0.7, and 2.8 vol % moisture. All specimens were electropolished prior to pretreatment.

The pins were tested in oxygen-pressurized 0.06 M UO_2SO_4 (15 g of uranium per liter) plus 0.015 M H_2SO_4 (25 mole % excess) for 200 hr at 250°C and 61 fps. Previous tests⁹ had shown that these conditions were convenient for sorting purposes. From the results summarized in Table II it can be seen that, for the short times considered here, optimum pretreatment conditions include low

moisture contents at high temperatures. Except for moisture control, these conditions are similar to those used in the full-annealing of type 300-series stainless steels. Type 309SCb appears to be more consistently satisfactory under these conditions than are types 304L and 347. On the other hand, at slightly higher moisture contents, type 309SCb may fail and types 304L and 347 may perform satisfactorily.

In view of the encouraging results with type 309SCb, pins and coupons of type 304L were subjected to chromizing treatments and subsequently heated to 1900°F for 1 hr in hydrogen containing 0.6 vol % moisture. The chromizing treatment developed chromium-rich diffusion layers on the specimens. Two chromized and preoxidized pins were inserted in a specimen holder along with both as-machined and pretreated pins and tested in 0.06 M UO_2SO_4 (15 g of uranium per liter) plus 0.015 M H_2SO_4 for 200 hr at 250°C and 68 fps. These pins showed scrubbed weight losses of 0.7 and 1.4 mg compared with an average of 130.2 mg for as-machined specimens and 139.1 for specimens preoxidized without prior chromizing. One chromized and preoxidized coupon was inserted in the ninth position of a ten-specimen, tapered-bore holder so as to be exposed to solution flow rates ranging from 45 to 55 fps in the same run. This coupon showed a scrubbed weight loss of only 26 mg compared with approximately 500 mg for as-machined specimens tested in this position under similar loop conditions in other runs.

Film studies on all specimens except those treated at 1850°F and those which had been chromized were performed by electron diffraction and microscopy and by x-ray diffraction and fluorescence analysis. These studies showed that specimens which exhibited satisfactory corrosion resistance were protected by pretreatment films containing both high-lattice-parameter spinels (8.39 to 8.40 kX units), of the iron chromite type, and chromic oxide ($\pm 10\%$ $\alpha\text{-Fe}_2\text{O}_3$). Indications were that the rhombohedral X_2O_3 phase was contained only in the inner layer of these films. Less satisfactory films were made up of spinels of lower lattice parameter and considerably less chromium. Films formed at higher moisture contents contained varying amounts of $\alpha\text{-Fe}_2\text{O}_3$.

⁹E. C. Miller and W. O. Harms, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p 17.

METALLURGY PROGRESS REPORT

TABLE 11. RESULTS OF DYNAMIC-CORROSION TESTS^a ON MOIST-HYDROGEN-PRETREATED AUSTENITIC STAINLESS STEEL PINS

PRETREATMENT CONDITIONS ^b			DEFILMED WEIGHT LOSSES ^c		
Temperature (°F)	Time (hr)	H ₂ O (vol %)	0 to 3 mg	12 to 15 mg	40 to 140 mg
700	1	0.2			304L (2)
		2.5			304L (2)
		5.6			304L (2)
1300	1	0.2			304L (2)
		2.4			304L (2)
		9.1			304L (2)
1900	1	0.2	304L (2)		304L (2)
		2.4			304L (2)
		4.6			304L (2)
1850	½	0.5	309 SCb (2)	304L (1) 309 SCb (1)	347 (1), 304L (2)
		0.7	309 SCb (2)		347 (2), 304L (1)
		2.8	304L (2), 347 (1)		347 (1), 309 SCb (1)
As-machined pins					309 SCb (3), 347 (1) 304L (4), 321 (2) 304 (1)

^aLoop run M-6: 0.06 M UO₂SO₄ (15 g of uranium per liter) plus 0.015 M H₂SO₄ (25 mole % excess), 250°C, 200 hr, 61 fps. This run also included eight specimens which were pretreated in air at 750°F for ½ hr and which lost from 107 to 127 mg in the test.

^bPrior to the pretreatments listed, all pins were fully annealed and electropolished.

^cSpecimens are listed as to AISI designation; the number of specimens tested is given in parentheses.

ANP METALLURGY

W. D. Manly

STATIC CORROSION

E. E. Hoffman

W. H. Cook

Fluoride Corrosion

Several thermal convection loop tests conducted by the Experimental Engineering Group had greater-than-average depths of attack. It was thought that this increased attack might be due to improper degreasing treatment of the loops prior to loading. Therefore, a static test was run in which six drops of oil and six drops of trichloroethylene were added to an Inconel tube and the solution was allowed to evaporate in an attempt to duplicate improper degreasing. This tube was then loaded with fluoride fuel No. 30 and run for 100 hr at 816°C (1500°F) under static conditions, along with a standard test for comparison. The results of the test are as follows:

	Weight Change (g/sq in.)	Metallographic Notes
Fluoride 30	-0.0063	2 to 3 mils of subsurface voids
Fluoride 30 plus oil and tri-chloroethylene	-0.0023	Maximum attack of 1 mil of subsurface voids

The specimen in the standard test had greater weight loss and depth of attack than did the specimen contaminated by the evaporation of the trichloroethylene-oil solution. It appears that, under

the conditions of this test, the contamination was not detrimental and might even be beneficial.

It was reported that molybdenum disulfide was being used as a Swagelok lubricant in fluoride production systems. The question arose as to whether increased corrosion of Inconel tubing would result if some of the MoS_2 were to contaminate the fluoride. Accordingly, two seesaw tests of fluoride 30 in Inconel tubing were run for 100 hr, and in one of these tests an addition of 3% MoS_2 , by weight, was made to the fluoride; the other test was run with no addition to the fluoride in order to have a standard test for purposes of comparison.

Upon metallographic examination of sections of tubing from hot and cold zones of both tests, it was found that more severe attack had taken place in the test with the MoS_2 addition. The cause of this increased corrosion is not known. The Climax Molybdenum Company states that no free sulfur is present in the MoS_2 and also "... on heating under non-oxidizing conditions, laboratory tests have shown no change in structure or composition even after heating to 1286°C (2350°F)." It is possible, of course, that some impurity in the MoS_2 carrier or the MoS_2 itself may have caused this increased corrosive attack. Test data and results are given in Table 12.

Static Tests of Brazing Alloys in Fluorides and Sodium

Brazed T-joints prepared by the Welding and Brazing Group have been static tested in fluoride 30 for 100 hr at 816°C. The brazing alloys used were the eutectics, 90%Ni-10%P and 80% Ni-10%

TABLE 12. CORROSION OF INCONEL BY FLUORIDE 30 CONTAMINATED BY MOLYBDENUM DISULFIDE IN SEESAW TESTS FOR 100 hr

	TEMPERATURE (°C)		METALLOGRAPHIC NOTES	
	Hot Zone	Cold Zone	Hot Zone	Cold Zone
Fluoride 30 in Inconel	815	690	Subsurface voids to 2 mils in depth	Very few subsurface voids to $\frac{1}{2}$ mil; not much attack
Fluoride 30 plus 3% MoS_2 in Inconel	815	715	Rather heavy attack in the form of subsurface voids varying from $\frac{1}{2}$ to 6 mils in depth	Subsurface voids of erratic occurrence to a maximum depth of $2\frac{1}{2}$ mils

METALLURGY PROGRESS REPORT

P-10% Cr, and both type 316 stainless steel and Inconel were used as the base materials. The details of the T-joint preparation and various properties of the brazed joints may be found in the Welding and Brazing section of this report.

The results of these tests are summarized in Table 13. As can be seen from the weight-change data, none of the specimens were attacked appreciably. The greater part of the weight loss may be attributed to attack on the base materials. The excellent resistance of the 90% Ni-10% P brazed joint to attack by fluoride 30 may be seen in Fig. 22. A layer ($\frac{1}{4}$ to 1 mil in thickness) of the nickel-rich solid solution formed on the surface of all the joints tested (see Fig. 23) except the 80% Ni-10% P-10% Cr on Inconel joint. These alloys seem to be very satisfactory from a corrosion standpoint, but the brittleness of the gray Ni_3P phase is well illustrated in Fig. 24.

Inconel and type 316 stainless steel joints brazed with 75% Ni-25% Ge have been tested in fluoride 30 and sodium. This alloy was corroded to an appreciable degree in both media. Results of examination following the tests are summarized in Table 14.

Several tests have been completed in the screening of materials for potential use in bearing and

hard-facing applications which would have corrosion resistance in molten fluorides. One set of specimens consisted of Hastelloys B, C, and D and also Stellites 1, 6, 12, 21, 25, 40, and 41 deposited on pieces of type 347 stainless steel. These composite specimens were tested in fluoride 30 for 100 hr at 816°C under static conditions. In these tests it appeared that Hastelloys B, C, and D and also Stellites 21, 25, and 40 stood up rather well against attack by the fluorides. Stellites 1, 6, 12, and 41 appeared to be attacked severely in this environment. As was reported previously, it is apparently the carbides in the Stellites which are preferentially attacked by the fused fluoride salts, and it appears that the Stellites of low carbon content are not so severely attacked. Results of the tests are presented in Table 15.

Various cermet specimens have been seesaw-tested in fluoride 30. These tests were run in Inconel tubes for 100 hr with the specimens restricted in the hot zone of the tubes. The results of the tests are given in Table 16. Of the various TiC plus nickel binder cermets tested, one specimen with 20% binder and another with 30% binder had the best resistance to attack. However, duplicate tests on each showed slightly heavier

TABLE 13. RESULTS OF STATIC TESTING OF BRAZING ALLOYS IN FLUORIDE 30 FOR 100 hr AT 1500°F

BRAZE ALLOY	BASE MATERIAL	WEIGHT CHANGE (%) [*]	METALLOGRAPHIC NOTES
90% Ni-10% P	Inconel	0.06	No attack on brazed joint; $\frac{1}{4}$ -mil nickel-rich phase on surface of braze fillet following test; no cracks in the brazed joint of either the as-brazed joint or the corrosion-tested joint
80% Ni-10% P-10% Cr	Inconel	0.07	Braze fillet attacked to a depth of 2 to 3 mils in the form of subsurface voids; voids resulted from attack on the globular particles of the nickel-rich phase
90% Ni-10% P	Type 316 stainless steel	0.06	Braze fillet unattacked by the fluoride; $\frac{1}{2}$ - to 1-mil layer of nickel-rich phase on surface of braze fillet; large cracks evident both in the as-brazed and tested joints
80% Ni-10% P-10% Cr	Type 316 stainless steel	0.18	Scattered subsurface voids in Ni_3P phase beneath $\frac{1}{2}$ -mil nickel-rich solid solution on the surface; surface layer itself unattacked; no cracks observed in either the as-brazed or the tested T-joint

^{*}Per cent weight change includes weight of brazing alloy (approximately 5% of total) and weight of base material of which T-joint is constructed.

attack. This discrepancy may be due to variations in the specimens themselves. Kennametal D4675 (WC plus 2.5% cobalt) had very good resistance, and additional tests are planned to confirm this result. In these tests the hot zone of the tubes was held at 816°C, while the cold zone was

approximately 700°C (1292°F). The attack on Carboloy 608 (Cr_3C_2 plus 2% WC and 15% nickel; see Fig. 25) seemed to indicate that the nickel binder was attacked preferentially, since Carboloy X3505, which is Carboloy 608 with no nickel binder, did not show this attack.

Fig. 22. Brazed Joint of 90% Ni-10% P on Inconel After 100-hr Static Test at 816°C (1500°F) in Fluoride Fuel No. 30. Specimen was nickel plated following test to preserve edge during polishing. 150X

TABLE 14. RESULTS OF STATIC TESTING OF 75% Ni-25% Ge BRAZING ALLOY IN FLUORIDE 30 AND SODIUM FOR 100 hr AT 1500°F

BASE MATERIAL	BATH	METALLOGRAPHIC NOTES
Inconel	Fluoride 30	Braze fillet attacked to a depth of 7 mils in several areas; attack confined to nickel-rich phase which formed on exposed surface of fillet during test
Inconel	Sodium	Very similar to specimen listed above, with voids to a maximum depth of 4 mils
Type 316 stainless steel	Sodium	Specimen attacked to a maximum depth of 9 mils; attack confined to nickel-rich phase

METALLURGY PROGRESS REPORT

Fig. 23. Brazed Joint of 90% Ni-10% P on Inconel After 100-hr Static Test at 816°C (1500°F) in Fluoride Fuel No. 30. Note uniform layer of nickel-rich solid solution which formed on surface of braze fillet during test. 1500X

Fig. 24. Brazed Joint of 90% Ni-10% P on Type 316 Stainless Steel Prior to Test. All cracks were in brittle Ni_3P phase. 1500X

TABLE 15. CORROSION OF HARD-FACING TYPE 347 STAINLESS STEEL COMPOSITE SPECIMENS IN FLUORIDE 30, 100 hr, 816°C, STATIC CONDITIONS

MATERIAL	COMPOSITION	METALLOGRAPHIC NOTES
Hastelloy B	Mo, 26-30%; Fe, 4-7%; C, 0.12% max; Ni, bal	A few voids to a depth of $\frac{1}{2}$ mil
Hastelloy C	Mo, 16-18%; Fe, 4.5-7%; C, 0.15% max; Cr, 15.5-17.5%; W, 3.75-5.25%; Ni, bal	A little spalling and a few voids to a maximum of 1 mil
Hastelloy D	Cu, 3%; Al, 1%; Si, 10%; Mn, 1%; Ni, bal; C, 0.12%	Subsurface voids to $1\frac{1}{2}$ mils
Stellite 1	Cr, 30.5%; W, 12.5%; Fe, 3% max; C, 2.5%; Ni, 1%; Co, bal	Many voids on Stellite to a depth of 5 to 10 mils
Stellite 6	Cr, 27.5%; W, 4%; Fe, 2-3% max; C, 1%; Co, bal	Stellite attacked erratically along carbides in grain boundaries up to 15 mils in depth
Stellite 12	Cr, 29.5%; W, 8.25%; Fe, 2-3% max; C, 1.4%; Ni, 1%; Co, bal	Erratic intergranular attack on Stellite, 0 to 13 mils in depth
Stellite 21	Cr, 25-30%; Ni, 1.5-3.5%; Mo, 4.5-6.5%; Fe, 2% max; Co, bal; C, 0.2-0.35%	A few voids to $\frac{1}{2}$ mil on Stellite
Stellite 25	Cr, 19-21%; C, 0.15%; Ni, 9-11%; W, 14-16%; Si, 1%; Mn, 1-2%; Fe, 2%; Co, bal	A few voids on Stellite to $\frac{1}{2}$ mil in depth
Stellite 40	Cr, 13.5%; C, 0.42%; Fe, 4.5% max; Si, 3.9%; Co, 1% max; Mn, 0.25%; B, 3.2%; Ni, bal	Voids to a depth of 3 to 5 mils on Stellite
Stellite 41	Si, 3.6%; Co, 1% max; Mn, 0.25%; B, 2.25%; Ni, bal; Cr, 12%; C, 0.42%; Fe, 4.5% max	Heavy erratic intergranular attack, 4 to 23 mils in depth on Stellite

Special tar-impregnated and fired graphite crucibles have been tested in fluoride 30 and sodium at 816°C for 100 hr (see Fig. 26). As can be seen in the photograph, the sodium completely penetrated the walls and caused them to crack and crumble. The crucible containing fluoride 30 had a weight loss of 0.012%, and the surface which was in contact with the fluoride had an etched appearance. The fluoride did not penetrate the graphite crucible wall.

Tests have been run to compare the corrosion resistance of two types of graphite in molten sodium at 816°C for 100 hr in a static system with type 304 stainless steel being used as the container material. One type of graphite tested was C-18 (reactor-grade graphite) and the other type was tar-impregnated and fired 16 times during its preparation. The purpose of the repeated impregnation and firing is to produce a high density and "tough skin" which could possibly help to

reduce penetration by various liquid media. The C-18 graphite was practically unaltered by the test (see Fig. 27). The surface of the specimen had an etched appearance and the sharp corners had been rounded slightly. The tar-impregnated and fired cylinder was cracked badly and spalled, as may be seen in Fig. 27.

Dissimilar Metals in Fluoride 30

A series of tests has been conducted to determine the effect of having dissimilar metals (type 316 stainless steel and Inconel) in contact with fluoride 30 in a dynamic system with a temperature differential. The tubes, one-half type 316 stainless steel and one-half Inconel, were joined in the center by heliarc welding. The hot zone in these tests was at 816°C and the cold zone was maintained at 680°C (1256°F). Both the type 316 stainless steel and Inconel sections were tested in the hot zone, and tests were conducted for 100

METALLURGY PROGRESS REPORT

TABLE 16. CERMETS SEESAW-TESTED IN FLUORIDE 30

MATERIAL	COMPOSITION	METALLOGRAPHIC NOTES
Kentanium K-150-A	TiC plus 10% Ni	Attacked to a depth of 4 mils
Kentanium K-151-A	TiC plus 20% Ni	A zone of slightly affected material to a depth of 1 or 2 mils
Kentanium K-151-A	TiC plus 20% Ni	Macro-examination revealed many blisters on surface of sample; attack extended to a depth of 6 mils
Kentanium K-152-B	TiC plus 30% Ni	Specimen attacked in only a few areas to a maximum depth of 2 mils; much less attack than on either K-150-A or K-151-A listed above
Kentanium K-152-B	TiC plus 30% Ni	Specimen attacked somewhat erratically to a depth of 4 to 7 mils; did not resist attack as well as sample of K-152-B listed above
Kentanium K-162-B	TiC plus 25% Ni and 5% Mo	Macro-examination of specimen revealed a surface which had the appearance of a plated specimen with portions of the plating removed; specimen attacked to a depth of 9 mils
Kennametal D4675	WC plus 2.5% Co	Specimen attacked in the form of subsurface voids to a depth of 1 mil
Firth Sterling Carboloy 608	TiC plus 7% Cr_3C_2 and 50% Ni Cr_3C_2 plus 2% WC and 15% Ni	Specimen attacked from 2 to 5 mils Exposed surface of specimen attacked to a depth of 4 mils
Carboloy X3505	Same composition as Carboloy 608 but with no Ni binder	No attack could be detected; both as-received and tested specimen very brittle and similar in appearance
Metamic LT-1 (not heat-treated)	77% Cr, 23% Al_2O_3	Specimen completely penetrated
Metamic LT-1 (heat-treated)	77% Cr, 23% Al_2O_3	Specimen completely penetrated

and 300 hr. The results of these tests are given in Table 17. Each tube was examined in the hot and cold zone and at the weld joining the two materials. It may be concluded from the results of these tests that type 316 stainless steel is inferior to Inconel in its ability to resist attack by molten fluorides even when the type 316 stainless steel occupies the cold zone in a dissimilar metal seesaw test. The heaviest attack found in these tests was to a depth of 6 mils in the type 316 stainless steel tube adjacent to the weld. The Inconel tube adjacent to the opposite side of this weld was attacked to a depth of 1 mil (see Fig. 28).

Thorium Oxide-Sodium Static Tests

A series of six different specimens in two different conditions was tested in sodium at 816°C. The specimens were as follows: ThO_2 , $ThO_2 + 1\% CaO$, $ThO_2 + 1\% MgO$, $ThO_2 + 1\% BeO$, $ThO_2 + 1\% PbO$, and $ThO_2 + 1\% ZnO$. One set of specimens was tested with as-cut surfaces, while another set of specimens was refired following cutting to densify the surface.

Visual observation of the specimens after they were tested was used to evaluate these materials. All specimens absorbed sodium during the test.

Fig. 25. Carboloy 608 (Cr_3C_2 plus 2% WC, 15% Ni). As-received condition (left); following seesaw test in fluoride fuel No. 30 for 100 hr (right). 250X

All specimens were heavily attacked, generally in the form of spalling, except the ThO_2 and the $\text{ThO}_2 + 1\% \text{CaO}$. The refined $\text{ThO}_2 + 1\% \text{MgO}$ also had good resistance. Refiring of the specimens to densify their surfaces seemed to improve their corrosion resistance.

Inconel X-Sodium Tests

A spinner test was run with Inconel X in sodium in which the specimens were not rotated. This test was run to determine whether the attack noted in the spinner test might possibly be due mainly to impurities in the sodium or in the atmosphere rather than to the velocity of test. Much lighter attack and less weight change were noted on these specimens than were observed on the Inconel X specimens that were run at 405 fpm; therefore most of the attack noted on specimens in spinner tests is believed to be due to velocity effects. A spinner test with type 405 stainless steel (12% chromium) has also been run at a velocity of 405 fpm. These tests were conducted at a temperature of 816°C for

TABLE 17. TYPE 316 STAINLESS STEEL-
INCONEL-FLUORIDE 30 SEESAW TESTS

MATERIAL	TIME (hr)	TEMPERATURE (°C)	DEPTH OF ATTACK (mils)
Inconel (hot zone)	100	815	0.3
Type 316 stainless steel (cold zone)		680	2
Inconel (hot zone)	300	815	0.5
Type 316 stainless steel (cold zone)		680	1
Type 316 stainless steel (hot zone)	100	815	2
Inconel (cold zone)		680	0
Type 316 stainless steel (hot zone)	300	815	2.5
Inconel (cold zone)		680	0

METALLURGY PROGRESS REPORT

100 hr in sodium. Results (along with a dynamic Inconel X test for comparison) are summarized in Table 18.

Fig. 26. Results of Static Tests on Tar-impregnated, Fired Graphite Crucibles for 100 hr at 816°C (1500°F). In sodium (left); in fluoride fuel No. 30 (right).

Fig. 27. Results of Static Tests on Graphite in Sodium for 100 hr at 816°C (1500°F). C-18 graphite (left); tar-impregnated graphite (right).

TABLE 18. SPINNER-TEST RESULTS

MATERIAL	SPECIMEN NO.	WEIGHT CHANGE (%)	METALLOGRAPHIC NOTES
Inconel X (static test)	1	+0.051	Light intergranular attack and voids to a depth of about $\frac{1}{4}$ mil
	2	+0.056	
	3	+0.056	
Inconel X	1	+3.22	One-mil surface layer with intergranular attack to 2 mils beneath it
	2	+2.96	
	3	+3.22	
Type 405 stainless steel	1	-0.46	Surface roughness to approximately $\frac{1}{2}$ mil; intergranular voids to a maximum depth of 3 mils
	2	-0.51	
	3	-0.48

Fig. 28. Results of Seesaw Test of Dissimilar Metals (Type 316 Stainless Steel-Inconel) for 100 hr at 750°C (1382°F) in Fluoride Fuel No. 30. Type 316 stainless steel weld zone (left); Inconel weld zone (right). 500X

"Chromalloyed" Steels in Liquid Metals

The surfaces of samples of type 304 stainless steel and 1035 carbon steel were impregnated with chromium by means of a gas reaction and diffusion process. The process used a reaction between a gaseous chromium compound and iron as a means of exchanging iron atoms for chromium at the surface of the steel. The reaction was accomplished by packing the parts to be treated in a powdered compound containing chromium, an energizer, and an inert material.

Both the "chromalloyed" type 304 stainless steel and 1035 carbon steel were seesaw-tested in sodium, 38% Pb-62% Sn, 82% Pb-18% Cd, 32% Cd-68% Sn, 60% Bi-40% Cd, and 45% Pb-55% Bi. In all cases the chromium-rich layer was found to have cracks in it, and the corrosion resistance of the base material was therefore unimproved. The appearance of the "chromalloyed" type 304 stainless steel before and following the test in 45% Pb-55% Bi may be seen in Fig. 31. These tests were conducted for 100 hr with hot- and cold-zone temperatures of 815°C (1500°F) and 660°C (1220°F), respectively.

Miscellaneous Tests

Core materials of UO_2 that had been clad with nickel, copper, types 304, 316, or 347 stainless steel were tested in sodium and sodium hydroxide for 100 hr at 816°C under static conditions. The specimens were prepared by the Fabrication Group, and the following data apply to their preparation.

	Rolling Temperature (°C)	Hot Reduction (%)
Type 302 stainless steel- UO_2 core clad with types 304, 316, or 347 stainless steel	1225	60
Nickel- UO_2 core clad with nickel	1100	60
Copper- UO_2 core clad with copper	1000	60

Also, specimens clad with nickel, types 304, 316, or 347 stainless steel were annealed for 15 min at 1000°C (1830°F) in hydrogen. Copper-clad specimens were annealed for 15 min at 450°C (842°F) in hydrogen. These specimens were approximately $1 \times 0.35 \times 0.050$ in. Thickness of the core and of each of the cladding layers was approximately 16 mils. In

sodium the specimens clad with nickel, types 304, 347, or 316 stainless steel showed no evidence of attack. The sample clad with copper had a slightly irregular edge and showed weight and dimensional increases after test. The many copper mass-transfer crystals attached to this specimen were probably caused by temperature gradients during the test. These results and the results of the tests with NaOH are summarized in Table 21. The tests with NaOH resulted in the copper- and the nickel-clad specimens being unattacked and the types 304, 316, and 347 stainless-steel-clad material being attacked more or less severely.

Vacuum Dry Box

Construction of a LaValle-type vacuum dry box and allied equipment has recently been completed. This system (see Fig. 32) has proved to be very satisfactory to the needs of the General Corrosion Group in the Metallurgy Division. Prior to loading containers to be tested, casting of bath materials into ingots, or heliarc welding of containers, the box is evacuated to less than $5\text{-}\mu$ pressure. The box is then charged with helium gas until atmospheric pressure is obtained. The tank helium is purified by passing it through a copper coil packed with activated coconut charcoal. The copper coil

METALLURGY PROGRESS REPORT

Fig. 31. Results of Seesaw Test of "Chromalloyed" Type 304 Stainless Steel in 45% Pb-55% Bi. Specimen was nickel plated prior to examination to prevent rounding over of edge during polishing. Specimen before test (left); following test (right). 500X

TABLE 21. RESULTS OF CORROSION TESTS OF FUEL PLATES CLAD WITH VARIOUS MATERIALS

Conditions: 100 hr, 816°C, vacuum

TYPE OF CLADDING	CORRODANT	METALLOGRAPHIC NOTES
Copper	NaOH	No evidence of attack
Copper	Na	Irregular edge with many copper mass-transfer crystals attached to specimen
Nickel	NaOH	No evidence of attack
Nickel	Na	No evidence of attack
Type 304 stainless steel	NaOH	10 to 12 mils of corrosion layer; unattacked material decreased from 48 to 34 mils
Type 304 stainless steel	Na	No evidence of attack
Type 316 stainless steel	NaOH	5-mil corrosion layer; unattacked material decreased from 56 to 51 mils
Type 316 stainless steel	Na	No evidence of attack
Type 347 stainless steel	NaOH	15 to 18 mils of corrosion layer; unattacked material decreased from 53 to 32 mils
Type 347 stainless steel	Na	No evidence of attack

Fig. 32. LaValle-Type Vacuum Dry Box.

PERIOD ENDING APRIL 10, 1954

METALLURGY PROGRESS REPORT

is immersed in liquid nitrogen. This system makes it possible to perform the entire loading operation of the corrosion test within the dry box.

DYNAMIC CORROSION

G. M. Adamson

The design of the standard thermal convection loops has been changed so as to eliminate the expansion pot and use only one size pipe or tubing. Schedule 40, $\frac{1}{2}$ -in. IPS pipe is still being used as the standard material, but will be replaced by $\frac{3}{8}$ -in. schedule 10 as soon as a supply is available. Another change in design that replaced the sharp bends with curved sections at both leg junctions should reduce the flow resistance and slightly increase the velocity.

Since longer circulation times are required to study mass transfer, loops are now operated for 1000 to 2000 hr instead of 500 hr. It has been necessary, therefore, to increase the number of loops in operation from 14 to 20, and instruments have been ordered for increasing to 31 loop stations.

Considerable difficulty has been encountered in obtaining reproducibility of the corrosiveness of various fluoride batches. The variation of gas-purging time during production is believed to be responsible for the variation in corrosion.

Operating Time

New results from a time series in which high-purity fluoride mixture 30 was circulated in Inconel at 1500°F confirm those previously reported,¹ which were obtained with impure fluorides. Results from loops filled with the same batch of fluorides and circulated for varying times are given in Table 22. Again, attack continued with time but at a lesser rate than in the initial stages. It is believed that the initial rapid attack may be caused mainly by impurities, while the slower second stage is a form of mass transfer. As can be seen in Fig. 33, which shows hot-leg sections from loops 345 and 329, the holes increased in size and became more concentrated in the grain boundaries with increasing time. The last column of Table 22 lists the average chromium concentration of fluorides taken from various areas around the loop after circulation. It shows that mass transfer may take place with very low and constant chromium concentrations in the fluorides. The depths of attack obtained with the long-time loops using high-purity fluorides are very similar to those previously reported for the one using impure fluorides.² It was expected that a decrease in the rate of attack, or mass transfer, would be found. Both the chemical and metallurgical results obtained from the 2000-hr loop conflict with the other tests in this series and with previous results.

¹G. M. Adamson, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p 30.

²G. M. Adamson, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p 26.

TABLE 22. EFFECT OF TIME VARIATION ON CORROSION

LOOP NO.	OPERATING TIME (hr)	ATTACK	MAXIMUM PENETRATION (mils)	TRAP AND COLD-LEG APPEARANCE	AVERAGE CHROMIUM CONCENTRATION (ppm)
345	500	General, moderate to heavy with small voids	6	Dark layer but no metal in trap; no layer on wall	620
327	1000	Moderate, general and intergranular	10	Metallic ring around trap wall; possibly thin layer on cold leg	550
328	2000	Moderate to heavy intergranular	7	Metallic ring around trap wall	250
329	3000	Heavy, intergranular with large voids	20	Layer of chromium in trap with layer on cold-leg wall	620

The values have been checked and are correct. As yet no satisfactory explanation has been found.

Fig. 33. Effect of Time on Growth and Concentration of Voids During Circulation of Fluoride Fuel No. 30 in Inconel Loop at 1500°F. (a) Loop 345, 500 hr. (b) Loop 329, 3000 hr. 250X. Reduced 22%.

An addition of zirconium hydride was made in order to further purify the fluorides in another loop in which a portion of the same high-purity fluorides was circulated for 3000 hr. This loop had a maximum hot-leg attack of $13\frac{1}{2}$ mils. While less than the attack found in the regular loops operated for as long, this extent of corrosion is not much less, if any, than that found after 500 hr of operation and provides additional evidence that the mass-transfer step is not extremely sensitive to the original fluoride batch purity.

It has been shown that mass transfer may also be obtained in long-time loops when fluoride mixtures that do not contain uranium are circulated. Metallic crystals were found in the traps and possibly on the cold-leg walls of loops in which fluoride mixture 31 was circulated for 2000 and 3000 hr. Analysis of the fluoride after operation gave only 100 to 200 ppm of chromium. The depths of attack were erratic and are still being studied.

Fluoride Batch Purity

Pilot-plant batches of fuel 30 that have received a 24-hr gas purification instead of the customary 8 hr or less are now available. This material is being specified for all thermal convection loop work. Corrosion results from four standard Inconel loops in which this material was circulated for 500 hr at 1500°F are presented in Table 23. These results confirmed those on loop 307 which had previously circulated a small batch that had been purified in the laboratory. This loop had shown a moderate to heavy attack with a maximum penetration of 5 mils.

When compared with the 9 mils maximum regarded as average for the standard production batches, the attack found in these loops is considerably

TABLE 23. CORROSION RESULTS ON STANDARD INCONEL LOOPS

LOOP NO.	MAXIMUM PENETRATION (mils)	AVERAGE FINAL CHROMIUM CONCENTRATION (ppm)	HOT-LEG CORROSION
345	Usually 3 but occasionally to 6	600	Moderate to heavy; mainly general but deepest penetrations are intergranular
352	$5\frac{1}{2}$	450	Light to moderate; mostly intergranular
353	3	600	Moderate to heavy; mainly general
421	5	800	Moderate to heavy

METALLURGY PROGRESS REPORT

reduced. Figure 34 shows the hot-leg section of a loop in which impure fluorides were circulated. Loop 298 is typical of those loops filled with the previous batches of impure fluorides, while 345, shown in Fig. 33, represents present high-purity batches. The reduction in attack is also reflected in the chromium pickup, which is now less than half the previous values. With the longer purification, some reduction is obtained in the amount of iron and nickel present but the major improvement is thought to have been achieved by reducing the hydrogen fluoride content by one-half as a result of the gas purging.

Loop Temperature

Considerable skepticism has been expressed about the conclusions previously presented³ that variations in hot-leg temperature from 1350 to 1650°F do not lead to large variations in attack. This range is almost twice as large as the difference between the hot- and cold-leg temperatures. As additional confirmation, loops were operated for 1000 hr with hot-leg temperatures of 1500 and 1650°F. In both loops the attack was moderate with a maximum penetration of 10 mils in the 1500°F loop and 8 mils in the 1650°F loop. The voids in both loops were larger than normal and were more concentrated in the grain boundaries. These two loops show again that, within the limits studied, temperature is not an important variable.

³G. M. Adamson, *Met. Semiann. Prog. Rep.* April 10, 1953, ORNL-1551, p 34.

Fig. 34. Attack of Impure Fluoride Fuel No. 30 on Inconel Loop 298 at 1500°F. 250X

It was noted previously,¹ in a loop operated at 1250°F, that only the upper portion of the hot leg was attacked and to a depth of only 3 mils. It was hoped that at slightly lower temperatures all attack would be eliminated. Two loops were therefore operated with a hot-leg temperature of 1200°F. Loops 390 and 350 produced a maximum hot-leg attack of 5 and 4 mils, respectively. The samples for these loops were cut from an area 2 in. further up the hot leg than were those in the 1250°F loop; so the values are not comparable. In both loops the attack was found only in the upper portion of the hot leg. The voids were very small and were general in nature. A hot-leg temperature of 1200°F is the lowest at which fluorides may be circulated in present loops.

ARE Fluoride Batch 31

One of the barren fluoride batches made from the low-hafnium zirconium oxide for use as the testing liquid and fuel carrier of the ARE was made available for corrosion testing. The batch was selected at random and so should be typical of this material. An entire series of Inconel loops was filled from it. The results from these loops are summarized in Table 24.

The maximum depth of attack obtained from this coolant is about the same as that reported in a previous section when the high-purity uranium-bearing fluoride 30 was circulated. The intensity of the attack is, however, much less with the fluoride 31. Figure 35 shows the hot leg of loop 341, which is typical.

The voids are larger and are more definitely concentrated in the grain boundaries. Just above the liquid-solid interface in the traps of these loops was found a gray layer about $\frac{1}{8}$ -in. thick. This layer was identified petrographically as being very fine needle-like metallic crystals, undoubtedly of chromium metal, dispersed in the fluorides. This fact, coupled with the low chromium values, is additional evidence that chromium mass transfer does occur with extremely low chromium concentrations in the fluorides.

High-Uranium Fluoride Mixture 44

After preliminary circulation in the ARE of mixture 31, sufficient uranium fluoride will be added to produce mixture 44. Except for being higher in uranium concentration, this mixture is the same as the mixture 30 which has received the majority

TABLE 24. CORROSION RESULTS OF ARE FLUORIDE BATCH 31

LOOP NO.	ATTACK		FINAL AVERAGE IMPURITIES (ppm)			VARIABLE
	Intensity	Maximum Penetration (mils)	Ni	Cr	Fe	
341	Light to moderate	5½	20	310	65	Standard conditions - 31 cleaned
348	Light	5	20	130	80	Standard conditions - 31 cleaned
336	Light to moderate	6	20	100	50	Standard conditions - degreased
342	Light to moderate	6	20	200	35	Standard conditions - degreased
337	Light	8	20	210	50	Two batches of 31 were circulated for a total of 575 hr
338	Moderate	4	20	480	50	First batch of 31 from loop 337 was circulated an additional 500 hr in this loop

Fig. 35. Hot Leg of Inconel Loop 341 After Circulation of Barren Fluoride Mixture 31 for 500 hr at 1500°F. 250X

of the testing. Three loops have been operated to determine the effect, if any, on corrosion of this increase in uranium. These fuels did not receive adequate purification, or even the same amount as

that given to mixture 30, during their production; so the depths should be compared with the 9 mils obtained with impure mixture 30. Because of the variation in purification, considerable variation was also found in the depth of attack. As values of 7, 10, and 16½ mils were measured after 500 hr of circulation at 1500°F, a definite conclusion cannot be drawn, but it does appear that no large increase in depth of attack is found with the increase in uranium. One difference in the behavior of this mixture is a definite segregation of uranium which is thought to have taken place during the cooling of the loop. The variation amounts to almost one-third the uranium value. The Materials Chemistry Division has been requested to produce batches of this mixture with a high purity so that the test may be repeated.

Variations in Uranium Percentage

A series of 31 base coolants with uranium additions varying from 0.5 to 15 wt % were produced by the Materials Chemistry Division and were circulated in Inconel loops. As this series also received inadequate and varying gas purges, the tests are being repeated. While the results of the

METALLURGY PROGRESS REPORT

series cannot be taken literally, the trends can be partially confirmed by other results. The two loops with low uranium concentrations, 0.5 and 2.8%, produced attacks much lower than were expected and that were not in line with the other loops. The purity of these two batches is thought to be higher than that of the remainder. In spite of the low attack a very thin, apparently metallic, deposit was found on the cold-leg wall of each loop. With the other three loops (5.1, 9.8, and 14.4 wt % of uranium) the attack increased linearly with increasing uranium. With the 5.1 wt % of uranium, a very thin layer was found in the cold leg but none was found with the other two concentrations. While depth of attack increases with increasing uranium, the possibility of layers being found in the cold leg decreases.

The above results are confirmed if results from mixtures ARE 31, high-purity fluoride 30, and the lowest penetration with mixture 44 are considered. Again, attack shows a small but linear increase, from 5 to 7 mils, with increasing uranium.

Inconel Loop Variations

Surface-to-Volume Ratio. Large differences have always been observed in the corrosion results obtained in the seesaw and in the loop tests. One of the differences between the two tests is the surface-to-volume ratios. To determine the effect of this variable, a loop, No. 349, was constructed from 1-in. tubing instead of the standard $\frac{1}{2}$ -in. IPS pipe. The loop from the 1-in. tubing had a surface-to-volume ratio of 4.6 sq in./cu in., while in a standard loop it is 6.5 sq in./cu in. Two loops made from $\frac{1}{2}$ -in. tubing with a surface-to-volume ratio of 10.5 sq in./cu in. were also operated. A maximum attack of 9 mils was measured for the loop with a surface-to-volume ratio of 4.6 sq in./cu in. and $5\frac{1}{2}$ mils in the one with a ratio of 6.5 sq in./cu in. The maximum attack found in the $\frac{1}{2}$ -in. tubing, ratio 10.5 sq in./cu in. (loop 359), which had been filled from the same batch of fluorides as the other two, was a moderate-to-heavy attack of 4 mils. Loop 362, also of $\frac{1}{2}$ -in. tubing, showed a similar attack to $3\frac{1}{2}$ mils with a few areas extending to 5 mils. A linear relationship is not obtained when attack vs ratio is plotted. With a thermal convection loop, both the velocity and temperature drop change with any change in pipe size. Variations in these quantities probably cause the deviation from the straight line.

Metal Purity. A series of high-purity, low-carbon heats of Inconel were made and sent to Superior Tube Company where $\frac{1}{2}$ -in. tubing was drawn. The tubing was then fabricated into thermal convection loops. Standard Inconel contains 0.08% carbon, but these heats contained only about 0.014%. To further tie up the carbon, one heat had 0.31% titanium added. One plain, low-carbon loop and the one with the titanium were filled from the same batch of fluorides as was used with the $\frac{1}{2}$ -in. commercial tubing discussed above. The low-carbon loop, 366, developed a moderate, general hot-leg attack with a maximum penetration of $3\frac{1}{2}$ mils. The one with added titanium, 367, showed a moderate-to-heavy, general hot-leg attack of $3\frac{1}{2}$ mils. Typical hot-leg sections from these three loops are shown in Fig. 36. Within the limits studied here, very little, if any, reduction in attack was found. A very slight reduction in depth is possible, but many more loops would be needed to confirm this. The Inconel was cleaner than typical hot-leg sections and did not contain so many inclusions.

One other low-carbon loop was filled from a different batch of fluorides, which turned out to be one of the several impure batches recently received. The hot-leg attack in this loop was heavy and penetrated to 13 mils. In addition, after circulation, a very large grain size was found in the Inconel. The loop is still being studied.

Additional Container Materials

Nickel. In report ORNL-1625⁴ results were presented that showed a very small amount of mass transfer in a nickel loop in which fuel 30 was circulated. Another nickel loop has been operated. High-purity fuel was used and the loop was cleaned by first circulating fuel 31. After circulation, no metallic crystals were visible in the fluorides either in the cold leg or in the trap. Metallographically, no layer could be identified on the cold-leg surface. The surface of the hot leg was bright and polished, and there were no subsurface voids or intergranular attack. The wall thickness was within commercial tolerances but on the low side. It seems likely that a small amount of removal had taken place, since the surface was polished; however, this seems to be the smallest amount of mass transfer or corrosion yet found.

⁴G. M. Adamson, *Met. Semiann. Prog. Rep.* Oct. 30, 1953, ORNL-1625, p 32.

Fig. 36. Attack of Fluoride Fuel No. 30 on Inconel Loops for 500 hr at 1500°F. (a) Commercial tubing, loop 359. (b) High-purity, low-carbon tubing, loop 366. (c) High-purity, low-carbon tubing with titanium addition, loop 367. 250X. Reduced 27%.

The 400-Series Stainless Steels. One type 430 stainless steel (0.12% maximum carbon, 14 to 18% chromium) loop has been operated with fuel 30 for 500 hr at 1500°F with no sign of plugging. A metallographic examination revealed an unexpected type of attack. The hot-leg attack was an even surface removal rather than the development of subsurface voids in the grain boundaries as was found with type 316 stainless steel. The hot-leg surface was smooth, with no subsurface voids or intergranular type of attack. A zone about 2 mils deep was present on the surface from which the carbides appeared to have been leached (or possibly to have gone back into solution) and in which considerable grain growth had taken place. The outer surface of the pipe was quite rough; so wall-thickness measurements are in doubt. Variations in thickness of from 0.106 to 0.109 in. were found. The specified thickness is 0.109 in.; so it would appear that no large amount of removal had taken place. That some removal had taken place was indicated by scattered metallic crystals adhering to the cold-leg surface. A second loop has been operated but not yet examined.

Loop 138 was constructed from type 410 stainless steel (0.15% maximum carbon, 11.5 to 13.5% chromium). Unlike the other 400-series loops studied, this composition is martensitic in nature. After 500 hr at 1500°F the hot leg was very rough with sharp depressions to $1\frac{1}{2}$ mils. There was no evidence of any intergranular or subsurface void type of attack. The outer surface was too rough to permit accurate wall-thickness measurements to be made; however, it seems likely that some thinning of the wall took place. The cold-leg wall was covered with a metallic layer and the fluorides were full of dendritic metallic crystals.

A third loop, No. 138, was constructed from type 446 stainless steel (0.35% maximum carbon, 23 to 27% chromium). After 500 hr the hot leg of this loop was rough and uneven, and, in addition, a heavy concentration of subsurface voids to a maximum depth of 10 mils was found. The cold leg had a very heavy deposit of metal with dendritic crystals in the fluorides. The cold-leg crystals from this loop and from the loop made from type 410 contained mostly iron, but chromium was also present. The ratio of chromium to iron was 1:12.5 in the crystals from the type 410 loop

METALLURGY PROGRESS REPORT

and 1:4.7 in those from the type 446 loop. The ratios in the original alloys were 1:6.5 and 1:3, respectively. It is obvious that with the change in chromium content of these two alloys a change in corrosion mechanism takes place. With type 430 it is an even removal, while with type 446 both an even removal and a subsurface void type of attack similar to that found in type 316 stainless steel are observed.

Izett Iron. A single loop of Izett iron was filled with mixture 30 and circulated at 1500°F. This loop was terminated in 39 hr because of a plug. In this short time the lower sections of the loop had collected many balls of needle-like dendritic iron crystals. These crystals are similar in appearance to those of nickel found in the hydroxide systems. A thick deposit was also found on the cold-leg wall. The hot-leg surface of this loop was very rough, and there were areas in which entire grains had been removed.

Hastelloys. One loop of $\frac{1}{2}$ -in. tubing was constructed from Hastelloy C (58% Ni, 17% Mo, 15% Cr, 5% W, 5% Fe). The loop was terminated when a leak occurred in the weld at the top of the hot leg after circulating fluoride mixture 30 for 456 hr at 1500°F. The hot leg showed a light subsurface void formation to a depth of $1\frac{1}{2}$ mils. The attack was mainly in the second phase found in these alloys. No attack or deposit was found in the cold leg.

Attempts were made to circulate several loops constructed from Hastelloy B (62% Ni, 30% Mo, 5% Fe). The loops varied from a 0.035-in. wall, $\frac{1}{2}$ -in. tubing to a 0.065-in. wall, 1-in. tubing, but all ended in failure. Two failures were due to poor handling, one to a poor weld, and the others to catastrophic oxidation. The oxidation took place under the Sauereisen cement used to protect the thermocouples. The Hastelloys are hot short in the temperature range of 1100 to 1600°F, which makes handling difficult. Loops are now being fabricated which will be given a high-temperature anneal to minimize the difficulties.

One loop constructed of 1-in. tubing was examined after it had operated at 1500°F for 91 hr before failing by catastrophic oxidation. The hot- and cold-leg surfaces of this loop were both rough. Fabrication cracks were visible in the cold leg but not in the hot leg. Since the surface of the hot leg had a matte finish, it is likely that some general removal had taken place, but no intergranular or subsurface void type of attack was visible.

Dissimilar-Metal Mass Transfer

A series of experiments was performed with various combinations of type 316 stainless steel or nickel in the hot and cold legs of Inconel loops in which mixture 30 was circulated. The purpose of this series is to study the effects of the presence of various amounts of these metals on the corrosion of Inconel. The results of the first loop experiment were reported in ORNL-1625⁵ and showed that a short length of type 316 in the top of the hot leg of an Inconel loop would reduce the attack on the Inconel but would cause increased mass transfer.

In loop 379, the second of the series, fuel was circulated with a length of nickel in an Inconel hot leg. The Inconel showed a heavy subsurface void attack to a depth of 5 mils. No change in attack in the Inconel was apparent as the nickel insert was approached. The nickel near the weld had a few scattered voids to a depth of 1 mil, while the rest of the insert appeared to be unattacked. If any even removal had taken place, it could not be determined. No deposit was found in the cold leg. If any reduction in attack was caused by the nickel, it was too low to pick up in a single loop.

Inconel Forced-Circulation Loop

The operation of an Inconel forced-circulation loop was described by Salmon.⁶ After termination, this loop was turned over to the Metallurgy Division for examination. The details of this examination were reported elsewhere,⁷ but a summary follows.

A normal subsurface void type of attack was found in the hot leg of this loop. The attack gradually increased in depth to a maximum of 11 mils in the hottest portion. The attack was both more intense and more concentrated in the grain boundaries than that found in the thermal loops under similar conditions. The depth is only slightly deeper but since turbulent flow was not obtained, a large increase would not be expected. Considerable carburization of the Inconel was found in the hot leg. The carbides must have originated from oil used to lubricate the gas seal of the pump. In the hottest portion a general layer of carbide precipitate to a depth of 14 mils was

⁵G. M. Adamson, *Met. Semiann. Prog. Rep.* Oct. 30, 1953, ORNL-1625, p 31.

⁶D. F. Salmon, *ANP Quar. Prog. Rep.* Dec. 10, 1953, ORNL-1649, p 29.

⁷G. M. Adamson and R. S. Crouse, *Metallographic Examination of Inconel Forced Circulation Loop No. 2*, ORNL CF-54-3-15 (March 3, 1954).

PERIOD ENDING APRIL 10, 1954

found, with an intergranular layer throughout the sample.

No deposit was found in any of the cold-leg sections examined. Some attack and carburization were found in the first or hottest section but not in the others.

Diffraction and petrographic examination of the fluorides, before and after circulation, failed to reveal any changes that might have caused plugging. It seems likely that the plugging in this loop was caused by a gradual freezing of the fluorides at a cold spot and not by corrosion.

47-51

METALLURGY PROGRESS REPORT

PHYSICAL CHEMISTRY

G. P. Smith

Mass Transfer in Fused Hydroxides

W. H. Bridges

Studies of the mass transfer of nickel in sodium hydroxide have been made in this laboratory at intervals over the past two years.¹⁰

Sodium hydroxide has very little corrosive effect on nickel at temperatures below 700°C as long as oxidizing atmospheres are excluded, hydrogen is not allowed to escape, and the system is isothermal. Studies of the effect of reducing atmospheres in systems with thermal gradients have shown that mass transfer is inhibited by a hydrogen atmosphere. Several different apparatus designs have been used in tests involving thermal gradients. The "stand-pipe"¹¹ is a long tube heated in the center and cooled at the ends. The seesaw apparatus¹² involves tilting a tube back and forth while heating one end and cooling the other. The thermal convection loop¹³ is a continuous length of tubing shaped like a parallelogram, one length of which is heated and the opposite length cooled. The cold finger¹⁴ consists of a small-diameter tube sealed off at one end and concentrically inserted into a larger pot containing the molten hydroxide. The larger pot is heated while the small tube is cooled by a jet of air. The inhibiting effect of hydrogen was first demonstrated with the use of the cold finger and subsequently in a seesaw test.

An extension of the hydroxide corrosion-testing program to determine the maximum temperatures and thermal gradients for various alkali hydroxides contained in various metals has been started. The cold finger type of apparatus was chosen because of the ease with which the thermal gradient can be controlled and a known atmosphere be maintained. The cost of expendable parts is not great, nor do the parts require many hours for fabrication.

The original cold-finger apparatus has been modified extensively to increase the mechanical strength and to allow the attainment of higher temperatures.

¹⁰Met. Quar. Prog. Rep. July 31, 1951, ORNL-1108, p 29.

¹¹Met. Quar. Prog. Rep. Oct. 31, 1951, ORNL-1161, p 25; A. deS. Brasunas and L. S. Richardson, Met. Quar. Prog. Rep. Jan. 31, 1952, ORNL-1627, p 72.

¹²A. deS. Brasunas and L. S. Richardson, Met. Quar. Prog. Rep. Jan. 31, 1952, ORNL-1627, p 67.

¹³Met. Quar. Prog. Rep. Oct. 31, 1951, ORNL-1161, p 39; G. P. Smith, J. V. Cathcart, and W. H. Bridges, Met. Quar. Prog. Rep. Jan. 31, 1952, ORNL-1267, p 74.

¹⁴G. P. Smith, Jr., J. V. Cathcart, and W. H. Bridges, Met. Quar. Prog. Rep. April 30, 1952, ORNL-1302, p 59.

A section of stainless steel pipe was sealed off at one end and flanged at the other as shown in Fig. 43. To the flange was bolted either a pyrex pipe bell reducer or a blind flange. A section of 1/2-in. tubing was inserted through a Swagelok fitting mounted in the center of either top piece. The 1/2-in. tubing was sealed off at one end, and a pot of the same material as the tubing was suspended concentrically. The pot contained the liquid media under test.

A few runs have been made in the pilot model. Under an argon atmosphere with a pot temperature of 700°C and a gradient of only 20°C, some mass transfer did occur in 48 hr. Under a hydrogen atmosphere with the same set of conditions, no mass transfer occurred. Increasing the thermal gradient to 200°C still resulted in no mass transfer in a hydrogen atmosphere. When the pot temperature was raised to 900°C with a thermal gradient of 170°C, mass transfer did occur. A multiple-unit

Fig. 43. Fused-Hydroxide Corrosion Test Apparatus.

rig is now being constructed which will accelerate gathering of the data.

Sodium-Alloy Flammability

M. E. Steidlitz

G. P. Smith

Studies¹⁵ of the flammability of jets of sodium alloys in moist and dry air at temperatures up to 800°C have been continued.

As mentioned previously, the test of combustion was whether or not a luminous fire was produced. According to this criterion the only alloys studied which did not burn were Na-Hg alloys containing less than 34 mole % sodium and Na-Bi alloys containing less than 40 mole % sodium. All other alloys burned to some degree ranging from slight to violent.

The combustible alloys were as follows: binary alloys containing 90 mole % aluminum, 50 to 60 mole % bismuth, 90 mole % indium, 90 mole % lead, 0.6 to 66 mole % mercury, 90 mole % silver, and 90 mole % zinc — each with the balance sodium; ternary alloys having a 45 mole % sodium-50 mole % bismuth base and containing 5% each of calcium, copper, magnesium, mercury, potassium, and silver; and ternary alloys having a 30 mole % sodium-65 mole % mercury base with 5 mole % each of aluminum, bismuth, calcium, copper, magnesium, potassium, and silver.

The humidity of the air was noted to have a very slight effect on the rate of combustion of jets of liquid sodium alloys and a somewhat more noticeable effect on the combustion of quiescent liquid sodium alloys.

Interfacial Equilibria in the Cu-Bi System

J. V. Cathcart

Investigations of the surface rearrangements occurring on single-crystal copper spheres immersed in a saturated solution of copper and bismuth have been continued. In these experiments, special care was taken to exactly saturate the bismuth solution with copper before it was brought into contact with the single crystals. Providing strict isothermal conditions were maintained during the experiments, it was felt that any surface rearrangements occurring on the copper crystals could be attributed to variations of surface free energy with

the crystallographic plane. Details of the experimental procedures and apparatus have already been reported.¹⁶

Since the last report, the temperature control for the experimental system has been improved to such a point that it has been possible to perform two experiments in which temperature variations at 400°C amounted to no more than $\pm 0.02^\circ\text{C}$. It is believed that under these conditions any surface rearrangements which could have been attributed to a solution-deposition mechanism would be at least an order of magnitude smaller than that actually observed.

The first of these experiments lasted 456 hr. Surface rearrangements similar to those previously reported were observed. The surfaces of the crystal were covered with a large number of small, flat, faceted regions from which bright specular reflections could be obtained when the crystal was rotated in a light beam. The crystallographic planes producing these reflections were identified as (111) and (110) planes and high index planes close to the (320) plane. This result was also in agreement with previous experiments.

The second experiment was designed to show the early stages of surface rearrangements. Specular reflections could not be obtained from this crystal, but when viewed under the highest magnification obtainable with an optical microscope, a slight but regular roughening was observed on the crystal surface. The examination of this specimen is still in progress.

Preliminary experiments in this investigation have indicated that small residual strains in the copper crystal produced an increase in the extent of surface rearrangements. For this reason great care was taken to avoid the introduction of mechanical strains into the crystal. They were grown in a spherical mold so that only a careful electropolish was necessary for their surface preparation. However, in order to mount the crystals in the reaction chamber, a small hole had to be drilled in the base of the stem of the crystal. This region, of necessity, remained in a slightly strained condition. It was observed that the surface rearrangement in the vicinity of the hole in the stem was much greater than that anywhere else on the crystal. Pyramid-like protuberances could be seen in this

¹⁵M. E. Steidlitz, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p. 45.

¹⁶G. P. Smith, J. V. Cathcart, and W. H. Bridges, *Met. Quar. Prog. Rep.* April 30, 1952, ORNL-1302, p. 59; *Met. Quar. Prog. Rep.* Jan. 31, 1953, ORNL-1503, p. 21.

METALLURGY PROGRESS REPORT

area. In future studies an effort will be made to learn more of the role played in surface rearrangements by small, residual strains.

Products of Hydroxide-Metal Reactions

H. L. Yakel, Jr.

G. P. Smith

Studies are being made to identify and to determine the properties of the compounds produced by hydroxide-metal reactions. Previous studies in this series were concerned with the action of lithium and sodium hydroxides on nickel in the presence of oxidizing agents.¹⁷ Current research is concerned with the reaction which occurs between sodium hydroxide and nickel when hydrogen is allowed to escape from the system.

Miller and Williams¹⁸ have shown the existence of an equilibrium of the type $\text{Ni} + \text{NaOH} = \text{H}_2 + \text{unknown products}$. They reported that when this equilibrium was displaced by evacuating at 900 to 1000°C until hydrogen evolution ceased, an "amorphous" product was obtained which had a gross composition corresponding to 1 mole of sodium oxide and 1 mole of nickelous oxide. Woltersdorf¹⁹ found that mixtures of sodium oxide and nickelous oxide react at temperatures as low as 250°C to produce various crystalline sodium nickelate(II) compounds. He was able to establish that sodium orthonickelate(II) has the empirical formula Na_2NiO_2 . Kruh²⁰ found that a mixture of NaOH and nickel heated to 700°C under flowing argon gave x-ray powder patterns which did not correspond to any patterns in the literature. Kertesz and Knox²¹ induced a reaction between sodium hydroxide and nickel by slowly removing a relatively small amount of hydrogen gas. X-ray powder patterns of the resulting material did not show any identifiable lines.

¹⁷L. D. Dyer, B. S. Borie, Jr., and G. P. Smith, *Alkali Metal-Nickel Oxides Containing Trivalent Nickel*, ORNL-1667 (Feb. 25, 1954).

¹⁸Reported by R. R. Miller and D. D. Williams in, *Sixth Progress Report on Thermal and Related Physical Properties of Molten Materials* (May 1 to August 1, 1953), Naval Research Laboratory Problem No. 32C11-06, p 1-2; and preceding reports in this series.

¹⁹G. Woltersdorf, *Z. anorg. Chem.* 252, 126 (1943).

²⁰Reported by R. F. Kruh in, *Progress Report, Subcontract No. 501 - Under W-7405-eng-26 - Report for the Period April 1, 1953 through June 30, 1953*, p 5, University of Arkansas, Institute of Science and Technology.

²¹F. Kertesz, private communication.

During the past few months a study has been made of the reaction which takes place when hydrogen is rapidly evacuated from the NaOH-Ni system. The primary product of this reaction was found to be a crystalline, sodium divalent nickelate, probably sodium orthonickelate(II). The crystal structure and chemical properties of this substance are now being determined.

In these studies the reaction chamber was a nickel tube (low-carbon grade) 1.27 cm OD and 44 cm long. The tube was welded closed at the bottom end and fastened at the top end to the rest of the all-glass apparatus by means of a standard, ground, ball joint. This nickel tube could be evacuated through either of two circuits by turning a stopcock. One circuit was relatively short and allowed fast pumping speeds. The other circuit contained a liquid-nitrogen cold trap. The pressure of the system was measured by means of a Pirani gage and an Octoil-S manometer similar to that described by Biondi.²² This combination of instruments provided pressure measurements from 1 to 1000 μ with a precision of $\frac{1}{5} \mu$ at the low pressure extreme and 20 μ at the high pressure extreme. The vacuum was produced by a Kinney CVM 3534 mechanical pump. Dry, carbon dioxide-free argon could be admitted to the apparatus when desired. The nickel reaction tube was heated by means of a tube furnace. Temperatures were measured with Chromel-Alumel thermocouples which were wired to the nickel tube. The method used for opening the reaction tubes at the end of an experiment did not make it practical to weld the thermocouples to the tube. Hence, the highest temperatures reported (950°C) may be in error by as much as $\pm 20^\circ\text{C}$.

The nickel reaction tube was loaded in the air with about 10 g of cp grade sodium hydroxide and then quickly attached to the apparatus. Dehydration of the hydroxide was accomplished by slowly heating to about 400°C under a vacuum. The circuit containing the cold trap was used to remove the water evolved. The course of the dehydration was followed by observing pressure changes, and some observations were made which are described elsewhere in this report.

After dehydration, the temperature was increased to a predetermined value while the gases evolved were pumped off through the short circuit. After reaction had proceeded as far as desired, the furnace was rapidly cooled. Then, dry, carbon

²²M. A. Biondi, *Rev. Sci. Instr.* 24, 989 (1953).

dioxide-free argon was admitted to the apparatus, and the reaction tube and its contents were removed to a dry box for examination.

Two reactions have been carried out and the reaction products examined. One reaction took place at 770°C. The pressure (assumed to be due to hydrogen) rose to a maximum of 200 μ and slowly decreased to 70 μ over a period of about 7 hr. The course of the second reaction is shown in Fig. 44. It had been intended that this reaction would be carried out at 950°C. However, as may be seen from Fig. 44, the pressure passed through its maximum before 950°C was reached. The shaded area connects the extremes of pressure fluctuations.

In Fig. 44 an area A taken under the curve for any time interval Δt is proportional to n , the number of moles of gas evolved during the time interval Δt . This may be seen as follows. The pumping speed s is defined to be $s = dV/dt$, where dV is the increment of gas volume passing through a given cross section of tubing in the time interval dt . By applying the ideal gas law in its usual form,

$$dn = \frac{sP}{RT} dt.$$

If s is constant over the pressure range under con-

sideration,

$$n = \frac{s}{RT} \int_{t_i}^{t_f} P dt = \frac{sA}{RT},$$

where $n \sim A$. For the pressure range represented in Fig. 44, the pumping speed varies by about 20% for the Kinney CVM 3534 pump.

The above idea applied to the plot (Fig. 44) shows that the reaction

cannot be said to cease at any definite time under the experimental conditions, undoubtedly because of the effect which the accumulation of reaction product has on the diffusion of sodium hydroxide to the nickel wall.

The nickel tubes containing the reaction products were opened in a helium-filled dry box. Microscopic examination showed that the reaction products consisted of fibers and a powder which were subsequently separated.

When very thin, the fibers were transparent green. They showed no recognizable crystal faces and were frequently bent or partially split along the fiber axis. They dissolved readily in 1 N hydrochloric acid, had an oxidizing power of less than

Fig. 44. Gas Evolution in the Reaction of Nickel with Sodium Hydroxide in a Continuously Evacuated System.

METALLURGY PROGRESS REPORT

0.08 meq/g (probably due to cobalt and manganese impurity), and reacted with moisture and carbon dioxide in the air to form a crust of sodium carbonate monohydrate. These chemical data suggest that the compound is a sodium nickelate(II). Preliminary x-ray evidence indicates that the fibers are not acted on by absolute alcohol during short exposure. Hence, alcohol was used to remove excess hydroxide in preparing the fibers for chemical analysis and density determination. The density determined by a displacement method was 3.82 g/cc.

A single fiber was sealed in a glass capillary in the dry box immediately after the nickel reaction tube was opened. This fiber was found to be a single crystal and was used for the structure determination work which is reported below.

Rotation, Weissenberg, and precession photographs of the single-crystal fiber show orthorhombic symmetry (Laue symmetry *mmm*). Unit cell dimensions were measured from all three types of photograph, and suitably averaged results are as follows:

$$\begin{aligned} a &= 8.28_4 \pm 0.011 \text{ \AA} , \\ b &= 10.14_9 \pm 0.008 \text{ \AA} , \\ c &= 2.81_5 \pm 0.008 \text{ \AA} , \\ V &= 236.67 \times 10^{-24} \text{ cc} . \end{aligned}$$

The extinctions observed in the single-crystal diffraction pattern are consistent with the three space groups *Amam*, *Ama2*, and *Ama2*₁. Piezoelectric or pyroelectric experiments might distinguish between the centrosymmetric space group *Amam* and the other, noncentrosymmetric, possibilities, but these experiments have not been performed because there is a lack of experimental equipment. A statistical averaging of the observed intensities may also permit a distinction between the possible space groups to be made.

The chemical evidence indicates the fibers to be a sodium nickelate(II). The work of Miller and Williams¹⁸ and of Woltersdorf¹⁹ suggests sodium orthonickelate(II). (Chemical analysis is now being made.) If it is assumed that the unit cell contains four formula weights of Na_2NiO_2 , a reasonable assumption in terms of atomic-packing consideration, then the x-ray density is computed to be 3.837 g/cc. This compares favorably with the measured density of 3.82 g/cc.

If it is assumed that the space group is *Amam*, all atoms in the unit cell must lie in either eight-fold or fourfold special positions. The oxygen atoms can be limited to the positions / (Wyckoff's

notation) by consideration of their packing in the *c* direction. The coordinates of these positions are $(0\ 0\ 0, 0\ \frac{1}{2}\ \frac{1}{2}) + x\ y\ 0, \bar{x}\ \bar{y}\ 0, \frac{1}{2} - x\ y\ 0, \frac{1}{2} + x\ \bar{y}\ 0$.

Qualitative examination of the intensities of the *h*00 reflections showed that the sodium atoms must also be in positions /. Nickel atoms may be in positions *c*, *b*, or *a*, for which the respective coordinates are $(0\ 0\ 0, 0\ \frac{1}{2}\ \frac{1}{2}) +$

$$\begin{aligned} &\frac{1}{4}\ y\ 0, \frac{3}{4}\ \bar{y}\ 0 \\ &0\ \frac{1}{2}\ 0, \frac{1}{2}\ \frac{1}{2}\ 0 \\ &0\ 0\ 0, \frac{1}{2}\ 0\ 0 \end{aligned}$$

The *z* coordinates of all the atoms are therefore 0 or $\frac{1}{2}$. This layering is confirmed by the x-ray data which show the intensities in the *hk*2 zone to be equal (allowing for differences in Lorentz and polarization factors and atomic form factors) to those in the *hk*0 zone and intensities of the *hk*3 zone to be equal to those in the *hk*1 zone.

The coordinates of the atoms (a total of five or possibly four parameters) remain to be determined. This may be accomplished stochastically by consideration of the most likely packing of the various atoms, or it may be accomplished by quantitative examination of the x-ray diffraction intensities. Following the latter approach, the Patterson section *P(uvo)* should determine most of the parameters, as it is an important Harker section of the space group *Amam*. This section will be computed after measurement of intensities in the *hk*0 and *hk*1 zones.

It should be re-emphasized at this point that the assignment of the space group *Amam* is an assumption which must be proved or disproved by the possibility or impossibility of deriving a satisfactory structure based on this space group. The layered structure suggested by the x-ray data does support this assumption, however.

Dehydration of Sodium Hydroxide

G. P. Smith

It is known that sodium hydroxide can be dehydrated by heating to 400°C under a vacuum. However, the details of this process have not previously been reported. In studies of the reaction of sodium hydroxide with nickel, as described above, it was possible to measure the evolution of water during the course of dehydration. It was found that virtually all the water evolution occurred near the melting points of sodium hydroxide mono-

hydrate and sodium hydroxide. This result is not surprising in view of the enhanced diffusion rates in the liquid as compared with those in the solid. However, the quantitative extent of this effect is greater than might have been predicted.

Figure 45 is a plot of pressure and temperature vs time during one of four similar dehydrations. As was shown in the preceding section, an area under the pressure-time curve for a specified time interval is proportional to the amount of gas evolved during that time interval. Hence, most of the water was evolved within the relatively narrow limits of two peaks or bands, the first corresponding to the melting of sodium hydroxide monohydrate and the second corresponding to the melting of sodium hydroxide. The shaded area on the second peak connects the upper and lower limits of rapid pressure fluctuations which were probably caused by the bursting of water-vapor bubbles.

Color Changes in Fused Hydroxides

C. R. Boston

M. E. Steidlitz

Color changes observed in fused hydroxides indicate the existence of species in thermal equilibrium other than the expected sodium ions and hydroxyl ions. Several years ago it was noted in this laboratory that fused sodium hydroxide in a nickel container under an atmosphere of hydrogen turned green above 500°C and returned to colorless on

cooling to below 500°C. This color change was at first thought to be due to a changing concentration of nickel ions with changing temperature. Subsequently it was found that the same color change took place when the hydroxide was contained in silver. These observations indicated that the color was not due to the presence of heavy-metal ions. This qualitative study of color changes has been greatly extended during the past few months.

The experimental method was as follows. The hydroxide was placed in a crucible that was contained in a quartz tube which could be evacuated with a mechanical pump and to which various atmospheres could be admitted. The crucible of hydroxide was heated by means of a small pot-type furnace which allowed observation of the hydroxide at temperature. The gases were either dried by passing them through a liquid-nitrogen cold trap or they were saturated with water vapor by bubbling them through water. In most of the experiments the crucibles were made of pure, sintered aluminum oxide, Morganite, in order to ensure the absence of heavy-metal ions. Morganite is very slowly and uniformly attacked by fused hydroxides. However, of the various ceramic crucibles available, Morganite was by far the most resistant to corrosion. In a few tests nickel crucibles were used. The lithium, sodium, and potassium hydroxides were cp grade. The rubidium and cesium hydroxides were supplied by L. G. Overholser of the Materials Chemistry Division.

Fig. 45. Water Evolution During Dehydration of Sodium Hydroxide at a Slow Heating Rate.

METALLURGY PROGRESS REPORT

A series of experiments was conducted in which the hydroxides were heated to approximately 600°C under specified atmospheres. At 600°C the initial atmosphere was evacuated and various atmospheres were successively admitted and evacuated. Finally, the hydroxide was cooled to room temperature. During each step the color changes were noted.

The colors of the hydroxides, contained in Morganite, which developed on standing in specified atmospheres at 600°C are shown in Table 25. For each fused hydroxide-atmosphere combination studied, the hydroxide was colorless below approximately 500°C and distinctly colored at 600°C. The colorless-to-colored transition was reversible with changing temperature. When the system was evacuated or filled with a specified gas, the color changed sometimes with startling abruptness after a brief induction period.

TABLE 25. COLORS OF HYDROXIDES CONTAINED IN MORGANITE AT 600°C AND IN VARIOUS ATMOSPHERES

ATMOSPHERE	COLORS* OF HYDROXIDES				
	LiOH	NaOH	KOH	RbOH	CsOH
Air	Y	Y, O	Y	Y	Y
Vacuum		Y, O	Y	Y	Y
H ₂		G	G	G	G
He		Y			
H ₂ O (g) in H ₂ or He		Colorless			

*Y - yellow

O - orange

G - green

Lithium hydroxide did not lend itself well to testing because of its tendency to decompose with the evolution of water.

After being heated for a long period in either air or vacuum, sodium hydroxide changed in color from yellow to a deep red-orange. This color, however, disappeared promptly on cooling or when the atmosphere was changed.

Several experiments were conducted with sodium hydroxide contained in nickel crucibles. The colors found here were the same as those observed with a Morganite container except that when an atmosphere of air was used reaction with the nickel quickly turned the hydroxide black.

Experiments were performed in which various sodium compounds were added to sodium hydroxide and the mixtures were heated under a vacuum to a temperature of about 400°C. These additives were of commercial purity. Metallic sodium and sodium hydride additions gave, at first, a blue color which turned to green with time. Sodium peroxide additions imparted an orange color. With sodium oxide additions the hydroxide was yellow. It should be noted that these colors were formed at a temperature at which the pure hydroxide would have been colorless. All the colors were retained upon cooling the hydroxide below its melting point.

These results are still too incomplete and too qualitative to permit specific conclusions as to the species giving rise to the various colors; nevertheless, a number of tentative speculations can be made. Various simple atmospheres such as oxygen, hydrogen, and water vapor can interact with the fused alkali metal hydroxide to produce different chemical species which can be characterized, at least to a limited extent, by their color. These interactions do not seem to be greatly altered by progressively changing the cation from sodium to cesium. Hence, they seem to be associated with the anion. The extent of interaction is rapidly established and thereafter seems to change only very slowly with time at constant temperature. The extent of interaction seems to increase markedly with increasing temperature.

It is significant that these hydroxide-gas interactions take place in the absence of free metal. It is well known that the atmosphere plays a dominant role in controlling the mass transfer of nickel. It is not entirely unlikely, then, that the chemical reactions causing mass transfer do not take place directly between nickel and the hydroxyl ion, as is generally believed, but take place between nickel and a chemical species whose concentration is dependent on an interaction between the hydroxyl ion and the atmosphere.

Electrical Conductivity of Fused Sodium Hydroxide

C. R. Boston

M. E. Steidlitz

Preliminary measurements have been made of the electrical conductivity of fused sodium hydroxide contained in silver exposed to the air at temperatures up to 550°C. The results are in fair agreement with those reported by Arndt and Ploetz²³

²³K. Arndt and G. Ploetz, *Z. physik. Chem.* 110, 237 (1924).

who give data up to 450°C. It is interesting to note that the conductivity was found to rise rapidly over the temperature range for which a color change is first noted (see preceding section). These measurements were temporarily discontinued in favor of the studies of color changes reported above.

Oxidation of Solid Sodium

J. V. Cathcart

The study of the oxidation of sodium at room temperature in oxygen has been continued. Oxidation rate measurements were made by following the pressure changes in a sealed reaction chamber with a sensitive differential manometer. The details of the apparatus have been described previously.²⁴

As already reported, preliminary rate measurements indicated that at room temperature sodium does not obey a linear oxidation rate law. The oxidation was characterized by the rapid formation of a thin oxide film followed by a sharp decrease in the oxidation rate. In this respect, the oxidation of sodium appeared to be similar to that of aluminum and copper. Not only were the results at variance with the oxidation mechanism generally proposed for sodium but they also indicate the possibility that the mechanism of oxidation generally accepted for such metals as copper or aluminum may also be applicable to sodium.

During the period covered by this report, an effort has been made to improve the reproducibility of oxidation measurements made on sodium. Approximately 20 measurements have been made of the oxidation rate of sodium at room temperature. All the results confirm the fact that sodium does not obey a linear oxidation rate law. However, satisfactory reproducibility for the oxidation curves has not yet been attained. It is believed that these difficulties have been due to the contamination of the sodium surfaces by trace quantities of impurities present in the reaction chamber. The source of these impurities has not definitely been established, but it appears possible that at least some of the trouble may have been caused by stopcock grease or by volatile impurities in the manometer fluid used. In order to eliminate this contamination, the experimental apparatus has been redesigned and is in the process of being rebuilt.

²⁴J. V. Cathcart, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p. 33.

As soon as a satisfactory procedure has been worked out for obtaining reproducible oxidation measurements, the oxidation rate of sodium will be determined at several temperatures.

WELDING AND BRAZING

P. Patriarca

J. Cisar

G. M. Slaughter

K. W. Reber

High-Temperature Brazing Alloy Development Program

Nickel-Phosphorus Brazing Alloy. The "electroless" method of preplating Ni-P brazing alloy, as described previously,²⁵ was applied to a practical, radiator fin problem. A commercially available system of plating solutions, under the trade name Lustralloy and manufactured by Metal Processing Company, Inc., has been found to give a satisfactory plate. A series of approximately one hundred 3 × 3 in. nickel fins were plated for brazing into a radiator assembly for the Griscom-Russell Co. As a preliminary test, two of these fins were sheared into $\frac{3}{4}$ -in. sections; nickel tubes were inserted into holes in these fins, and the mock assembly was placed into the hydrogen furnace at 1020°C for approximately 10 min. The specimen was then cooled slowly under a hydrogen atmosphere. The finished specimen was bright, and the joints were well brazed. A similarly brazed assembly is shown in Fig. 46. As can be seen, the brazing alloy, originally uniformly distributed on the fins and absent on the tubes, was drawn to the capillary. Figure 47, a photomicrograph of the tube-to-fin joints, shows the excellent quality of the braze.

A disadvantage to this method of applying this brazing alloy is that it is time consuming; hence, it would be desirable to find a method for producing Ni-P powder for application in the usual manner.

Attempts to make a Ni-P alloy by conventional melting methods proved to be unreliable with respect to phosphorus retention, homogeneity, and contamination in subsequent crushing and grinding operations on the as-cast ingots. However, a Ni-P alloy can be prepared by cataclysmic precipitation from a conventional "electroless" plating bath. It was found that an excess of the sodium hypophosphate addition agent would cause a precipitation of Ni-P alloy as flakes on the bath container

²⁵P. Patriarca and G. M. Slaughter, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p. 48-9.

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Fig. 46. Tube-to-Fin Test Specimen Fabricated by Assembly of Preplated Type 304 Stainless Steel Fins and Type 316 Stainless Steel Tubes Followed by Brazing at 1800°F in Dry Hydrogen.

walls and as powder in the bath. The flakes can easily be ground into a powder. Chemical analysis showed the phosphorus content of alloy precipitated in either form to be 11 to 12.5%, which is slightly higher than the phosphorus content in the binary eutectic but similar enough to retain a low melting point and other good brazing properties.

Researchers at the New York Testing Laboratories, Inc. have developed a process for obtaining Ni-P coatings in which a slurry of nickelous oxide, dibasic ammonium phosphate, and water is prepared and is fired in a hydrogen atmosphere at approximately 930°C. Since this method appeared to offer a promising means for obtaining Ni-P alloy, a series of experiments was performed to evaluate the technique. However, metallic nickel powder was used instead of the oxide, since the oxide would be reduced to nickel in the dry hydrogen atmosphere. Calculations based on 100% phos-

phorus retention indicated that a phosphate-to-nickel ratio of 2:1 should produce 90% Ni-10% P eutectic composition. Such an ingot was made, and chemical analysis showed it to be of the eutectic composition. Experiments performed to determine the optimum conditions for producing Ni-P alloy by this method resulted in the following observations:

1. The particle size of the nickel powder was found to have an extremely important effect on phosphorus retention. Fine powders were found to be desirable; subsieve powder reacted with the phosphate to yield better results than those yielded by -200-mesh powder.

2. The effect of temperature was less critical as the particle size decreased. However, firing at higher temperatures than the calculated equilibrium temperature was found to be desirable because the rate of alloying increased as compared

Fig. 47. Section of Tube-to-Fin Assembly Shown in Fig. 46 Illustrating the Feasibility of Tube-to-Fin Fabrication by the Preplate Method. Etchant: glyceria regia. 50X

with the rate of phosphorus loss by vaporization.

3. The use of nickelous oxide was also found to be satisfactory in the production of homogeneous melts.

4. Preliminary experiments indicated that alloy additions such as chromium and iron could be made by including these elements as elemental metal powders in calculated quantities in the initial mixture.

Nickel-Germanium Brazing Alloy. The Ni-Ge system has been investigated at other installations, but its suitability for liquid-metal or fused-salt service has not been established.²⁶ Therefore, Ni-Ge and Ni-Ge-Cr alloys were made for evaluation with respect to oxidation resistance and static-corrosion resistance.

The 75% Ni-25% Ge alloy used as a master alloy has a melting point of 1151°C and has exhibited favorable flowability at 1180°C. The results of corrosion tests conducted in liquid sodium and in fluoride salt mixtures are considered promising (cf. "Static Corrosion," this report). Metallographic examination of an Inconel T-joint brazed with this alloy and exposed to air for 100 hr at 1500°F showed negligible attack. These results, along with evidence that the alloy can be hot-worked, indicate that the Ni-Ge system merits serious consideration for ANP applications.

Alloy additions of chromium and phosphorus have resulted in a substantial decrease of the melting point. A 10% chromium addition lowered the flow point to 1100°C. It is expected that oxidation resistance and corrosion resistance in sodium will also be favored by the chromium addition. However, it appears that chromium additions make the alloy more brittle.

²⁶ Aircraft Nuclear Propulsion Project Engineering Progress Report No. 4, April 1, 1952 - June 30, 1952, APEx-4, p 220.

METALLURGY PROGRESS REPORT

Germanium Additions to Existing, Brazing Alloy Systems. The role of germanium additions in lowering the melting point of existing Ni-Cr-base brazing alloys has been effectively demonstrated. Additions of varying amounts of germanium to the G-E No. 62 alloy (69% Ni-20% Cr-11% Si) resulted in a series of alloys which appeared to have sharper and lower melting ranges. An alloy of 68.2% Ni-12.0% Cr-6.6% Si-13.2% Ge (wt %) appeared to have a solidus and liquidus within 30°C of each other, complete melting having been observed at 1100°C. This alloy will be further investigated by increasing the silicon content in

increments to 11% silicon to determine melting-point effects.

Oxidation Resistance of Brazing Alloys. A group of commercially available and experimental brazing alloys was used to assemble Inconel T-joints which were subsequently sectioned and subjected to oxidation in air at 1500°F. The results of metallographic examination of the specimens after intervals of 200 and 500 hr are presented in Table 26.

Brazing of High-Conductivity Radiator Fins

Although the problem of brazing Inconel-clad-copper high-conductivity fin material to Inconel

TABLE 26. OXIDATION RESISTANCE OF DRY-HYDROGEN-BRAZED T-JOINTS

Parent metal - Inconel

Average fillet throat - 0.015 in.

Air temperature - 1500°F

Exposure time - variable

ALLOY	COMPOSITION (wt %)	BRAZING TEMPERATURE (°F)	EXTENT OF ATTACK*	
			After 200 hr	After 500 hr
Commercial Microbraz	70 Ni-14 Cr-6 Fe-5 B- 4 Si-1 C	2150	Slight	Slight
Low-melting Microbraz	80 Ni-5 Cr-6 Fe-5 Si- 3 B-1 C	1920	Slight	Slight
Coast Metals 52	89 Ni-5 Si-4 B-2 Fe	1840	Very slight	Slight
Mond Nickel Co. alloy	64 Ag-33 Pd-3 Mn	2150	Severe internal oxidation	Severe internal oxidation
Copper	100 Cu	2050	Complete	Complete
Experimental Nickel base				
General Electric 81	66 Ni-19 Cr-10 Si-4 Fe- 1 Mn	2150	Very slight	Slight
Ni-Ge	75 Ni-25 Ge	2150	Slight	Slight
Ni-Cr-Ge	65 Ni-25 Ge-10 Cr	2140	Very slight	Slight
Electroless Ni	88 Ni-12 P	1740	Very slight	Slight
Ni-Cr-P	80 Ni-10 P-10 Cr	1830	Very slight	Slight and moderate
Ni-Sn	68 Ni-32 Sn	2150	Slight	Moderate
Ni-Mn	40 Ni-60 Mn	1920	Complete	Complete
Precious-metal base				
Au-Ni	82 Au-18 Ni	1830	Very slight	Slight
Au-Cu	80 Au-20 Cu	1740	Moderate	Complete
Pd-Al	92 Pd-8 Al	2020	Very slight	Very slight

*Very slight - less than 0.001 in. penetration; slight - 0.001 to 0.002 in. penetration; moderate - 0.002 to 0.005 in. penetration; complete - fillet completely destroyed.

tubing was satisfactorily resolved, as described in the previous report,²⁷ the subsequent determination of the detrimental effects of diffusion of nickel and copper has proved to be a limitation of the method. Accordingly, a group of other high-conductivity fin materials was fabricated for brazing tests.

Several brazing alloys having more favorable melting-point ranges have been under investigation. The Ni-P, Ni-P-Cr, and Coast Metals, Inc. No. 52 alloys (see Table 26) have been found to have suitable wettability. Their oxidation resistance in conjunction with stainless-steel-clad copper and Inconel tubing after a 500-hr exposure to air at 1500°F is being evaluated, and it is expected that deleterious changes, if any, in the metallurgy of the brazed joint and parent materials as a result of diffusion will be revealed during this examination.

Test specimens for the qualitative evaluation of the heat transfer efficiency of various fin materials are being fabricated in the Welding and Brazing Laboratory. These specimens consist of $\frac{3}{16}$ -in.-OD, 0.025-in.-wall Inconel tubing, 6 in. long, with disk fins brazed to the center 2 in. of the tube. A typical specimen, shown in Fig. 48, utilized $\frac{3}{4}$ -in.-OD, 0.010-in.-thick nickel fins brazed 25 to the inch with Microbraz. Copper leads for voltage-drop measurements were brazed to the specimen with low-melting Microbraz. Four of these specimens are connected in parallel and heated by electrical resistance. The temperature of the exit air blown

across the specimens will be considered as a measure of the fin efficiency. Test specimens of the following materials are being fabricated in both 15 and 25 fin-per-inch spacings:

Fin Material	Total Fin Thickness (in.)
Type 304 stainless steel	0.010
Nickel	0.010
0.004-in. copper clad with 0.002 in. of Inconel	0.008
0.006-in. copper clad with 0.002 in. of Inconel	0.010
0.004-in. copper clad with 0.002 in. of type 310 stainless steel	0.008
0.006-in. copper clad with 0.002 in. of type 310 stainless steel	0.010
0.004-in. copper clad with 0.002 in. of type 430 stainless steel	0.008
0.006-in. copper clad with 0.002 in. of type 446 stainless steel	0.010
94% Cu-6% aluminum bronze	0.010

Since Microbraz and low-melting Microbraz proved to be satisfactory on previous tests and since sufficient quantities were available, Microbraz was used to braze the first two specimens above; low-melting Microbraz or Coast Metals 52 was used to braze the others because the melting point of the clad fin materials would not permit the high brazing temperatures necessary for fabrication with Microbraz. It has been found that the aluminum bronze fin material must be plated with approximately 0.001 in. of nickel or chromium before adequate wetting is obtained.

A duplicate set of Inconel-clad copper specimens will be made from sheet oxidized for 500 hr to determine the effect of diffusion on the heat transfer efficiency.

Sufficient fin material of Inconel-clad copper, type 310 stainless-steel-clad copper, and type 430 stainless-steel-clad copper is on hand for the fabrication of conventional sodium-to-air radiators for core-element tests. The results of the above experiments will determine the type of material to be used in these full-scale tests.

²⁷P. Patriarca and G. M. Slaughter, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p 45-8.

Fig. 48. Typical Specimen for Heat Transfer Efficiency Experiment.

METALLURGY PROGRESS REPORT

Sodium-to-Air Radiator Fabrication

It was stated in the previous report that the G-E No. 62 brazing alloy (69% Ni-20% Cr-11% Si) appeared to be suitable for use on ANP type of sodium-to-air radiators.²⁸ Stainless steel and Inconel joints brazed with this alloy were considered to possess adequate resistance to cracking on thermal cycling. It was found that this alloy exhibited excellent resistance to high-temperature oxidation. A metallographic section of a joint of an Inconel tube brazed to a type 304 stainless steel fin and exposed in static air for 1200 hr at 1500°F is shown in Fig. 49. It can be seen that the extent of attack is negligible. Previous tests had also shown that this alloy was adequately resistant to molten sodium at 1500°F in a 100-hr test. The sodium-to-air radiator shown in Fig. 50 was fabricated by brazing the tube-to-fin joints with G-E No. 81 alloy (66% Ni-

19% Cr-10% Si-4% Fe-1% Mn), which is equivalent to G-E alloy No. 62, and heliarc-welding tube-to-header and manifold joints. This method of fabrication was found to be the most reliable one for obtaining a pressure-tight system with one brazing operation.

The tube-to-header welds were inert-gas tungsten-arc welded, manually, with argon as the shielding gas and helium as the backup gas. The header caps and the manifold were also heliarc-welded by using suitable joint designs to permit complete penetration. The sequence of manifold and header-cap welding was such that the Ni-Cr-Si alloy could always be applied to the underside of the joint after tube-to-header welding when complete weld penetration was impossible to achieve. For example, each tube-to-header weld was supplemented with this brazing alloy. A typical heliarc-welded joint backed up with the Ni-Cr-Si braze after brazing is shown in Fig. 51.

The completed assembly was then dry-hydrogen

²⁸P. Patriarca and G. M. Slaughter, *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p 51-2.

Fig. 49. Metallographic Section of Ni-Cr-Si Brazed Tube-to-Fin Joint After Being Tested in Air for 1200 hr at 1500°F. Etchant: glyceria regia, 75X

Fig. 50. Sodium-to-Air Radiator Fabricated by Brazing the Tube-to-Fin Joints and Backing Up the Previously Heliarc-Welded Tube-to-Header and Manifold Joints with Brazing Alloy.

brazed by using the thermal cycle shown in Fig. 52. A preheat of 1600°F was utilized so as to permit an equalization of temperatures over the assembly. The thermocouple, which was placed directly on the radiator, indicated that a maximum temperature of 2150°F was attained and that the unit was held above 2100°F for approximately 30 min. The brazing technique used for this fabrication ensured a relatively slow cooling rate, and so a tendency toward cracking upon cooling as a result of uneven thermal contractions would be minimized.

Helium leak-testing at less than 0.03- μ vacuum revealed that all welded and brazed joints in the radiator were leak-tight.

The success of the brazing procedure used in this fabrication is evidenced by the service history of the radiator described above. To date it has seen sodium-to-air service for a period of approximately 1000 hr in the temperature range 1200 to 1500°F

Fig. 51. Typical Heliarc-welded Tube-to-Header Joint Backed Up with Ni-Cr-Si Braze. Etchant: glyceria regia. 30X. Reduced 50%.

METALLURGY PROGRESS REPORT

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Fig. 52. Thermal Cycle Used in Brazing the Radiator Shown in Fig. 50. Temperatures were obtained with a Chromel-Alumel thermocouple secured to the heat exchanger.

without failure. The service test will be continued to the destruction of the radiator by progressively increasing the operating temperature in an attempt to fully determine the integrity and reliability of the system.

Inert-Arc Plug-Welding of Solid Fuel Elements

An inert-arc plug-welding technique was applied to the assembly of stainless-steel-clad fuel plates into fuel elements of the size and configuration of interest for Package Reactor service. The configuration investigated consisted of a 0.026-in.-thick type 304 stainless-steel-clad type 304 stainless steel sheet 24 in. long that was to be joined on the edge at 2-in. intervals to a 0.041-in.-thick type 304 stainless steel side plate.

The joint design considered to be optimum for plug-welding is shown in Fig. 53. A hole was drilled in a header sheet to receive a projection obtained by edge-milling the 0.026-in.-thick type

304 stainless-steel-clad fuel-plate sheet. The 0.084-in. extension of the projection above the header sheet was predetermined from the following consideration: (1) the volume of the 0.067-in.-dia, 0.041-in.-deep header hole was 0.00015 cu in.; (2) the volume of the 0.062 × 0.026 × 0.125 in. projection was 0.0002 cu in.; (3) the excess of 0.00005 cu in. would ensure adequate weld buildup and could be removed by finish-machining.

A series of these specimens was welded with variations in arc current, arc time, arc distance, and welding sequence. Since precise control of these variables was required, cone-arc²⁹ equipment was used throughout the study. The welds were examined metallographically for penetration and flaws.

Examination of test specimens indicated that the most favorable weld geometry could be achieved by

²⁹P. Patriarca and G. M. Slaughter, *Cone-Arc Welding*, ORNL-1514 (April 10, 1953).

Fig. 53. Assembly of Type 304 Stainless Steel Components Prior to Application of Inert-Arc Plug-Welding Procedure.

two separate inert-arc welding operations. The projection was melted into a "rivet" by an initial choice of arc current, arc time, and arc distance. The arc distance was then reduced, and an additional application of current was used to form the finished weld, the fillet metal being provided by the rivet.

The rivet formed during the first operation by using the optimum welding conditions is shown in Fig. 54, which is a section through the weld joint corresponding to section A-A in Fig. 53. The plug weld formed in the second operation is shown in Fig. 55. Note that the penetration of the type 304 stainless-steel-clad sheet was complete and reasonably uniform, which indicated that a sound weld joint was obtained. It thus appears that inert-arc plug-welding may be one alternative method of fabrication of these assemblies and could be pursued by further experiment. The results of brazing experiments (cf. "Component Assembly by Brazing," this report) are considered to be encouraging, however, and it appears that further plug-welding experiments will not be necessary.

³⁰E. S. Bomar, J. H. Coobs, and H. Inouye, *Met. Semiann. Prog. Rep.* April 10, 1953, ORNL-1551, p 55-6; *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p 52-4.

Fig. 54. Section of "Rivet" Formed by Initial Application of 30-amp Arc Current for an Arc Time of 2 sec at an Arc Length of 0.140 in. Etchant: aqua regia. 21X. Reduced 33%.

Fig. 55. Section of Completed Weld Formed by Application of 30 amp for 4 sec at an Arc Length of 0.060 in. to the Rivet Shown in Fig. 54. Etchant: aqua regia. 21X. Reduced 31%.

FABRICATION

ANP Radiator

H. Inouye

Previous reports³⁰ describe the investigation of high-thermal-conductivity fin material in which it was found that copper could be adequately protected from air oxidation with the absence of diffusion by types 446 and 310 stainless steel. In addition, copper alloys containing 6 and 8% aluminum showed promise. Inconel-clad copper was

METALLURGY PROGRESS REPORT

found to be unsatisfactory because of diffusion. Electroplates and vapor plates were unsatisfactory because there was nonadherence or brittleness.

The work covered during this period includes the investigation of diffusion barriers for Inconel-clad copper, the fabrication of small quantities of the clad material for heat exchangers, and other miscellaneous tests.

Diffusion Barriers. Barrier material between Inconel and copper was selected on the basis of low solubility in copper and high melting point. The barrier materials studied were tungsten, molybdenum, titanium, zirconium, tantalum, vanadium, types 310 and 446 stainless steel, iron, and iron plus silver.

The several composites were hot-rolled approximately 50% at 1800°F and finished cold to 0.008 in. to determine the rolling characteristics. The final composite was calculated to be 0.004 in. of copper clad on both sides with 0.002 in. of cladding.

The refractory metal barriers were calculated to be 0.0002 in. Bonding was not achieved between molybdenum and Inconel or between vanadium and Inconel. The other metals were unsuccessful because discontinuous layers were formed during rolling because of either fracturing of the barrier material or the difference in strength at the rolling temperature. In the latter case, the barrier material was found to be embedded within the copper.

Diffusion barriers of iron and of types 310 and 446 stainless steel were successful in preventing diffusion. Barrier thicknesses of 0.0005 and 0.001 in. showed no deleterious effects up to 1000 hr at 1500°F.

Composites of the configuration Inconel-Ag-Fe-Cu-Fe-Inconel could not be fabricated because there was difficulty in keeping the silver and copper apart during rolling at 1652°F. Further tests were not made, since the silver was found to be unnecessary and because its rather low melting point would cause difficulty in the assembly of structures by brazing.

Some of the earlier tests of Inconel-clad copper showed the absence of diffusion voids. In this connection, a few tests were made to determine the effect of surface preparation on void formation. For this study, oxide layers were formed on Inconel by heat-treating in air and in wet hydrogen at 1350°F for various times up to 1½ hr. Composites fabricated with such oxide layers did not prevent the formation of diffusion voids.

In order to establish which of the clads on copper is most suitable as a fin material for heat exchangers and also to determine the effect of diffusion on the heat transfer properties of a heat exchanger, approximately 15 sq ft of the following claddings on copper has been made: Inconel and types 310 and 446 stainless steel. The fin material is 0.010 in. thick in the ratio 2-6-2. Diffusion couples between copper and the following alloys were made: types 310 and 446 stainless steel, Inconel, and 8% Al-Cu. The couples were heated for 500 hr at 1500°F, and successive 0.001-in. layers were analyzed. The results shown in Table 27 confirm the metallographic observations that Inconel and 8% aluminum bronze vs copper suffer considerable diffusion.

TABLE 27. COPPER DIFFUSION INTO VARIOUS ALLOYS AFTER 500 hr AT 1500°F

COUPLE	COPPER AT INTERFACE (%)	
	Initial	Final
8% aluminum bronze-copper	8.4*	5.97*
Inconel-copper	None	31.2
Type 310 stainless steel-copper	None	0.46
Type 446 stainless steel-copper	None	1.4

*Per cent aluminum by chemical analysis; all others by spectrographic analysis of copper.

The General Plate Div. of Metals and Controls Corp. has fabricated 0.008-in. clad copper up to 5 in. wide and in a single piece up to 50 ft long. Types 430 and 310 stainless steel have been received and tested. The materials are satisfactory with respect to oxidation and diffusion.

Samples of the clad copper have been tested up to 1000 hr at 1500°F. These materials include the barrier metals for Inconel-clad copper. The results show that significant diffusion did not occur and that no alteration of the copper core was apparent.

Efforts to obtain uniform and thinner clads are being investigated by employing seam-welding techniques as proposed by The Glenn L. Martin Company. Material of the final desired thickness is used, and thus far samples 4 in. long with clads 0.001 in. thick have been produced. Under the test conditions employed, it appears that the mini-

mum clad thickness is limited only by the ability to fabricate the composites. The behavior of these composites under stress is unknown and may ultimately dictate the clad thickness required.

Special Alloys Fabrication

Inconel-Type Alloys. The fabrication of seven vacuum-melted Cr-Fe-Ni alloys has been completed except for the final drawing operation to finished size. Difficulty was experienced in this operation because some of the extruded tubes were heavily scored. Apparently the extrusion ratios were too great. It was found, however, that malleablizing elements are unnecessary for good forgeability when the alloys are melted under vacuum and that chromium losses are not severe. The maximum impurity content is about 0.3%, most of which is accounted for from the analysis of the ferrochromium (Table 32).

Extrusions were made in a 750-ton press with the billets heated in a salt bath. A straight mandrel and a 25-deg cone die with a radius at the throat were used. The tools were fabricated with rock wool in the container and glass wool on the billet and mandrel.

No difficulties were experienced in making the extrusions around 2200°F at extrusion ratios as

high as 32:1. However, tool wear was high and surfaces were not good. For the alloy containing 10% molybdenum (DPI-18) temperatures of 2350°F and extrusion ratios of 13:1 were necessary to produce tubing. A good surface and minimum die wear occur at ratios of about 9:1.

Nickel-Molybdenum Alloys. Two vacuum melts have been made of nominal composition 24% Mo-76% Ni and 20% Mo-80% Ni. Attempts to extrude the 24% Mo-76% Ni at 2350°F at an extrusion ratio of 13:1 were unsuccessful. At the same temperature and an extrusion ratio of 9:1, the die insert fractured. A solid die has been made and will be tried.

MECHANICAL TESTING

R. B. Oliver

D. A. Douglas, Jr.

J. W. Woods

Stress-rupture tests of sheet Inconel specimens have been conducted in molten fluoride fuel mixture 30 and in argon at temperatures of 1300, 1500, and 1650°F. Some of the specimens were annealed at 1650°F before test and the remainder at 2050°F. Figure 57 shows the rupture time vs stress plot for each condition and environment. The rupture curve for the tube burst type of tests in molten fluoride at 1500°F is also shown. The relative position of this curve falls considerably below the tensile-stressed specimens at this temperature and compares roughly with these tests at 1650°F. It is thought that the tube burst type of test is a more realistic test from the standpoint of the present reactor designs. In view of the rather large differences in rupture properties shown in the data, it

TABLE 32. CHEMICAL ANALYSIS OF INCONEL-TYPE ALLOYS

MELT NO.	NOMINAL COMPOSITION (%)	ANALYSIS* (%)						
		Cr	Ni	Fe	Si**	Mn	Mo	C
DPI-14	18 Cr-7 Fe-75 Ni	17.62	75.88	6.79	0.20	0.09		0.018
DPI-15	10 Cr-15 Fe-75 Ni	9.80	75.61	14.46	0.15	0.07		0.007
DPI-16	5 Cr-20 Fe-75 Ni	4.79	76.11	19.78	0.08	0.05		0.028
DPI-17	10 Cr-7 Fe-83 Ni	9.82	83.40	6.66	0.14	0.07		0.041
DPI-18	5 Cr-10 Fe-75 Ni-10 Mo	6.00	74.42	10.05	0.06	0.05	9.78	0.001
DPI-19	15 Cr-7 Fe-78 Ni	14.42	78.74	6.58	0.19	0.09		0.033
DPI-20	15 Cr-7 Fe-78 Ni	14.68	77.98	6.44	0.19	0.10		0.008

*S, <0.005; by spectrographic analysis: Al, <0.004; Ti, <0.006; Mg, <0.003; B, <0.002; Co, <0.007.

**By spectrographic analysis.

Fig. 57. Stress vs Rupture Time for Sheet Inconel Specimens at Various Conditions.

seems imperative that this particular testing program be expanded so that the multiaxial stress system can be more thoroughly studied.

In previous reports the sensitivity of Inconel to both its test environment and its annealing temperature has been shown by comparing the times to rupture for the various test conditions. However, it should be emphasized that the selection of the best annealing temperature or environment when using rupture time as the criterion would not necessarily prove to be the best conditions if some other reference mark, such as 1% total strain, were the limiting factor. Figure 58 is a bar graph showing the time required to reach several selected extensions and rupture. The bars are arranged from left to right in order of increasing time to 1% elongation. It can be seen that many of the bars are out of order if extension is neglected and if rupture time is used for a comparative basis. The total elongation at rupture is about the same regardless of the annealing temperature or the environment, except for tests in air and sodium. In the case of

sodium it has been found that the specimen is markedly decarburized during test, which would account for the increased ductility. No explanation has yet been found for the greater elongations reached in air.

Examination of the bar-graph plot shows that the most obvious cases of misfit, with reference to rupture times, are the coarse-grain specimens which were tested in molten fluoride and in argon. The explanation for this discrepancy can be shown in a comparison of the creep curves for the coarse- and fine-grain specimens at 3500 psi. Two such curves are shown in Fig. 59 for tests conducted in argon. The pattern would be similar though of different magnitudes for tests in fluoride. These curves show that for the first 200 hr the fine-grain specimen has a much slower creep rate but that a transition occurs and a new and faster creep rate is established and maintained till fracture. Thus, up to 700 hr and about 4.5% elongation, the fine-grain material will show better creep properties, but after that the coarse-grain specimen will be superior.

Fig. 58. Time Required to Reach Several Selected Extensions and to Rupture for Inconel Tested in Various Environments. All tests at 3500 psi and 815°C.

Fig. 59. Creep Curves for Coarse- and Fine-Grain Inconel Specimens. Test conditions: 3500 psi, 1500°F, argon environment.

Another variable which must be considered when studying the stress-rupture properties of Inconel is the amounts of such trace elements as aluminum, titanium, and boron which are introduced into the heat during deoxidation. The effect of these elements is quite significant even though they are present in very small percentages. Figure 60 is a plot showing rupture curves for two different heats of Inconel. Heat B, which is appreciably higher in these residual elements, has a rupture life from two to three times as long as that of heat A. An analysis of the effect of annealing temperature on the stress-rupture properties of the two heats shows that the 2050°F anneal producing a coarse-grain specimen does not improve the properties of heat A. However, in the case of heat B this same treatment produces a marked improvement in the rupture properties at stresses below 4500 psi. This improvement can also be attributed to the increased content of these residual elements, since the creep curves show an apparent precipitation-hardening effect taking place during test.

Many metallurgical problems, and particularly those associated with the reactor development programs, involve bonded multimetallic layers or the joining of several sections of metal. A method of evaluating the strength of these bonds is imperative both to give the design engineer qualitative strengths to use in his calculations and to allow the metallurgist to evaluate the various fab-

Fig. 60. Stress vs Rupture Time for Two Heats of Inconel. (A) Heat NX4511, low in aluminum and titanium. (B) Heat NX8004, high in aluminum and titanium.

rication variables. Testing methods previously available have been inadequate because either they were not quantitative or they were not capable of resolving the applied load to a simple stress pattern in a plane or a thin layer.

A simple device patented by Schaevitz and fabricated by Baldwin-Lima-Hamilton Corp. converts the tensile load of a testing machine into a torsion stress (Fig. 61). This loading method has been explored with SR-4 strain gages bridged to detect bending moments and axial loads. These extraneous stresses are less than $\frac{1}{2}\%$ of the applied shear stress; thus a joint or interface is tested in pure shear.

Fourteen metallic composites formed by hot-rolling have been tested. The test specimen is prepared by punching a $\frac{3}{4}$ -in. disk from the compos-

ite plate and brazing steel bars to the opposite surfaces. This assembly is then machined to 0.588 to 0.590 in. in diameter by 6 in. long. A reference line is scribed on the surface prior to test, and the specimen is loaded until either failure occurs or the load passes through a maximum value.

Figure 62 illustrates the results of the test on eight composites. In only one case did failure occur at the braze joint attaching the specimen to the torsion rod. Much more experience is needed before a critical evaluation can be made of this type of test. However, it does show that with these specimens shear stresses less than 26,000 psi could be tolerated without failure. It is planned to use this test on a series of butt brazes to evaluate the several alloys and thicknesses of braze metal.

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Fig. 61. Testing Machine for Converting Tensile Load to Torsion Stress.

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PHOTO Y-1023

SPECIMEN BEFORE TEST

2.7F9-Fe-Ni-Mo-Th-Mo-Ni-Fe
 $S_s = 26,900$ psi

2.7E3-2-Fe-SS-Mo-Th-Mo-SS-Fe
 $S_s = 38,400$ psi

2.7E3-1-Fe-SS-Mo-Th-Mo-SS-Fe
 $S_s = 34,500$ psi

2.7F10-Fe-Ni-Mo-Th-Mo-Ni-Fe
 $S_s = 26,000$ psi

Fe-SS-Ni-SS-Fe
 $S_s = 26,100$ psi

2.7F7-Fe-Ni-Mo-Th-Mo-Ni-Fe
 $S_s = 27,100$ psi

Fe-SS-Cu-SS-Fe
 $S_s = 26,400$ psi

2.7F8-Fe-Ni-Mo-Th-Mo-Ni-Fe
 $S_s = 27,800$ psi

Fig. 62. Shear Tests of Multimetallic Composites.

PACKAGE POWER REACTOR PROGRAM

J. E. Cunningham

Metallurgical studies were initiated recently to develop and produce inexpensive, reliable stainless steel fuel and control-rod components for long-time service in a 10-Mw Package Power Reactor power plant. The proposed reactor will be powered with highly enriched fuel, will be cooled and moderated with light water, and, tentatively, will have an expected minimum service life of three years on the replaceable fuel elements.

The fuel plates conceived for service in the reactor consist of a stainless steel-uranium dioxide-boron carbide sintered core mixture clad on all sides with wrought type 304 stainless steel by the picture-frame technique. Eighteen of these plates will be assembled into a flat-plate element by brazing in a manner similar to that employed in the manufacture of MTR type of fuel assemblies.

Initial results of experimental work on the preparation of the sintered core mixture, composite cladding, component assembly, corrosion studies, and control-rod development are described in the following sections.

PREPARATION OF UO_2 -STAINLESS STEEL- B_4C POWDER CORE

E. S. Bomar

Clad plates containing 0 to 50 wt % UO_2 in the core mixture have been successfully prepared. An addition of B_4C in the amount of 0.44% goes into solid solution in the mixture, but a 0.66% addition precipitates the excess at the grain boundaries and on the crystallographic planes across the particles. An 0.81% addition of BN shows no similar precipitation effect. Present specifications on the sintered core mixture of the fuel plates call for 65.47 wt % stainless steel, 34.05% UO_2 enriched to the 93% level, and 0.48% B_4C .

The materials used in the preparation of the core mixture were commercial grade -325-mesh stainless steel powder, -100-mesh UO_2 powder which contained a large percentage of fine particles (5μ), and -325-mesh B_4C . No binder was employed in compacting the powder mixture, but a binder may be necessary to avoid classification if larger particles of UO_2 are specified. The use of larger-sized UO_2 particles may be desirable to minimize

fission-fragment damage during in-pile service.

Powder-metallurgy techniques were employed in the initial preparation of the core mixture. The steps taken in sequence consisted in (1) weighing and blending the powders and (2) consolidating by cold-compacting under pressure of 33 tons/sq in. and sintering for 2 hr at 2100°F. Sintered core compacts, $2\frac{1}{4} \times 2 \times 0.275$ in., were prepared in this manner.

FABRICATION OF STAINLESS-STEEL-CLAD FUEL PLATE

R. J. Beaver

Preliminary specifications for the fuel plate designed for service in the Package Reactor call for core dimensions of $2\frac{1}{2}$ in. in width by 22 in. in length and an over-all width and length of 2.760 in. and 23 in., respectively. The clad-core-clad thickness in mils is 5-20-5.

A total of 32 composite plates containing normal UO_2 has been fabricated by roll-cladding. Originally, picture frames for the cores were prepared by welding four rectangular bars at right angles to each other to form the frame. An exhaust tube was provided for evacuating the interior of the jacketed billet after closure by welding. Inspection of these composites after rolling revealed unbonded areas in the frame where the weld of the four-piece frame was incomplete. Fabrication methods were therefore confined to solid, one-piece frames. At the same time, evacuation was eliminated. Present practice is the insertion of the core in the frame, drying in an oven at 150°C along with the cover plates for 12 hr, and welding the cover plates to the frame as quickly as possible after removal. More than a dozen plates have been fabricated from billets prepared in this manner without any evidence of poor bonding or formation of blisters during a subsequent quality-treatment test.

Experiments were performed to establish a satisfactory procedure for fabricating the fuel plates. Heating and rolling of type 304 stainless steel test samples in air at 1225°C resulted in excessive surface oxidation. Similar tests on samples heated in a hydrogen muffle furnace reduced the thickness of the surface scale to less than 0.5 mil. Some isolated pitting caused by

rolled-in mill scale was encountered, but close metallographic inspection disclosed such pitting to be superficial. The temperature of the furnace from which the billets were rolled was maintained at 1225°C. Obviously, as the plate becomes thinner during the reduction process, the actual rolling temperature is decreased, and when the plate is 0.050 in., the temperature at which the plate is being rolled is estimated to be less than 900°C. The amount of reduction per pass was varied from 10 to 40%. A 40% reduction per pass seems to contribute greatly to the bonding process. It was found, however, that in rolling the plate below approximately 0.080 in. the great reduction per pass, combined with the lower rolling temperature, resulted in a cross-warp in the plate. The present practice is to make four passes at 40%, two at 20%, and two at 12%. Total hot reduction was varied from 89 to 93%, and total cold reduction was varied from 8 to 56%. It appears that the surface quality of the finished plate improves with increasing cold reduction. Indications are that a 30% reduction will yield a plate of satisfactory surface quality. The practice established for fabricating the fuel plates is to roll the plate as it emerges from a hydrogen muffle furnace at 1225°C, hot-roll 89%, anneal after hot-rolling, remove scale, and cold-reduce 30%. Total reduction of the finished plate is 92.5%.

After hot-rolling, the scale is removed by acid-pickling in 15% HNO_3 -5% HF -80% H_2O solution heated to 140°F. Isolated areas where scale is not removed by the acid pickle appear to be satisfactorily cleaned by wire-brushing prior to the cold reduction.

Plate dimensions have been closely checked. Core length and width are measured fluoroscopically. It was observed that the spread in core width during fabrication is related to the width of the frame. A frame with a $1\frac{1}{2}$ -in. shoulder is considered optimum and confines the core spread to approximately 0.080 in. in $2\frac{1}{4}$ in. Numerous transverse sections of several plates have been measured microscopically to determine an average value for both the clad and the core thickness; 180 clad and 90 core measurements were made on four typical stainless-steel-clad fuel plates. The average values and limits obtained are listed in Table 34. Tolerances represent maximum and minimum values actually observed.

TABLE 34. CLAD-CORE THICKNESS MEASUREMENTS OF PACKAGE REACTOR FUEL PLATES

PLATE NUMBER	CORE THICKNESS AND TOLERANCE (in.)	CLAD THICKNESS AND TOLERANCE (in.)
2	0.0205 ± 0.0015	0.0045 ± 0.00075
3	0.0190 ± 0.0010	0.0045 ± 0.0010
4	0.0210 ± 0.0010	0.0048 ± 0.0007
23	$0.0205 + 0.0015$ $- 0.0010$	$0.0045 + 0.0005$ $- 0.0010$

COMPONENT ASSEMBLY BY BRAZING

R. J. Beaver

The fuel plates have been joined by brazing, and as the assembly is similar to the MTR assembly, the same jiggling technique should be applicable. Alsimag 202, silicon carbide, alundum, JM 20, and graphite were tested for compatibility as jig materials, but only graphite appeared to be satisfactory for use at elevated temperatures in the dry hydrogen atmosphere required for brazing stainless steel. Coating of the graphite with a mixture of organic lacquer and alumina effectively prevented reaction between stainless steel and carbon during the brazing treatment.

Nicrobraz, applied in a vehicle of Nicrobraz cement, has been chosen as the braze metal until corrosion tests in progress on several potential brazing alloys indicate a better choice.

The stainless steel side plates have been machined with little difficulty. Side-plate thickness and groove depth have been varied to determine optimum groove design. Slight ridging on the outside of the plate occurred with deep cuts but was not observed when 0.020 in. was left below the finished cut. Satisfactory plates 0.050 in. thick with grooves 0.030 in. deep have been successfully machined. Distortion of the plate, which occurred during machining, was removed by press-annealing at 1150°C.

Results obtained from brazing dummy stainless steel plates into a parallel flat plate type of assembly have proved the feasibility of the technique of assembly of the plates and dummy fuel plates in position while the braze metal was applied along the side plate-fuel plate junction with an eyedropper. The Nicrobraz-cement mixture hardened

METALLURGY PROGRESS REPORT

rapidly after application, and a short time later the assembly was sufficiently rigid for removal and for placing in the graphite jig. Figure 63 illustrates the stainless steel assembly in the alumina-coated graphite jig.

Brazing of the assembly was done inside a welded stainless steel can provided with inlet and outlet tubes for constant purging of the interior of the can with dry hydrogen. A thermocouple permitted measurement of the temperature close to the assembly. The procedure employed was to purge the can at room temperature for 1 hr, place the can in a Hevi Duty furnace heated to 1200°C, and permit the assembly to heat to 1180°C. The assembly was then slow-cooled to 900°C, removed from the furnace, and cooled to room temperature. After the can was opened by sawing through the rear end of the can, the brazed assembly was removed. A typical time-temperature curve plotted during

brazing of assembly No. 3 is shown in Fig. 64. Visual and metallographic examinations have revealed the soundness of the joints, and it can be concluded that the procedure for brazing in this manner is adequate for obtaining satisfactory Microbrazed joints.

The experiments were designed primarily to determine whether or not a package reactor assembly as brazed could meet the tolerances specified for the MTR assembly. Dimensional results have been extremely encouraging. Figure 65 is a cross section of assembly No. 4. It will be observed that all but the top and bottom plates appear to be uniformly parallel. Actual measurements of the 17 plate spacings revealed that 15 of the spacings fell within the 10% tolerance established for the MTR assembly spacings. It is felt that the bow in the top and bottom plates is a result of excess heat radiation and that it can be corrected.

Fig. 63. Dummy Stainless Steel Package Reactor Fuel Assembly in Self-locking Alumina-coated Graphite Jig Prior to Brazing.

PERIOD ENDING APRIL 10, 1954

CORROSION STUDIES

R. J. Beaver

Fig. 64. Time-Temperature Data in Brazing Package Reactor Assembly No. 3.

Fig. 65. Cross-Sectional View of Representative Portion of Dummy Stainless Steel Package Reactor Assembly No. 4 After Brazing.

Some preliminary corrosion tests were conducted under simulated reactor conditions on several potential brazing alloys. These tests were designed to determine the more promising brazing alloys for use in the construction of package reactor fuel elements.

Brazing alloys of 18 different compositions were prepared and were used to braze wrought type 304LC stainless steel strip T-joints for corrosion testing. The samples were tested in an autoclave containing distilled water at a temperature of 295°C and a pressure of 1200 psi. Weight-change data and remarks on inspection after 656 hr in test are listed in Table 35.

Inspection of the 60 wt % Pd-40 Ni and the 60 Pd-37 Ni-3 Si alloys showed essentially no attack, while the 60 Ni-20 Cr-11 Si, although attacked, showed negligible weight change. After additional exposure, all samples will be sectioned and examined metallographically to permit a more reliable evaluation.

CONTROL-ROD DEVELOPMENT

J. H. Coobs

Rolling experiments were conducted to investigate the possibility of cladding a sintered mixture of 16% B_4C -84% copper with stainless steel for possible service in the absorber section of the Package Reactor control rod.

Initial attempts to prepare such a composite by hot-rolling at 1000°C were not successful. The cladding-to-core bond was rather poor and failed completely in several places along the edges when it was shear-tested. The poor results are believed to be due to a volatile impurity in the B_4C which forms a dark surface film on the stainless steel during heating prior to rolling. Another attempt will be made after the core compact is pretreated in water to remove B_2O_3 and soluble borate impurities. A 5-mil copper layer will be placed between the core and the cladding in an effort to prevent surface contamination of the stainless steel cladding.

METALLURGY PROGRESS REPORT

**TABLE 35. PRELIMINARY CORROSION DATA ON BRAZED T-JOINTS OF TYPE 304LC STAINLESS STEEL
TESTED 656 hr IN DISTILLED WATER AT 295°C AND 1200 psi**

BRAZING ALLOY COMPOSITION (wt %)	WEIGHT CHANGE (mg/sq cm)	REMARKS
100 Cu	-0.20	Attack
80 Ni-10 Cr-10 P	+0.03	Attack
70 Ni-15 Cr-5 Fe-5 Si-5 B	-0.07	Attack
69 Ni-20 Cr-11 Si	-0.01	Attack
49 Ni-28.3 Fe-11.4 Si-4.5 P-3.8 Mo-0.6 Mn-0.4 Cr	-0.02	Attack
88 Ni-4.2 Si-4.0 B-1.6 Fe	-0.97	Attack
91.3 Ni-4.5 Si-2.6 B-0.6 Fe	-0.05	Attack
91.9 Ni-3.7 Si-2.6 B	-0.07	Attack
82 Au-18 Ni	-0.02	Attack
60 Mn-40 Ni	-0.21	Attack
80 Ni-5 Cr-5 Fe-5 Si-5 B	Negligible	Attack
90 Ni-10 P	-0.11	Attack
60 Pd-40 Ni	+0.01	No attack
60 Pd-37 Ni-3 Si	Negligible	No attack
92 Cu-8 Si	-0.77	Attack
75 Ni-25 Ge	-0.08	Possible attack
68 Ni-32 Sn	-0.13	Attack
72 Ag-28 Cu	-0.42	Attack

CERAMICS RESEARCH

J. M. Warde
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S. D. Fulkerson
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PETROGRAPHIC EXAMINATION OF
FLUORIDE FUELS

Petrographic examinations of some 2000 specimens of compositions of interest to the ARE fuel program were made. The examinations included synthesized fuel compounds, quenched samples from phase studies, reduction products from loops and filtration residues and filtrates, fuel subjected to irradiation, and evaluation of purity of materials and phases in ARE fuels.

It was found from petrographic examination that the presence of moisture absorbed from the air has no observable effect on the radiation stability of ANP fuel 30.

Petrographic examinations were made of ANP fuels 30 and 44 which had been irradiated a maximum of 492 hr in the MTR. Unirradiated control samples were examined at the same time. These fuel compositions normally are composed of NaZr(U)F_5 , which is green in color, and perhaps a very small amount of a lower refractive index complex which is designated E-2. The irradiated samples were normal except for the NaZr(U)F_5 having a slightly low refractive index and being slightly reduced. There was no difference between the control samples and the irradiated samples which could be observed with a petrographic microscope.

GLASS-TYPE PUMP SEALS

Work continued on the development of a suitable, viscous, high-temperature seal for the ANP Experimental Engineering Group. Ten test rings, $2\frac{1}{2}$ -in. ID, $3\frac{1}{2}$ -in. OD, and $\frac{7}{16}$ in. thick, of a beryllium fluoride glass¹ were prepared by melting the glass batch in a platinum crucible and casting the glass in graphite dies. The rings were cooled slowly in a blanket of glass wool to minimize cracking. The finished rings were sent to the ANP group for trial. Figure 66 shows a specimen of the rings.

¹J. M. Warde et al., *Met. Semiann. Prog. Rep.* Oct. 10, 1953, ORNL-1625, p 71.

CERAMIC BEARINGS

At the request of the ANP Experimental Engineering Group, bearing shapes are being supplied in BeO and high-density graphite. The BeO shapes are being cut from excess hot-pressed ANP BeO moderator blocks by the Beryllium Machine Shop. High-density graphite bearing shapes (1.92 density) were prepared by M. Cory, consultant to the Ceramics Laboratory, and furnished to the ANP group for test.

CERAMIC CONTAINER FOR FUEL STUDIES

Work continues on the production of a suitable ceramic container for use in the investigation of the electrical resistivity of the fluoride fuels as requested by the Heat Transfer and Physical Properties Group of the ANP Division. Specimens of BeO supplied by Clifton Products Company were tested for this service and found to have a density of 2.62. This ware was not impervious to the fluoride fuel. A rod $1\frac{3}{4}$ in. in diameter $\times$ 11 in. long was prepared by isostatically pressing BeO.

Fig. 66. Specimen Ring in Vitreous Pump-Seal Development. Composition (by weight): BeF_2 , 50%; KF , 25%; MgF_2 , 16%; AlF_3 , 9%.

METALLURGY PROGRESS REPORT

powder (-325 mesh) bonded with carbowax and sintered to 1850°C and holding for 1½ hr at this temperature. Test of this rod showed that it was not impervious to the fuel. A body was prepared of the composition 48 moles BeO, 1 mole Al₂O₃, 1 mole ZrO₂, derived by National Bureau of Standards for dense BeO work. The body was made up into a small, ¾-in.-ID × 4-in.-high crucible by slip-casting and firing to 1850°C and holding for 1½ hr at this temperature. Again the ware was not impervious to the fluoride. Further work with the use of minor additions of CaF₂ and other materials is in progress.

BORON CARBIDE-IRON CERMETS

Six boron carbide-iron (30-70) disks, ¾ × 6½ in. in diameter, were prepared by hot-pressing (1025°C and 1750 psi) for the Solid State Division. Final density of the ware was 3.56. These disks are required for shielding in connection with in-pile loop studies of ANP fuels.

RARE-EARTH CERAMICS

It has been found that Sm₂O₃ produces well-sintered and strong ceramic bodies when it is first calcined at about 1500°C, then pressed into shape and refired at 1500°C. Densities thus obtained were 99% theoretical (given as 7.43) and the bodies were nearly impervious (porosity = 0.5%).

The Sm₂O₃ as received was anisotropic, probably hexagonal; the form is given as cubic in the literature. The thermal expansion coefficient was established at 9.3×10^{-6} in./in./°C. No change in structure was shown to 1130°C by thermal expansion on differential thermal analysis; the reported change above 1150°C has been tentatively verified by x ray.

The fact that samarium oxide ceramics react with boiling water disqualifies them for some applications. Reaction with BeO ceramics was noted at about 1520°C and with alumina at about 1600°C.

Gadolinium oxide (mol wt = 351.8) has a slightly lower melting point (1950 ± 20°C) than Sm₂O₃ (mol wt = 348.8) (mp 2300 ± 20°C as previously reported); it fires into well-sintered ceramics provided the powder as received is precalcined at 1350 to 1500°C. The density, 7.51, of the fired bodies was higher than the reported theoretical density of 7.41, which may be accounted for by the presence of 2% of terbium in the Gd₂O₃.

The thermal expansion coefficient of the Gd₂O₃ ceramics was 10.3×10^{-6} in./in./°C. The cubic form was stable to 1000°C according to the thermal expansion behavior and the differential thermal analysis; this coincides with its behavior as reported in the literature.

Gadolinium oxide ceramics (unlike Sm₂O₃) were found to be stable toward boiling water. Their machining properties were very good.

Al-UO₂ CERMETS

A specimen of Al-UO₂ cermet was fabricated in the form of a rod 1.1 in. in diameter and 4 in. long by isostatic pressing as part of a fabrication study in connection with "J" slug development.

ThO₂ INVESTIGATIONS

Thoria pellets in the form of small cylinders, ⅛ in. in diameter × ⅛ in. in height, have been fabricated for the HRP. These cylinders will be tested for abrasion resistance in contact with both themselves and with stainless steel and zirconia. The abrasive tests will be carried out in moving water to simulate conditions expected in the proposed breeder blanket.

A 1.1-in.-dia × 4-in.-long thoria rod containing 1 mole % CaO was prepared by isostatic pressing and sintering to 1850°C and holding at this maximum temperature 1½ hr. Final density of the rod was 95% of theoretical. This rod will be canned in alumina and sent to the Solid State Division for radiation stability tests.

CERAMIC COATINGS

Especially prepared enamel high in boron and lead was applied to a plate approximately 55 to 60 in. in diameter. The plate was sent to the Reactor Shielding Group for test. Ceramic coating A-418 was applied to Inconel. These coated specimens are to be used in creep experiments. Specimens of type 309 stainless steel were also coated with the A-418 enamel. These specimens will be supplied to the HRP for corrosion tests.

HIGH-DENSITY GRAPHITE

Specimens of high-density graphite (Graph-i-tite) supplied by Graphite Specialties Corporation were sent to the Metallurgy Division's Corrosion Group for compatibility tests with the fluorides and other molten salts and molten metals. Typical properties of the Graph-i-tite as given by the manufacturer

are as follows:

Apparent density, g/cc	1.85 to 1.92
Transverse breaking strength, psi	4000 to 4500
Modulus of elasticity, lb/sq in./in./in.	20×10^5 to 25×10^5
Electrical resistance, ohm-in.	0.00032 to 0.00040
Permeability	
1.85 density	Impermeable to water at 40 psi, room temperature, 10 min minimum
1.92 density	Impermeable to air at 40 psi, room temperature, 10 min minimum

A model of a core design, suggested by Fraas of the ANP Division for the Reflector-Moderated Reactor, was prepared in high-density graphite, 1.85 to 1.92 (Fig. 67), by Graphite Specialties Corporation for the Ceramics Laboratory.

HIGH-DENSITY K_3CrF_6 RODS

A near-theoretical-density (96% of theoretical) rod of K_3CrF_6 was prepared by isostatic pressing. This rod is intended for use in conductivity measurements by ANP.

Fig. 67. Model of a Core Design Made from High-Density Graphite. (a) Side view. (b) Top view.

FUNDAMENTAL PHYSIOMETALLURGICAL RESEARCH

L. K. Jetter

METHODS OF REPRESENTING PREFERRED ORIENTATION DATA

L. K. Jetter

W. C. McHargue

It was pointed out previously¹ that quantitative study of the fiber-texture type of preferred orientation requires precise information on the orientation distribution of the fiber axis with respect to the crystallographic axes of the grains. Such information denotes specifically the most preferred crystallographic direction of the fiber axis for each component of the texture, the symmetry of the orientation distribution about these preferred directions, and the relative volumes of material associated with the various components.

For good delineation of a fiber texture, then, it is necessary that the orientation distribution of the diffracting-plane poles with respect to the fiber axis, as given by the pole figure, be converted into the orientation distribution of the fiber axis on a standard stereographic projection.

It was proposed that the "density of poles" is related to the "density of fiber axes" by the

following expression:

$$(1) \quad R(\phi) = \frac{\int_0^{\beta_{\max}} T(\phi, \beta) d\beta}{\beta_{\max}} = \bar{T}(\phi),$$

where $R(\phi)$ is the normalized diffraction intensity from planes of a form $\{hkl\}$ as a function of ϕ , the angle between the fiber axis and the diffracting-plane poles, and is equal to the normalized pole density; $T(\phi, \beta)$ is the normalized axis density as a function of ϕ and β , the angle between the fiber axis and some arbitrary zero point along the path through the unit stereographic triangle traced out by the locus of points ϕ degrees from the diffracting-plane poles (see Fig. 71); and $\bar{T}(\phi)$ is the average value of T along this angular path of total length $\beta_{\max}$.

$$(2) \quad R(\phi) = \frac{I(\phi)}{I_{\text{ren}}}$$

and

$$(3) \quad T(\phi, \beta) = \frac{S(\phi, \beta)}{S_{\text{ren}}},$$

where $I(\phi)$ is the diffraction intensity from planes

¹L. K. Jetter, *Met. Semiann. Prog. Rep.* April 10, 1953, ORNL-1551, p 6.

METALLURGY PROGRESS REPORT

of the form $\{hkl\}$, corrected for any change in diffraction geometry with specimen orientation, and is proportional to the volume fraction per unit solid angle having the designated angular relationship between the fiber axis and the diffracting plane poles; and $S(\phi, \beta)$ is the volume fraction per unit solid angle having the designated angular relationship between the fiber axis and the crystallographic axes.

Furthermore,

$$(4) \quad I_{ran} = \int_0^{\pi/2} I(\phi) \sin \phi \, d\phi ,$$

$$(5) \quad S_{ran} = \frac{N}{4\pi} ,$$

and

$$(6) \quad \beta_{max} = 2\pi \frac{p}{N} \sin \phi ,$$

where N is the maximum multiplicity for the crystal system and p is the multiplicity of the diffracting planes $\{hkl\}$.

These relationships were derived for an ideal fiber texture and, consequently, require for experi-

mental confirmation the examination of a sample having a homogeneous and ideal fiber texture. Such conditions might be expected to prevail in the center of an extruded rod. To confirm this, an 0.89-in.-dia aluminum rod was extruded from a 3.125-in.-dia ingot (extrusion ratio 12.3) at a temperature of 450°F and a speed of 0.1 fpm. The extruded rod was water-quenched at the die to retain the as-deformed structure.

On a 0.19-in. spherical specimen taken from the center of the rod, pole distribution data were obtained by the spectrometric method described previously.^{2,3} Since these earlier reports, however, the goniometer supporting the specimen has been modified for use with the Norelco Type 42202 high-angle G-M spectrometer. Figures 72 to 74 show the new arrangement.

The pole distribution charts (R vs ϕ) for a number of the diffracting planes are given in Figs. 75 to 79. They were obtained by applying Eqs. 2 and 4 to the diffraction data I vs ϕ ; the values of I_{ran} were obtained by graphical integration of the function $I \sin \phi$ from $\phi = 0$ to 90 deg for the various $\{hkl\}$'s (see Table 39).

The axis distribution chart (T vs ϕ, β) deduced from these pole distributions is given in Fig. 80. On this chart the contours indicate angular locations of equal normalized axis density T . Exact values of T for locations corresponding to the poles of the diffracting planes were obtained directly, that is, $T(\phi = 0) = R(\phi = 0)$ (see Table 39). The values of T for other locations were assigned after careful inspection of the pole distribution charts. The over-all axis distribution was then checked by applying Eq. 1 to determine how well it reproduced the pole distributions. The reproducibility is shown in Figs. 75 to 79. The angular path through the unit triangle along which T was averaged to obtain $R(\phi = 66 \text{ deg})$ for the $\{111\}$ is illustrated in Fig. 81.

The axis distribution chart shows the most preferred crystallographic directions of the fiber axis to be the $\langle 111 \rangle$ and the $\langle 100 \rangle$. The axis density at first falls off rapidly and symmetrically from the peaks at these locations but then asymmetrically

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Fig. 71. Standard Stereographic Projection on a Unit Triangle Showing an Angular Path β from 0 to β_{max} . In this projection, $\{hkl\}$ is $\{110\}$ and $\phi = 50$ deg.

²L. K. Jetter, *Met. Quar. Prog. Rep.* Jan. 31, 1952, ORNL-1267, p 21.

³L. K. Jetter and B. S. Borie, Jr., "A Method for the Quantitative Determination of Preferred Orientation in Metals," *Proceedings of the Spring Metallurgy Conference*, March 24-26, 1952, Vol. 2, TID-5084 (June 1952), p 529.

Fig. 72. Left, Front, Closeup View of Fiber Texture Goniometer.

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Fig. 73. Right, Front, Closeup View of Fiber Texture Goniometer.

Fig. 74. Left View of Fiber Texture Goniometer and Diffraction Specimen Mounted on High-Angle X-Ray Spectrometer.

METALLURGY PROGRESS REPORT

Fig. 75. Pole Distribution Chart {111} for 0.89-in.-dia As-extruded Aluminum Rod (Specimen 118).

Fig. 77. Pole Distribution Chart {222} for 0.89-in.-dia As-extruded Aluminum Rod (Specimen 118).

Fig. 76. Pole Distribution Chart {311} for 0.89-in.-dia As-extruded Aluminum Rod (Specimen 118).

Fig. 78. Pole Distribution Chart {400} for 0.89-in.-dia As-extruded Aluminum Rod (Specimen 118).

to form a "saddle" along the [110] zone. This is indicated by the finite value of $R(\phi = 0 \text{ deg})$ for the {311} pole distribution chart and is shown very clearly in the axis distribution chart.

Table 40 gives the volume fraction of each of the two components computed from the relation

$$(7) \quad F_c = \frac{p}{2p_c} \frac{\int_{\phi_1}^{\phi_2} I(\phi) \sin \phi d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi d\phi},$$

where $\phi_1 - \phi_2$ is the separable range of the function $I \sin \phi$ attributable to one component only, and p/p_c is the fraction of the total multiplicity associated with this range.

The results show the volume fraction of the $\langle 111 \rangle$ and $\langle 100 \rangle$ components to be 0.475 and 0.525, respectively; the ratio $\langle 111 \rangle / \langle 100 \rangle$ is 0.90.

For diffracting planes where no separable range of the function $I \sin \phi$ could be attributed to one component only, a comparison was made of the

METALLURGY PROGRESS REPORT

and calculated from

$$(9) \quad \frac{2}{p} (p_{c_1} F_{c_1} + p_{c_2} F_{c_2}) ,$$

assuming $F_{c_1} = 0.475$ and $F_{c_2} = 0.525$. The comparisons for the various diffracting planes are shown in Table 41.

The remarkable consistency of these data for the various diffracting planes over the range of ϕ from 0 to 90 deg, which corresponds to a distance of 0.09 in. from the center of the extruded rod, proves that the sample had a homogeneous, ideal fiber texture and experimentally confirms the mathematical relationships previously derived for this type of preferred orientation.

FUNDAMENTAL STUDIES OF ALLOYING

J. O. Betterton, Jr.

The Group IVA elements, titanium, zirconium, and hafnium, are transition elements in that part of the Periodic Table where a relatively small number of d electrons are present in the valency electron distribution and where the properties of these ele-

ments in the metallic state are intermediate between those of the alkaline-earth metals and the iron or platinum group transition elements in which d electrons are more numerous. Within the approximation by which ionic radius can be used in considering solid metals, these metals have smaller underlying inner electron shells and therefore are more "open" than later members of the transition group and metals such as copper, silver, and gold. This may be one reason why intermediate phases are favored at the expense of extensive solid terminal solutions in such A-Group metals. Another reason may be that these elements are in such a position on the Periodic Table that there is likely to be an important electrochemical difference between the solvent and most of the solutes which would be alloyed. This factor would favor the formation of ordered types of intermediate phases at the expense of terminal solid solutions. In spite of these inherent restrictions on the solid solutions of Group IVA elements, the alloying of these metals is of considerable importance. For instance, the aqueous corrosion resistance is very good, and when this is combined with the low neutron cross sections of titanium and zirconium, the combination makes the two elements attractive reactor materials.

The investigation has started with additions of B-subgroup elements, silver, cadmium, indium, tin, and antimony, to zirconium. Since these B-subgroup elements are of nearly the same atomic size as zirconium and since their metallic valencies are known, the addition to zirconium should show the effect of valency. In addition, the allotropic change of crystal structure in zirconium permits the effect of these alloying elements to be compared in both types of crystal structure.

Factors Affecting the α/β Boundaries

J. H. Frye, Jr.

J. O. Betterton, Jr.

As a first approximation, the assumption is made that the equilibrium between the two allotropic metallic phases, as represented, for example, by the α/β phase boundaries in Group IVA elements, depends solely on the changes in electronic energy at 0°K and that the relative changes in free energy between the two forms, with equal additions of solute elements, are not a function of temperature. This is equivalent to saying that the alloying additions are assumed, in approximation, to shift the free energy vs temperature curves of the two crystal forms to the same extent at 0°K as at the

Fig. 81. Standard Stereographic Projection on a Unit Triangle Showing the Angular Path β for Diffracting Plane $\{111\}$ and $\phi = 66$ deg as Shown in Fig. 80. This is the path over which T is averaged to obtain R ($\phi = 66$ deg).

TABLE 40. COMPUTATION OF THE VOLUME FRACTION F_c FOR EACH COMPONENT

COMPONENT. $\langle uvw \rangle \rightarrow$			$\langle 111 \rangle$				$\langle 100 \rangle$					TOTAL AREA $A_{c_1} + A_{c_2}$	$\langle 111 \rangle / \langle 100 \rangle$
Diffracting Plane $\{hkl\}$	Plane Multiplicity $p\{hkl\}$	Angle ϕ	Component Multiplicity p_{c_1}	Component Area A_{c_1}	Unit Area A_{c_1}/p_{c_1}	Component Fraction F_{c_1}	Angle ϕ	Component Multiplicity p_{c_2}	Component Area A_{c_2}	Unit Area A_{c_2}/p_{c_2}	Component Fraction F_{c_2}		
{111}	8	0° 0'	1	493.70	493.70	0.476	54° 44'	4	2189.56	547.39	0.528	2683.26	0.90
		70° 32'	3	1465.71	488.57	0.471		—	—	—	—	1465.71	0.89
		—	4	1959.41	489.85	0.472		4	2189.56	547.39	0.528	4148.97	0.89
{200}	6	54° 44'	3	1387.61	462.54	0.476*	0° 0'	1	506.30	506.30	0.524*	1893.91	0.91
			—	—	—	90° 0'	2	—	—	—	—	—	—
			3	1387.61	462.54	—	3	—	—	—	—	—	—
{220}	12	35° 16'	3	728.88	242.96	0.471*	45° 0'	4	1086.47	271.62	0.529*	1815.35	0.89
		90° 0'	3	—	—	—	90° 0'	2	—	—	—	—	—
		—	6	—	—	—	6	—	—	—	—	—	—
{222}	8	0° 0'	1	152.63	152.63	0.499	54° 44'	4	648.96	162.24	0.530	801.59	0.94
		70° 32'	3	422.88	140.96	0.460		—	—	—	—	422.88	0.87
		—	4	575.51	143.88	0.470		4	648.96	162.24	0.530	1224.47	0.89
{400}	6	54° 44'	3	410.16	136.72	0.484	0° 0'	1	140.21	140.21	0.496	550.37	0.98
			—	—	—	90° 0'	2	297.36	148.68	0.526	297.36	0.92	
			3	410.16	136.72	0.484	3	437.57	145.86	0.516	847.73	0.94	
						$A_v = 0.475$						$A_v = 0.525$	$A_v = 0.90$

*Computed from the $\langle 111 \rangle / \langle 100 \rangle$.

PERIOD ENDING APRIL 10, 1954

METALLURGY PROGRESS REPORT

TABLE 41. COMPARISON OF VARIOUS DIFFRACTING PLANES

DIFFRACTING PLANE $\{hkl\}$	ANGLE ϕ	COMPONENT $\langle uvw \rangle$	COMPONENT MULTIPLICITY p_c	AREA		RELATIVE AREA		
				Calculated $p_c F_c$	Experimental $\int_c^{\phi_2} I \sin \phi \, d\phi$	Calculated $2A/p$	Experimental A/A_t	
{111}	0° 0'	$\langle 111 \rangle$	1	$1 \times 0.475 = 0.475$	493.70	0.119	0.119	
	54° 44'	$\langle 100 \rangle$	4	$4 \times 0.525 = 2.100$	2189.56	0.525	0.528	
	70° 32'	$\langle 111 \rangle$	3	$3 \times 0.475 = 1.425$	1465.71	0.356	0.353	
			8	4.000	4148.97	1.000	1.000	
{200}	0° 0'	$\langle 100 \rangle$	1	$1 \times 0.525 = 0.525$	506.30	0.269	0.267	
	54° 44'	$\langle 111 \rangle$	3	$3 \times 0.475 = 1.425$	1387.61	0.731	0.733	
	90° 0'	$\langle 100 \rangle$	2	$2 \times 0.525 = (1.050)$				
			6	(3.000)	1893.91	1.000	1.000	
{220}	35° 16'	$\langle 111 \rangle$	3	$3 \times 0.475 = 1.425$	728.88	0.404	0.402	
	45° 0'	$\langle 100 \rangle$	4	$4 \times 0.525 = 2.100$	1086.47	0.596	0.598	
	90° 0'	$\langle 111 \rangle$	3	3×0.475				
		$\langle 100 \rangle$	2	2×0.525	(2.475)			
		12	(6.000)	1815.35	1.000	1.000		
{311}	25° 14'	$\langle 100 \rangle$	4	4×0.525				
	29° 30'	$\langle 111 \rangle$	3	3×0.475	3.525	1277.90	0.294	0.272
	58° 31'	$\langle 111 \rangle$	6	6×0.475				
	72° 27'	$\langle 100 \rangle$	8	8×0.525	8.475	3423.96	0.706	0.728
	79° 58'	$\langle 111 \rangle$	3	3×0.475				
			24	12.000	4701.86	1.000	1.000	
{222}	0° 0'	$\langle 111 \rangle$	1	$1 \times 0.475 = 0.475$	152.63	0.119	0.125	
	54° 55'	$\langle 100 \rangle$	4	$4 \times 0.525 = 2.100$	648.96	0.525	0.530	
	70° 32'	$\langle 111 \rangle$	3	$3 \times 0.475 = 1.425$	422.88	0.356	0.345	
			8	4.000	1224.47	1.000	1.000	
{400}	0° 0'	$\langle 100 \rangle$	1	$1 \times 0.525 = 0.525$	140.21	0.175	0.165	
	54° 44'	$\langle 111 \rangle$	3	$3 \times 0.475 = 1.425$	410.16	0.475	0.484	
	90° 0'	$\langle 100 \rangle$	2	$2 \times 0.525 = 1.050$	297.36	0.350	0.351	
			6	3.000	847.73	1.000	1.000	
{381}	22° 0'	$\langle 111 \rangle$	3	$3 \times 0.475 = 1.425$	341.25	0.119	0.119	
	46° 30'	$\langle 100 \rangle$	8	8×0.525				
	48° 32'	$\langle 111 \rangle$	3	3×0.475	5.625	1316.47	0.469	0.457
	76° 44'	$\langle 100 \rangle$	4	4×0.525				
	82° 23'	$\langle 111 \rangle$	6	6×0.475	4.950	1222.27	0.412	0.424
			24	12.000	2879.99	1.000	1.000	
{420}	26° 34'	$\langle 100 \rangle$	4	4×0.525				
	39° 14'	$\langle 111 \rangle$	6	6×0.475	4.950	1233.20	0.413	0.406
	63° 26'	$\langle 100 \rangle$	4	4×0.525				
	75° 2'	$\langle 111 \rangle$	6	6×0.475	7.050	1801.32	0.587	0.594
	90° 0'	$\langle 100 \rangle$	4	4×0.525				
		24	12.000	3034.52	1.000	1.000		

TABLE 41. (continued)

DIFFRACTING PLANE $\{hkl\}$	ANGLE ϕ	COMPONENT $\langle uvw \rangle$	COMPONENT MULTIPLICITY p_c	AREA		RELATIVE AREA			
				Calculated $p_c F_c$	Experimental $\int_{\phi_1}^{\phi_2} I \sin \phi \, d\phi$	Calculated $2A/p$	Experimental A/A_t		
{422}	19° 28'	<111>	3	3 × 0.475	3.525	1085.67	0.294	0.293	
	35° 16'	<100>	4	4 × 0.525					
	61° 52'	<111>	6	6 × 0.475	8.475	2625.74	0.706	0.707	
	65° 54'	<100>	8	8 × 0.525					
	90° 0'	<111>	3	3 × 0.475					
			<u>24</u>		<u>12.000</u>		<u>3711.41</u>	<u>1.000</u>	<u>1.000</u>

temperatures near the α/β boundaries and involve the assumption that the difference in specific heats does not depend upon solute concentration. At the allotropic transition temperature for pure zirconium, $F_\alpha = F_\beta$, where F_α is the free energy of the alpha, hexagonal phase and F_β is the free energy of the beta, cubic phase. In order to avoid difficulties of having to treat the actual phase boundaries of the $(\alpha + \beta)$ region in the alloys, the following treatment will be restricted to a hypothetical intersection of the free energy vs temperature curves for the two phases, which, by the graphical construction shown in Fig. 82, should always lie within the two-phase region. The differential equation given below is then obtained for conditions at the intersection.

$$dF_\alpha = dF_\beta,$$

$$\left(\frac{\partial F_\alpha}{\partial T}\right) dT + \left(\frac{\partial F_\alpha}{\partial N}\right) dN = \left(\frac{\partial F_\beta}{\partial T}\right) dT + \left(\frac{\partial F_\beta}{\partial N}\right) dN,$$

$$\left(\frac{\partial F_\alpha}{\partial T} - \frac{\partial F_\beta}{\partial T}\right) dT = \left(\frac{\partial F_\beta}{\partial N} - \frac{\partial F_\alpha}{\partial N}\right) dN.$$

In the above expressions the symbol N refers to the electron concentration.

The entropy change in the $\alpha \rightarrow \beta$ transition in pure zirconium is about 0.624 cal/deg/mole, or 0.000027 ev/deg/atom. The term

$$\left(\frac{\partial F_\alpha}{\partial T} - \frac{\partial F_\beta}{\partial T}\right)_N$$

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Fig. 82. Hypothetical Free-Energy Curves for Isothermal Equilibrium Between Two Phases. Note that the point of intersection of the two curves is intermediate in composition to the two common tangency points.

is evaluated approximately by this means, and on the basis of the assumptions which were made about the effects of temperature on the relative energies of the two phases,

$$\left(\frac{\partial E_\beta}{\partial N} - \frac{\partial E_\alpha}{\partial N}\right)$$

is substituted for

$$\left(\frac{\partial F_\beta}{\partial N} - \frac{\partial F_\alpha}{\partial N}\right),$$

METALLURGY PROGRESS REPORT

where E is the energy of the electron at 0°K. Thus

$$0.000027 \frac{dT}{dN} = \left(\frac{\partial E_{\beta}}{\partial N} - \frac{\partial E_{\alpha}}{\partial N} \right)$$

Measurement of the low-temperature specific heat of the hexagonal form of pure zirconium gives a value for $N(E_{\max})_{\alpha}$ of 0.615 levels/ev/atom, or 1.23 electrons/ev/atom.⁴ Hence

$$\begin{aligned} \frac{1}{N(E_{\max})_{\alpha}} &= \frac{dE_{\alpha}}{dN} \\ &= \frac{1}{1.23} = 0.813 \text{ ev/atom/electron} \end{aligned}$$

Substituting this value in the equation results in

$$0.000027 \frac{dT}{dN} = \left(\frac{\partial E_{\beta}}{\partial N} - 0.813 \right),$$

and if the density of states of beta zirconium were known, the change of the temperature of the intersection of the two free energy curves as a function of addition or subtraction of electrons could be calculated. For example, if $N(E_{\max})_{\beta}$ were smaller than $N(E_{\max})_{\alpha}$, as might be presumed from the tendency for metals with higher $N(E)$ to be more stable at low temperatures, then dT/dN would be positive; this crude calculation then indicates that the α/β boundaries would rise with increases in electron concentration. On the other hand, a value for dT/dN may be estimated experimentally from the zirconium and titanium phase diagrams by the following procedure. First, it is observed that alloying elements to the right of Group IIB generally result in rising α/β boundaries, whereas those to the left of Group IIB result in falling α/β boundaries. The valency of titanium and zirconium is therefore estimated as being equal to cadmium — for this example taken as 2 — although it is not essential to the discussion to assign any definite value to either metal but only to assign differences in valency. Next, in each phase diagram a point half way between the two phase boundaries [$\alpha/(\alpha + \beta)$] and [$\beta/(\alpha + \beta)$] is arbitrarily selected, and composition of this point is expressed in terms of electron concentration by taking the following values for the element valencies: Cu and Ag, 1;

In and Al, 3; Sn and Pb, 4; Sb, 5; Zr and Ti, 2. The resulting plot (Fig. 83) shows the variation of the mean points of the ($\alpha + \beta$) region vs electron concentration, and the value for dT/dN estimated from this figure is 1300 deg/electron.

Fig. 83. Dependence of α/β Boundaries of Titanium and Zirconium Alloys upon Electron Concentration.

When this value is substituted in the above equation, a value for $\partial E_{\beta}/\partial N$ of 0.85 ev/atom/electron or for $N(E_{\max})_{\beta}$ of 1.18 electrons/ev/atom is obtained. This approximate calculation therefore indicates that the density of states of beta zirconium would have to be only slightly smaller than that in alpha zirconium to account for the phase boundaries at elevated temperatures.

Experiments on the low-temperature specific heat of a retained beta, or body-centered-cubic zirconium, should be carried out as soon as a satisfactory series of retained beta alloys can be prepared. This experiment would be of interest not only in testing the approximations above but also in considering the choice of valency scheme for these metals, since for most parts of the treatment the Pauling scheme of valencies could be used with equally satisfactory results if the $N(E_{\max})_{\beta}$ is chosen larger than the $N(E_{\max})_{\alpha}$.

EXPERIMENTAL INVESTIGATION OF PURE ZIRCONIUM

The $\alpha \rightarrow \beta$ Transition Temperature

G. W. Cunningham J. O. Betterton, Jr.

Zwicker⁵ first concluded from resistivity-temperature measurements that an allotropic transition

⁴I. Estermann, S. A. Friedberg, and J. E. Goldman, *Phys. Rev.* 87, 582 (1952).

⁵C. Zwicker, *Physica* 6, 361 (1926).

existed in zirconium. The temperature of this transition was reinvestigated by Vogel and Tonn,⁶ and the value of $862 \pm 5^\circ\text{C}$ is the one generally used in the literature. Vogel and Tonn made a thermal and dilatometric analysis of iodide-decomposition zirconium supplied by deBoer. The critical experiments from which the 862°C value was obtained were cooling curves determined by using thermal analyses specimens of 12 g run at the rate of $60^\circ\text{C}/\text{min}$, which is high for this type of work. Vogel and Tonn did not include heating-curve results in this value; so the temperature, 862°C , may be expected to be somewhat lower than the true equilibrium point. This temperature, however, was substantiated by deBoer, Clausing, and Fast,⁷ who found a transition temperature of $865 \pm 10^\circ\text{C}$ by the electrical resistivity method in which optical pyrometer temperature readings were used.

More recently, McGeary⁸ has made a dilatometric study of iodide-decomposition zirconium. McGeary found, as did Vogel and Tonn, that the transition took place over a 35 to 75°C range of temperature rather than at one single temperature. Since McGeary found no significant effect of 1.58% hafnium impurity in his zirconium, a typical curve from grade 1 material of this type will be used as an example of his results. During heating, the transition contraction began gradually at 863°C , occurred more rapidly in the interval 880 to 890°C , and finally stopped at 903°C with the resumption of normal thermal expansion. During cooling, the transition expansion of the same specimen began gradually at 887°C , occurred at a maximum rate in the range 877 to 866°C , and then finally stopped at 853°C with the resumption of normal thermal contraction. McGeary did not choose a single temperature as the $\alpha \rightarrow \beta$ point, but if the point where the major part of the transition begins is arbitrarily taken as the significant one for purposes of averaging, the mean of these points in heating and cooling would be about 878°C for the above example. Other specimens were similar, and it is clear that

in this zirconium the transition occurs at a somewhat higher temperature than 862°C .

At Oak Ridge National Laboratory, the zirconium transition temperature was investigated by means of thermal analysis in an argon-filled, silica capsule. A cylindrical specimen of iodide-decomposition zirconium, weighing 30 to 40 g, and with a hole drilled into the center, was homogenized at 800°C for one week. It was then vacuum-degassed at about 800°C in a silica capsule before being sealed off. The thermal analysis capsule was provided with a thermocouple sheath leading to the interior of the sample. The silica sheath was of about $\frac{1}{2}$ -mm wall thickness and 3-mm OD and a calibrated, Pt-Pt + 10% Rh thermocouple could be moved inside this sheath during the experiments to test for temperature gradients. The variation of the calibration of the thermocouple used in the experiments over the period of time concerned is shown in Fig. 84, and by interpolations between these curves, the temperature reading at any particular time could be corrected. The same Rubicon type B potentiometer and the same furnace were used for the calibrations as for the thermal analysis, and it is estimated that temperatures were measured to an accuracy of $\pm 0.25^\circ\text{C}$.

The determination was based on four different batches of grade 1, iodide zirconium supplied by the Foote Mineral Company. The analysis of this zirconium is given in Table 42 before and after the thermal analysis. The results are given in terms of atomic percentage of solute in order to emphasize the importance of the lighter elements as impurities. Hydrogen, for example, when present to the extent of 10 ppm by mass ratio becomes about 900 ppm by atom ratio. The analyses were by spectroscopic means, except for carbon, oxygen, nitrogen, and hydrogen, which were done by direct combustion and vacuum fusion analyses. The principal impurities in this zirconium were hydrogen, carbon, oxygen, and iron.

The ranges of temperature over which the $\alpha \rightarrow \beta$ thermal arrest occurred for each of these batches are given in Table 43, and some typical curves for two batches are shown in Fig. 85. As will be observed in this figure, the heating and cooling rates varied between $\frac{1}{2}$ and $2^\circ\text{C}/\text{min}$, and the arrests took place over a range of temperatures. The best arrests were found in cooling curves, which, in three cases, showed supercooling and an actual plateau of constant temperature. The numbers 1, 2, 3, and 4 in Fig. 85 refer to the first

⁶R. Vogel and W. Tonn, *Z. anorg. Chem.* 202, 262 (1931).

⁷J. H. deBoer, P. Clausing, and J. D. Fast, *Rec. trav. chim.* 55, 450 (1936).

⁸R. K. McGeary, "Dilatometric Investigation of Zirconium, Zirconium-Uranium, Zirconium-Oxygen, and Zirconium-Nitrogen Alloys," *Proceedings of the Metallurgy and Materials Information Meeting, April 16-18, 1951, TID-5061 (Jan. 1, 1952), p. 419.*

Fig. 84. Calibration Curves of Platinum-Platinum + 10% Rhodium Thermocouple.

inflection point, the beginning of the region of minimum rate, the end of the region of minimum rate, and the end of the arrest, respectively. The temperatures corresponding to these points are given in Table 43.

Two methods of controlling the furnace power were used. In the first experiments the simple method of adjusting the furnace variac to give a slow heating and cooling rate was used. In later experiments the method described by Smith⁹ was adopted, and a small temperature difference between the specimen and a surrounding heat conductor (of Inconel or Inconel-jacketed copper) was maintained constant by a controller. An improvement in the magnitude of the arrest was observed with the latter method, as shown in Fig. 85, and the end of the reaction could be observed because the rapid change of temperature immediately following an arrest is eliminated.

A schematic diagram, Fig. 86, has been drawn to show that the major portion of each arrest occurs above and below a single temperature, represented

by the horizontal lines in this figure. It is apparent that this part of the arrest, chosen by graphical inspection as the region of minimum rate of change, agrees with the hysteresis effects which might be expected in ordinary rate phenomenon in heating and cooling. The gradual rounding of the curves before and after the arrests, indicated by the dotted lines in Fig. 86, is different in that these effects occur at higher temperatures in cooling than they do in heating. They are presumed to be an effect of impurities¹⁰ and have not been considered in averaging the results of the experiments. Rather, the major part of the arrest, or the region of minimum rate of change given in Table 43, has been considered. The principal impurities in this zirconium, as discussed earlier, are hydrogen, oxygen, carbon, and iron. The variation of the temperature as indicated by the horizontal lines in Fig. 86 suggests that impurities may also affect the major part of the arrest.

¹⁰The temperature gradients found in the specimens during the experiments were 0.1 to 0.4°C/cm, and this effect could hardly explain the rounding of the curves observed.

⁹C. S. Smith, *Metals Technol.* 6, T.P. 1073 (1939).

TABLE 42. ANALYSIS OF CRYSTAL-BAR ZIRCONIUM USED IN THERMAL ANALYSIS OF $\alpha \rightarrow \beta$ TRANSITION

Values in atomic percentage of solute

ELEMENT	BATCH NO. 1		BATCH NO. 2		BATCH NO. 3			BATCH NO. 4	
	Before	After	Before	After	Before	After		Before	After
						Specimen 1	Specimen 2		
Al	0.010	0.007	0.010	0.006	0.010	0.006	0.008	0.016	0.012
Ca	0.002	0.003	<0.001	0.002	0.005	0.003	0.003	0.002	0.002
Cr	0.007	0.002	0.006	0.002	0.004	0.003	0.001	0.002	0.001
Cu	0.004	0.006	0.002	0.010	0.002	0.004	0.003	0.003	0.003
Fe	0.09	0.13	0.06	0.11	0.03	0.03	0.03	0.065	0.057
K	0.003	0.003	<0.002	0.005	0.009	0.002	0.003	0.007	0.001
Mg	<0.001	0.002	<0.001	0.003	0.002	0.004	0.002	0.002	0.001
Ni	0.02	0.02	0.003	0.009	0.006	0.004	0.006	0.004	0.004
Ti	0.004	0.002	<0.001	<0.001	0.001	<0.001	<0.001	0.001	<0.001
Hf	0.005	0.004		0.006	0.010	0.008	0.005	0.009	0.005
C		0.175		0.224	0.13	0.09	0.18	0.14	0.21
O	0.05	0.10	0.02	0.09	0.02	0.03	0.02	0.015	0.005
N	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007
H	0.13	0.27	0.18	0.31	0.46	0.10	0.45	0.155	0.158
Vickers hardness	86	90	76	85	59	67	75	73	57

Figure 87 is a plot which is intended to show the effects of two of the impurities, hydrogen and oxygen, and the result is in agreement with what might be expected from the phase diagrams Zr-H and Zr-O. An attempt could be made to also correct for the carbon and iron impurities on the same basis, and the phase-diagram information which is available indicates that they might be expected to approximately cancel one another. Assuming that this is true, only oxygen and hydrogen need be considered, and an approximately extrapolated value to zero hydrogen and zero oxygen from Fig. 87 would give $870 \pm 3^\circ\text{C}$ for the $\alpha \rightarrow \beta$ transition in zirconium. A direct average of the results in column 2 of Table 43 without regard for impurities gives 867.5°C , which is within the range chosen above.

Annealing of Pure Zirconium

D. S. Easton

J. O. Betterton, Jr.

The investigation of the effects of annealing pure zirconium in silica capsules was continued by determining the effect of breaking the hot capsule under water and of heat-treating for three days at 1200°C . It had been observed previously in high-temperature annealing of zirconium alloys that crushing the silica capsule to obtain a fast cooling rate resulted in the development of a thin, black film on the alloy. Further, zirconium annealed at 1011°C for four days in a protective zirconium foil gave a Vickers hardness number of 96.5 when the capsule was crushed in water and of 79.5 when the capsule was cooled unbroken under the water, the starting hardness in each case being 83. An

METALLURGY PROGRESS REPORT

TABLE 43. RESULTS OF THERMAL ANALYSIS OF DIFFERENT BATCHES OF CRYSTAL-BAR ZIRCONIUM

SPECIMEN IDENTIFICATION	TEMPERATURE (°C)			DURATION (min)	
	First Inflection Point ^a	Range of Minimum Rate of Change			End of Arrest ^d
		Beginning ^b	End ^c		
Batch No. 1					
Cooling 1 ^e	872.3	869.1	867.3	8	
Cooling 2	875.4	869.9	864.9	12	
Heating 1 ^e	863.2	870.5	874.7	3	
Heating 2	863.4	868.8	874.1	5	
		Av 869.6			
Batch No. 2					
Cooling 1	871.4	868.8	865.5	6	
Cooling 2	872.3	869.1	865.1	6	
Heating 1	865.1	868.2	874.1	4	
Heating 2	868.2	870.0	873.6	3	
		Av 869.1			
Batch No. 3, Specimen No. 1					
Cooling 1		868	867.0	8	
Cooling 2	870.6	869.0	867.8	17	
Heating 1	867.8	870.6	872.0	10	
Heating 2	862.1	870.4	872.6	13	
		Av 869.5			
Batch No. 3, Specimen No. 2					
Cooling 1	Supercooling	862.6		10	
Cooling 2 ^f	Supercooling	862.4	853.0	21	
Cooling 3 ^f	Supercooling	863.4	853.9	34	
Heating 1 ^f	857.6	863.9	868.0	7	
Heating 2 ^f	860.0	863.9	868.6	44	
		Av 863.4			
Batch No. 4					
Cooling 1 ^f	Supercooling	865.1	864.8	55	
Heating 1 ^f	826.7	866.6	867.2	175	
		Av 865.9			

^aCorresponds to No. 1 in Fig. 85.

^bCorresponds to No. 2 in Fig. 85.

^cCorresponds to No. 3 in Fig. 85.

^dCorresponds to No. 4 in Fig. 85.

^eEvacuated capsule, rather than argon-filled capsule.

^fDifferential controller.

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Fig. 85. Typical Thermal Analysis Curves of Iodide Crystal-Bar Zirconium.

investigation of these effects was incorporated into the annealing program at 1200°C where various types of materials were tested as jackets to prevent any reaction between the pure zirconium specimen and the quartz capsule. The results are given in Table 44.

All the specimens were degassed by slowly heating to 700°C and holding for 30 min under a pressure of 2×10^{-5} mm Hg. Sufficient purified argon was admitted to give a pressure of 1 atm of argon at 1200°C and the capsules were sealed off. Heat treatment was for three days at 1200°C. The cylindrical specimens used were of approximately 1 g in weight and of the analysis described in Table 42 as batch No. 3. The starting condition was as-received crystal bar with a hardness of 68. Reannealing the water-quenched specimens was done at 2×10^{-5} mm Hg for 30 min at 800°C, and the specimens were wrapped in pure zirconium foil. The refractory oxides used were Norton RA 84

Al_2O_3 , T.A.M. stabilized ZrO_2 , and BeO containing 1% Al, 0.15% Si, 0.05% Ca, and 0.05% Fe from Bureau of Mines, Norris, Tennessee.

It will be observed that the annealing experiments with the use of molybdenum and tantalum foil jackets resulted in no appreciable hardening of the zirconium crystal bar, where the capsules were not broken during quenching. The refractory oxide crucibles all resulted in an appreciable gain in hardness, as did the use of a silica tube without a protective interface. A zirconium foil jacket which has been used successfully at temperatures up to 1000°C resulted in some significant hardening of the specimen at 1200°C. These results have led to the use of molybdenum or tantalum foils for anneals in the phase-diagram program above 1000°C. The principal disadvantage in the use of molybdenum – and presumably the same would be true to a lesser extent for tantalum – is that wherever good contact is established between the specimen

METALLURGY PROGRESS REPORT

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ORNL-LR-DWG 1367

Fig. 86. Schematic Diagram of the $\alpha \rightarrow \beta$ Arrests in Zirconium.

TABLE 44. RESULTS OF PURE-ZIRCONIUM ANNEALING EXPERIMENTS

CRUCIBLE OR JACKET SEPARATING ZIRCONIUM FROM QUARTZ	SPECIMEN A - CAPSULE UNBROKEN DURING QUENCH		SPECIMEN B - CAPSULE BROKEN DURING QUENCH		SPECIMEN B REANNEALED AND SLOWLY COOLED	
	Vickers Hardness, 10-kg Load	Weight Change (%)	Vickers Hardness, 10-kg Load	Weight Change (%)	Vickers Hardness, 10-kg Load	Weight Change (%)
None	142	0.00				
Molybdenum	68	-0.12	84	+0.05	67	-0.09
Tantalum	67	-0.24	81	-0.31	63	-0.06
Zirconia	222	+0.13				
Alumina	168	-0.20				
Beryllia	330					
Zirconium	95	+0.37	124	+0.10	124	-0.05

PERIOD ENDING APRIL 10, 1954

and the molybdenum foil there is localized diffusion which must be removed by grinding. An extreme case of this effect is illustrated in Fig. 88, which

Fig. 87. Approximate Extrapolation of the $\alpha \rightarrow \beta$ Zirconium Transition Temperature.

shows two similarly machined surfaces that were shrunk together and heat-treated for five days at 1100°C. This photograph illustrates the extent of diffusion which occurs when a tight contact is made between the zirconium and molybdenum. The structures from left to right are considered to be molybdenum, retained beta zirconium solid solution, basket-weave transformed beta, and serrated alpha structure of pure zirconium. The $ZrMo_2$ phase apparently was not retained in polishing. The foil jackets can be used successfully for annealing zirconium if care is taken to remove any isolated areas of molybdenum-contaminated material from each specimen after the anneal.

The microstructures of the pure zirconium annealed in the various crucibles and jackets were examined and the results are given in Table 45. At the start of this examination numerous small markings were observed in the microstructures, as shown in Fig. 89. By variation in the proportions

Fig. 88. Diffusion Couple Between Molybdenum (Left) and Zirconium (Right) After Five Days at 1100°C. Bright-field illumination after chemical etch with 46% H_2O , 46% HNO_3 , 8% HF . 100X. Reduced 7%.

METALLURGY PROGRESS REPORT

of water, nitric acid, and hydrofluoric acid in the etching reagent, by more careful polishing operations, and by a neutralizing rinse after etching, the markings were eliminated. They are now regarded as etch-pitting or other manifestation of the metallographic technique rather than as a characteristic of the impurities in the metal. The same specimen shown in Fig. 89 is shown again in Fig. 90 with the more careful etching procedure. The large serrated grains are typical of the transformation structure of pure beta zirconium, but when oxygen

or some other impurity or solute element is dissolved in beta zirconium, the transformation structure changes in appearance to that known as the "basket-weave" structure. An example of this is shown in Fig. 91, which is of a specimen annealed in a silica tube without any protective interface. It will be observed by comparing Tables 44 and 45 that the hardest specimens are those with the basket-weave microstructure. An exception is the specimen annealed in BeO. Extensive reduction of the BeO by the zirconium occurred,

Fig. 89. Zirconium Annealed for Three Days at 1200°C in Molybdenum Foil. Polarized light illumination; capsule not broken in the quenching water; first etching results. 250X. Reduced 31%.

Fig. 90. Same Specimen as in Fig. 89 Etched More Carefully with 47.5% H₂O, 47.5% HNO₃, 5% HF Followed by Neutralizing Rinse. 100X. Reduced 30%.

TABLE 45. PURE-ZIRCONIUM ANNEALING EXPERIMENTS - METALLOGRAPHIC RESULTS

CRUCIBLE OR JACKET MATERIAL	CAPSULE UNBROKEN DURING QUENCH	CAPSULE BROKEN DURING QUENCH
None	Basket-weave structure	
Molybdenum	Serrated alpha without twins	Serrated alpha with twins; small amount of basket-weave structure in region near edge
Tantalum	Serrated alpha with some twins	Serrated alpha with twins and with one small area of basket-weave structure near edge
Zirconia	Coarse basket-weave structure	
Alumina	Coarse basket-weave structure	
Beryllia	Chilled liquid eutectic structure formed between BeO and zirconium	
Zirconium	Serrated alpha with very few twins; smaller grains near edge	Serrated alpha with some twins and one small area of basket-weave structure near edge

and the amount of oxygen and beryllium introduced into the zirconium was sufficient to make most of the zirconium specimen consist of two phases. A photograph of the liquid region which formed between BeO and zirconium is shown in Fig. 92.

The effect of breaking the capsule during the quenching is threefold. First, small areas near the surface of the sample occasionally show the basket-weave structure, indicating possible hydrogen or oxygen alloying; secondly, the microstructures contain more twins, presumably because of the increased quenching stresses; thirdly, the Vickers hardness is increased (Table 44). To investigate the nature of the hardening effect, specimens which had been exposed to the quenching water in molybdenum, tantalum, and zirconium foil jackets were reannealed at 800°C for 30 min to relieve quenching and transformation stresses. In the cases of molybdenum and tantalum the specimens were restored to the original crystal-bar hardness, but in the third case (zirconium foil) the hardness remained the same. Since the investigations of rapidly cooled arc-castings, to be described in the

next section, revealed similar hardening effects on cooling and since these hardening effects were found to be softened by alpha-annealing, the third specimen is considered to be an exception. The probable conclusion is that water-quenched specimens from the beta region will include a hardening effect from transition stresses which is independent of any contamination of the specimens by foreign atoms.

Vacuum fusion analysis confirmed that the hardening effect in quenching was not gas contamination. The analyses were part of a series of experiments for investigating the changes in gas content with the arc-casting, degassing, and etching operations used in the course of phase-diagram work. The results are given in Table 46. It will be observed by comparing analysis 192 with analyses 194 and 195 that the hydrogen content was effectively reduced by vacuum-degassing. Further, when the surface of the specimen was cleaned by an etchant, 46% H₂O-46% HNO₃-8% HF at room temperature, no increase in hydrogen content was observed. The same type of specimen, when degassed and then quenched by breaking the capsule under water, did not change in either hydrogen or oxygen contents significantly. The arc-casting operation, on the other hand, resulted in an increase in hydrogen content. This is thought to be due to an inadequate performance of the hydrogen remover in the argon purification train at the time that this experiment was done, and corrective steps have been taken.

Arc-Melting of Zirconium

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S. C. Bennett

The alloys necessary for phase-diagram studies have been prepared by arc-melting the proper charge in a nonconsumable-electrode furnace similar to that used by other investigators for titanium alloys and zirconium alloys.

Several unalloyed zirconium ingots have been melted numerous times in order to determine the optimum melting practice and to provide information on the contamination introduced during melting.

The furnace used consists of a water-cooled copper hearth and a water-cooled nonconsumable tungsten electrode mounted inside a vacuum chamber through a metal bellows which makes it possible for the arc to be played over the surface of the charge during melting. A diffusion pump backed by a mechanical vacuum pump is used to evacuate

Fig. 91. Zirconium Annealed for Three Days at 1200°C in a Silica Capsule Without a Protective Foil. Capsule was not broken in quenching. Etchant: 47.5% H₂O, 47.5% HNO₃, 5% HF followed by neutralizing rinse. Polarized light illumination. 100X.

Fig. 92. Reaction Between Zirconium and Beryllia After Annealing for Three Days at 1200°C. Phases in sequence (from the left) are thought to be a two-phase region of ($\alpha + \beta$) zirconium, a (Zr-Be-O) compound, a zirconium-rich Zr-Be-O eutectic, and BeO. Etchant: 47.5% H_2O , 47.5% HNO_3 , 5% HF followed by neutralizing rinse. Bright-field illumination. 100X

the system prior to filling with a protective atmosphere of argon. A 200-amp, d-c arc-welding generator supplies sufficient power for the melting of 5- to 20-g charges.

The general melting procedure was to evacuate the furnace to approximately 10^{-5} mm Hg with hot water flowing through the hearth and electrode assembly and then flush with purified argon. The evacuation and flushing were repeated three times with a static pressure of argon set at 500 mm Hg on the final filling. The cooling water for the electrode and hearth was then turned on and the arc was struck on a tungsten striker and then transferred to the charge. When the charge was thoroughly molten, the arc was extinguished and the ingot allowed to cool, after which it was turned over and remelted. Charges of grade 1 zirconium

crystal bar were prepared for the melting experiments by sand-blasting and by pickling in 46% H_2O -46% HNO_3 -8% HF.

Ingots were made which had been melted 2, 4, 6, 8, and 10 times without the furnace being opened between melting of any given ingot, and the initial and final hardnesses were measured to give an indication of the amount of contamination.

The hardness values plotted against the number of times the ingots were melted are presented in Fig. 93, and the change in hardness for a given ingot vs the number of times it was melted is presented in Fig. 94. The ingots were from a January 1953 lot, arc-cast in 25 in. argon, evacuated to 4×10^{-5} mm Hg, annealed 2 hr at $800 \pm 25^\circ\text{C}$ at 4×10^{-5} mm Hg. An increase in hardness of 20 to 40 Vickers points was found to occur in every case.

TABLE 46. CHANGES IN GAS CONTENT OF PURE ZIRCONIUM* DURING ARC-CASTING, DEGASSING, QUENCHING, AND ETCHING OPERATIONS

ANALYSIS NUMBER	HEAT TREATMENT	SURFACE PREPARATION	NUMBER OF SPECIMENS IN AVERAGE	WEIGHT (ppm)**	
				Oxygen	Hydrogen
192	Crystal bar	Etched	5	39	17
193	Crystal bar arc-cast	Etched	5	47	46
194	Degassed 30 min at 1000°C at 1×10^{-6} mm Hg	Filed	3	29	5
195	Degassed 30 min at 1000°C at 1×10^{-6} mm Hg	Etched	2	30	5
196	Degassed 30 min at 1000°C; hot specimen in silica capsule broken under water	Filed	2	35	7

*Material used throughout was a single piece of batch No. 4, grade 1 zirconium crystal bar. The results were by vacuum fusion analysis performed by W. Wolkowitz and H. Davis in a molten iron bath and a graphite crucible.

**Nitrogen content reported to be 10 ppm in all tests.

Fig. 93. Hardness of Arc-Cast Zirconium.

Since stresses introduced by the rapid cooling through the $\alpha \rightarrow \beta$ transformation would also appear as an increase in hardness, the ingots were then annealed in vacuum for 2 hr at 800°C and slowly cooled. It was found that the hardness was

Fig. 94. Hardness Changes During Casting and Annealing of Zirconium.

decreased in every case by the annealing treatment; therefore the increase in hardness due to contamination during melting is not nearly so great as that occurring from the stresses introduced by rapid cooling through the $\alpha \rightarrow \beta$ transformation.

Figure 94 shows the hardness increase due to contamination of the ingot during melting to be approximately 1.3 Vickers points per melting cycle.

METALLURGY PROGRESS REPORT

EXPERIMENTAL INVESTIGATION OF ALLOYS

The Ag-Zr System

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J. O. Betterton, Jr.

The present determination of the Ag-Zr system is a continuation of the work reported earlier¹¹ in which the Group IB element silver is alloyed with the Group IVA element zirconium. Since the beginning of this work, a new Ag-Zr phase diagram has been reported by Kemper¹² and an x-ray structure investigation of the intermediate phases has been reported by Karlsson.¹³ These results are in general agreement with the present experiments.

Experimental Procedure. The alloys were prepared by arc-casting 99.99% silver and grade 1, iodide-decomposition zirconium on a water-cooled, copper hearth in purified argon with a nonconsumable, tungsten electrode. Prior to annealing, the alloys were wrapped in a protective foil (Zr, Mo, or Ta, depending upon the temperature) and then placed in individual silica tubes. Precautions were taken to see that everything inside the tubes was chemically cleaned, and the alloys were then degassed by heating slowly to 1000°C and holding for 30 min at $<5 \times 10^{-5}$ mm Hg to remove hydrogen. The alloys were then sealed off in a silica tube under a partial pressure of purified argon. During annealing in these capsules, the temperature was measured repeatedly with a calibrated Pt-Pt + 10% Rh thermocouple. The movements of this thermocouple, in order to determine the temperature difference along the length of the capsule, added to the uncertainty of the annealing temperature finally used. The specimens after the anneal were quenched by breaking the capsule under water with the use of a specially built, foot-operated hammer. The annealing times used varied somewhat, depending upon the alloy, with the following values being typical.

Number of Days	Temperature (°C)
2	1200
5	1100
8	1000
15	850
20	820
30-45	700-800
45-60	600

The hypereutectoid alloys over 3.5% silver were not very ductile and became even less ductile as

the silver content increased. Cold deformation by forging or rolling therefore could be used only with the hypoeutectoid alloys to reduce the time to attain equilibrium.

Thermal Analysis. The method of thermal analysis used for the Ag-Zr alloys was the same as that already described for the investigation of the $\alpha \rightarrow \beta$ transition of pure zirconium. The alloys were arc-cast into 30- to 40-g ingots, degassed, and homogenized for five days at 1000°C. To investigate the extent of the segregation of silver, samples for chemical analysis were removed from three different locations on the annealed ingot, just prior to the thermal investigation. The analytical results are given in Table 47, together with the location in the sample from which they were taken. The silver was fairly uniformly distributed in the lower silver alloys (within 0.1 at. %), but in the higher silver alloys silver segregations of 0.4 to 0.9% silver were observed. The observed variation in silver content should not affect the determination of the eutectoid temperature, but it does influence the detection of the $[\beta/(a + \beta)]$ and $[\beta/(\beta + \gamma)]$ boundaries, as will be discussed later.

The homogenized buttons were again degassed and then sealed into thermal-analysis capsules with re-entrant thermocouple sheaths. Each capsule was then placed in a 6-in. length of Inconel heavy-walled tube positioned inside an electrical resistance muffle. Gradient tests were made by moving the calibrated Pt-Pt + 10% Rh couple, and in no case did the gradient exceed 0.2°C/cm. Power control of the furnace was by means of simple variac settings, and each specimen was first heated overnight in the beta region, cooled 1 to 2°C/min into the $(a + \gamma)$ region, held overnight, and reheated 1 to 2°C/min into the beta region. The process of cooling was then repeated after several hours in the beta region. Finally, the specimens were examined microscopically in the slowly cooled condition.

The results of these thermal analyses are given in Table 48. The arrests from the eutectoid reaction, $\beta \rightleftharpoons a + \gamma$, began in cooling in the temperature range of 770 to 820°C. Progressively

¹¹J. O. Betterton, Jr. and T. M. Kegley, Jr., *Met. Quar. Prog. Rep.* Jan. 31, 1952, ORNL-1267, p 39; *Met. Quar. Prog. Rep.* July 31, 1952, ORNL-1366, p 21.

¹²R. S. Kemper, Jr., *The Zirconium-Silver System*, Oregon State College thesis, June 1952.

¹³N. Karlsson, *Acta Chem. Scand.* 6, 1424 (1952).

PERIOD ENDING APRIL 10, 1954

TABLE 47. DETAILS OF THE PREPARATION OF THERMAL-ANALYSIS ALLOYS
AND RESULTS OF CHEMICAL ANALYSIS

SILVER CONTENT OF ALLOY (at. %)	NUMBER OF REMELTINGS	PURE ZIRCONIUM CONTROL- BUTTON HARDNESS	HOMOGENEIZATION HEAT TREATMENT		LOCATION* OF ANALYSIS SAMPLE	CHEMICAL ANALYSIS (at. %)		
			Number of Days	Temperature (°C)		Silver	Zirconium	Total
0.5	9	97	5	1012	O	0.44	99.49	99.93
					T	0.55	99.48	100.03
					B	0.57	99.41	99.98
0.8	9	99	4	1008	O	0.72	99.20	99.92
					T	0.79	99.20	99.99
					B	0.81	99.17	99.98
1.0	9	84	6	1003	O	0.85	99.13	99.98
					T	0.93	99.10	100.03
					B	1.03	98.94	99.97
1.3	9	97	7	1012	O	1.15	98.88	100.03
					T	1.40	98.58	99.98
					B	1.38	98.61	99.99
2.1	9	90	10	1000	O	1.94	98.03	99.97
					T	2.19	97.81	100.00
					B	2.29	97.65	99.94
2.4	12	77	12	1014	O	2.09	97.94	100.03
					T	2.26	97.81	100.07
					B	2.80	97.29	100.09
3.7	9	81	5	1000	O	3.32	96.71	100.02
					T	3.90	96.14	100.04
					B	3.95	96.02	99.97
6.3	9	84	7	1022	O	5.75	94.26	100.01
					T	6.65	93.30	99.95
					B	6.55	93.42	99.97
9.5	9	81	3	1005	O	9.44	90.60	100.04
					T	9.64	90.38	100.02
					B	9.27	90.74	100.01
29.61	9	70	13	1027	O	29.52	70.52	100.04
				(4 days)				
				1102				
				(9 days)				
					T	29.58	70.35	99.93
					B	29.64	70.34	99.98

*O: Outside surface on the side of the ingot.

T: Outside half of hole drilled into the end of the ingot.

B: Interior half of hole drilled into the end of the ingot; represents the center of the ingot.

TABLE 48. RESULTS OF THERMAL ANALYSES OF Ag-Zr ALLOYS

SILVER CONTENT OF ALLOY (at. %)	BEGINNING OF EUTECTOID ARREST		[$\beta/(\alpha + \beta)$] BOUNDARY*		[$\beta/(\beta + \gamma)$] BOUNDARY*	
	Cooling (°C)	Heating (°C)	Beginning of Arrest When Cooling (°C)	End of Arrest When Heating (°C)	Beginning of Arrest When Cooling (°C)	End of Arrest When Heating (°C)
0.5			858 858	868		
0.8			855 856	866		
1.0			849 847 846	859		
1.3	782 779	823	845 844	(830- 858?)		
2.1	796 796	820	842 848	(830- 840?)		
2.4	795 794	819 819	834 838 835 836	834 847		
3.7	806 806	816				
6.3	815 814	812			947	942
9.5	820 820	820				

*For all except alloys in the range 0.5 to 1.0 at. % silver, these arrests were very slight and uncertain.

lower temperatures were observed as the silver content was reduced, the arrests becoming weaker in hypoeutectoid alloys, and no effects were detected below 1.3 at. % silver. On the other hand, a maximum arrest occurred in the alloy with 3.7 at. % silver. Two possible explanations could be considered for the variation in what should be a constant temperature. One is a kinetics effect in which the rate of the reaction depended upon the silver content and in which the cooling rate, 1 to 2°C/min, was fast enough to depress the eutectoid in the lowest silver contents. The other is that the impurities in the alloys were sufficient to cause a variable eutectoid temperature, the effect being greatest in the more dilute alloys. No conclusion has yet been drawn as to which of these

explanations is correct. More satisfactory agreement was obtained in the heating curves, where the beginning of the reaction was observed in the same alloys at temperatures 812 to 823°C, the average being 817.5°C. The average both in heating and cooling of the hypereutectoid alloys only was 815°C, just slightly less than the average of all alloys in heating, and this value is considered to be the best present estimate of eutectoid temperature from the thermal analysis.

The inflections in the heating and cooling curves at the [$\beta/(\alpha + \beta)$] boundary were quite pronounced in alloys of 0.5, 0.8, and 1.0 at. % silver and indicated clearly that the [$\beta/(\alpha + \beta)$] boundary was depressed with additions of silver. In the 1.3, 2.1, and 2.4 at. % alloys, more gradual and weaker

effects were found, and the points noted in Table 48 were the best selections which could be made by plotting a rate analysis. A comparison of these thermal-analysis results with the phase boundaries determined by annealing and quenching experiments to be described later is shown in Fig. 95. It will be seen that the $[\beta/(a + \beta)]$ thermal arrests lie below the phase boundary determined by the annealing method. The rectangular symbols in this figure represent the major part of the arrest, the part which would be taken as the temperature range of the arrest under ordinary circumstances. However, because of the present case of complicated thermal effects inside a two-phase region and of composition differences within the 1.3, 2.1, and 2.4 at. % alloys of 0.25 to 0.71% silver, it seemed desirable to add to the graph the dotted portions which include all the very weak effects and slight deviations of the regular rate of heating or cooling.¹⁴

¹⁴Composition variations make composition-dependent thermal inflections diffuse because not all parts of the specimen react at the same temperature.

These dotted portions are more significant before the arrest than afterward because of the temperature gradient effect, but both have been included in Fig. 95. The symbols have been plotted at the minimum silver analysis, since this is the part of a hypoeutectoid alloy which results in the highest temperature inflections. Considering the tops of the dotted portions as indicating the beginning of the $(a + \beta)$ region, a somewhat better agreement is obtained with the annealing method; but, in general, the thermal-analysis results have been disappointing as far as the $[\beta/(a + \beta)]$ boundary is concerned, probably as a result of the composition differences in various parts of the alloys. Similar considerations apply to the $[\beta/(\beta + \gamma)]$ boundary, although the inflections observed in the 6.3 at. % alloy did agree quite well with the microscopically determined boundary.

The thermal-analysis specimens, after the experiments, were in the slowly cooled condition from about 900°C. The microstructures in this condition are shown in Fig. 96. The eutectoid

Fig. 95. The Ag-Zr System.

METALLURGY PROGRESS REPORT

Fig. 96. Slowly Cooled Ag-Zr Alloys in the Vicinity of the $\beta \rightleftharpoons \alpha + \beta$ Eutectoid. (a) 0.51 at. % Ag, 1000X. (b) 1.32 at. % Ag, 2000X. (c) 2.18 at. % Ag, 1000X. (d) 3.73 at. % Ag, 1000X. (e) 5.88 at. % Ag, 2000X. (f) 9.47 at. % Ag, 1200X. Reduced 31.5%.

structure observed in the grain boundaries of the alpha phase of the 0.51 at. % alloy indicates that the alpha solid solubility is certainly less than 0.5 at. % silver. The 3.7 at. % alloy consisted almost wholly of the eutectoid structure, whereas the 6.3 and 9.5 at. % alloys both showed larger crystals of the $\gamma(\text{AgZr}_2)$ phase intermixed with the eutectoid structure.

Alpha- and Beta-Phase Boundaries According to Annealing Experiments. The results of annealing alloys containing 0.1, 0.2, 0.3, and 0.4 at. % silver for 45 days at 600 and 700°C indicated that the alpha solid solubility was less than 0.12 at. % Ag at these temperatures. The microstructures shown in Fig. 97 are typical of these results. At higher temperatures, the temperature at which the alpha phase changed from equilibrium with the $\gamma(\text{AgZr}_2)$ phase to equilibrium with the beta phase appeared to vary with the history of the alloy. For example, the 0.2 at. % alloy, after being annealed for 29 days at $796 \pm 3^\circ\text{C}$, was in the $(\alpha + \beta)$ region, whereas the 0.6 at. % alloy, which had been prepared independently from another batch of zirconium and had been annealed for 35 days at $800 \pm 1^\circ\text{C}$, was in the $(\alpha + \gamma)$ region. In addition, $(\alpha + \text{traces of } \beta)$ microstructures were observed in 0.1, 0.2, and 0.3 at. % alloys at 805°C and in 0.2 and 0.3 at. % alloys at 815°C, both temperatures being below the eutectoid temperature found at higher silver contents. Finally, although the 0.12 at. % alloy in anneals at 600, 700, 805, and 856°C was never found to be homogeneously alpha, the 0.8 at. % alloy after 11 days at 847°C consisted of only 20% beta (80% alpha) and another 0.83 at. % alloy after 11 days at 803°C consisted of only 3% beta (97% alpha). Both these results indicated that the maximum alpha should be closer to 0.6 to 0.7% silver. Behavior such as this can be understood in terms of an insoluble impurity which also undergoes a eutectoid reaction with zirconium at some temperature less than 800°C. In the future, zirconium batches will be used to make silver alloys only if they can be annealed in the unalloyed state without two-phase effects. With the present zirconium, the maximum solid solubility of silver in the alpha phase should be considered to be less than 0.1%, as there are more results supporting this conclusion than there are for the higher figure of 0.6 to 0.7% solubility which could conceivably be true for purer zirconium.

The results of annealing experiments in the vicinity of the $[\beta/(\alpha + \beta)]$ boundary are shown in

the phase diagram in Fig. 98. Similarly, the results of annealing experiments in the vicinity of the $[\beta/(\beta + \gamma)]$ boundary are shown in the same figure. In both cases a number of compositions, or temperature brackets, were obtained, which were then confirmed by examination of both sides of the specimens to ensure the absence of composition segregation, and the actual microscopical specimen was analyzed. Examples of two of these brackets are shown in the photomicrographs of Fig. 99. In the first, the 1.64 and 1.84 at. % alloys at 853°C are in the $(\alpha + \beta)$ and the beta region, respectively, the pattern in the beta phase being the characteristic transformation structure. Similarly, two other alloys are shown to be on either side of the $[\beta/(\beta + \gamma)]$ boundary in Fig. 99c and in 99d. The example shown in Fig. 99f of a beta microstructure, obtained when high-silver alloys are quenched from the homogeneous beta region, is one in which there is no microscopically apparent transformation to a lower temperature phase.

The eutectoid composition and temperature indicated by the intersection of the $[\beta/(\alpha + \beta)]$ and $[\beta/(\beta + \gamma)]$ boundaries are 3.5 at. % silver and 820°C. When this result is compared with that of Kemper's, there is only approximate agreement; Kemper's conclusions for the eutectoid reaction from thermal analysis and slowly cooled microstructures were $\beta (4.7) \rightleftharpoons \alpha (0.1) + \text{AgZr}_2$ at $810 \pm 5^\circ\text{C}$, whereas the present results from thermal analysis and slowly cooled microstructures were $\beta (3.7) \rightleftharpoons \alpha (0.5) + \text{AgZr}_2$ at $815 \pm 5^\circ\text{C}$. Attempts to establish the eutectoid temperature more accurately by annealing above and within the $(\alpha + \gamma)$ region have led to certain inconsistencies. For example, the 2.8 at. % alloy annealed at 816.5°C was in the field $(\alpha + \gamma)$, while the 3.9 at. % alloy at 815°C was in the field $(\beta + \gamma)$. Furthermore, a whole series of alloys made from batch No. 4 zirconium consisted of three phases $(\alpha + \beta + \gamma)$ when annealed at the two temperatures 814 and 817°C. The eutectoid temperature and the upper limits of the $(\alpha + \gamma)$ region are now being re-examined with other batches of zirconium in connection with the alpha solid solubility limit near the eutectoid temperature.

The equilibrium is reached fairly slowly in this part of the phase diagram. For example, in the $(\alpha + \beta)$ region, three-day anneals do not produce the same type of isothermal $(\alpha + \beta)$ microstructure as do twelve-day anneals. Similarly, in the $(\alpha + \gamma)$ region, annealing for even 70 days is not sufficient

Fig. 97. Typical Microstructures of the Alpha Phase and $(\alpha + \gamma)$ Alloys in the Ag-Zr System. Annealed for 45 days at 600°C. (a) Pure zirconium, alpha phase, 500X. (b) 0.13 at. % Ag, trace, 500X. (c) 0.27 at. % Ag, $(\alpha + \gamma)$, 750X. Reduced 18.5%.

Fig. 98. The β -Phase Region of the Ag-Zr System.

to completely spheriodize the particles of the gamma phase at 800°C (Fig. 99e).

The Gamma Phase. The intermediate phases of the Ag-Zr system were reported earlier¹¹ to be near the compositions AgZr_2 and AgZr . This was on the basis of some preliminary annealing experiments involving only six alloys; for convenience in the following, the AgZr_2 phase will now be called gamma, and the AgZr phase, delta. The gamma phase was then presumed to form by peritectic reaction from the melt on the basis of the cast microstructure of the 23.3 at. % alloy, but recently Kemper¹² has interpreted similar "as-cast" microstructures to indicate a (liquid $\rightleftharpoons \beta + \gamma$) eutectic reaction at 10.3 at. % silver and 1250°C. The difference in interpretation appears to depend upon whether an aggregated structure observed in the castings is the result of a eutectic reaction or a gamma-precipitation effect in the primary beta crystals as a result of the rapidly declining beta solid solubility with temperature.

New experiments have now been completed which show that the peritectic formation of the gamma phase is the correct interpretation. Eight alloys were cast in the composition range 28.7 and 32.3 at. % silver, and after homogeneization at 1100°C, the alloys up to 31 at. % silver were found to be ($\beta + \gamma$). Higher silver alloys, in the range 31.5 to 32.3 at. % silver, unfortunately were not completely annealed in eight days at 1100°C but appeared as principally gamma phase with about equal trace amounts of both beta and delta phases. For this reason, the composition limits of the gamma phase are shown as dotted lines in the phase diagram, Fig. 100, although they are known with certainty to be between the limits 29.58 and 34.10 at. % silver.

Some typical photomicrographs of these alloys are shown in Fig. 101, which includes a typical cast structure of an alloy in the gamma-phase region. The dendritic crystals are beta phase, whereas the matrix consists of gamma phase, formed

Fig. 99. Quenched Ag-Zr Alloys in the Zirconium-rich Region. (a) 1.64 at. % Ag, ($\alpha + \beta$) microstructure, 17 days at 853°C, 500X. (b) 1.82 at. % Ag, transformed β , 17 days at 853°C, 500X. (c) 3.7 at. % Ag, transformed β , 17 days at 848°C, 750X. (d) 4.3 at. % Ag, ($\beta + \gamma$) microstructure, 14 days at 855°C, 750X. (e) 2.3 at. % Ag, ($\alpha + \gamma$) microstructure, 70 days at 800°C, 500X. (f) 13.68 at. % Ag, retained β , two days at 1120°C, 500X. Reduced 31.5%.

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ORNL-LR-DWG 1373

Fig. 100. Tentative Ag-Zr Phase Diagram to Illustrate the Results at Higher Silver Contents.

during the peritectic reaction of the liquid and the beta phase. Within the gamma matrix, some areas of delta phase may also be seen. These are due to the incomplete peritectic reaction and represent a coalesced $(\gamma + \delta)$ eutectic. Although not shown here, the actual noncoalesced eutectic structure has been observed in other cast specimens. The effect of annealing this peritectic structure is next illustrated by Fig. 101b and 101c. The three-phase structure persisted after four days at 1027°C and two and one-half days at 1100°C, and a total of nine days at 1100°C was required to reach an equilibrium $(\beta + \gamma)$ microstructure. This slow attainment of equilibrium at temperatures near the melting point is a further indication of a peritectic-cast structure. The temperature of the peritectic horizontal was placed at $1175 \pm 10^\circ\text{C}$, and the temperature of the $(\gamma + \delta)$ eutectic horizontal was placed at $1160 \pm 6^\circ\text{C}$ by melting-point anneals, illustrated by the specimen in Fig. 101d. The photograph shows the gamma-phase surface of the two-phase $(\beta + \gamma)$ specimen, which has melted at 1177°C to form the $(\gamma + \delta)$ eutectic. Since the

melting-point studies involved some uncertainties in interpretation, these experiments will be discussed in detail below.

In the first experiment a thermal-analysis sample of 29.58 at. % silver was annealed to a $(\beta + \gamma)$ microstructure and then was slowly heated to 1173°C without a melting-point arrest being encountered. In removing the specimen from the furnace, the specimen temperature rose an estimated 3 to 8°C higher. Upon examination the quenched microstructure was found to consist of $(\beta + \gamma)$ with some parts of the gamma melted, leading to the conclusion that the gamma melting point is only slightly higher than 1173°C. A second set of experiments was performed by the solidus-annealing method in which short, 10- to 60-min, anneals in silica capsules were done at progressively increasing temperatures. The 30.5 at. % alloy was found to melt slightly on the surface at the temperatures 1161 and 1170°C, more deeply at 1177°C, and still more deeply at 1186°C. In each case the beta phase was unaffected, whereas the gamma phase did melt, the chilled liquid consisting of the $(\gamma + \delta)$ eutectic.

Fig. 101. Results of Homogenization and Solidus Experiments in the Vicinity of the Gamma Phase of the Ag-Zr System. (a) 31.8 at. % Ag, as-cast microstructure, 250X. (b) 29.6 at. % Ag, annealed four days at 1027°C and 2½ days at 1100°C, 500X. (c) 29.6 at. % Ag, annealed nine days at 1100°C ($\beta + \gamma$) microstructure, 500X. (d) 30.5 at. % Ag, annealed eight days at 1100°C and 10 min at 1177°C, incipient melting of the gamma phase, 500X. Reduced 24%.

The very slight surface melting of the samples at 1161 and 1170°C was disregarded because these surfaces were near the molybdenum foil, and an unidentified "Mo-Si-Zr" compound phase was observed in the same area. Since the 1177 and 1186°C specimens were wrapped with zirconium foil and then tantalum foil before being enclosed in a silica capsule, the results are thought to be valid representations of the melting in the sample. The peritectic temperature for $\beta + \text{liquid} \rightleftharpoons \gamma$ is $1175 \pm 10^\circ\text{C}$, based on the absence of thermal effect in thermal analysis to 1173°C and on the incipient melting observed in the Zr-Ta wrapped specimen at 1177°C.

The $(\gamma + \delta)$ eutectic horizontal was investigated on the other side of the gamma phase by using the 32.3 at. % alloy. The temperatures 1143, 1150, 1154, and 1166°C were investigated, and, as before, slight surface melting was observed over a range of temperature (as low as 1150°C). However, in this alloy the shape of the delta-phase grains in the interior of the sample could be used to choose the melting temperature. Up to 1154°C the grains of the delta phase were rounded, but at 1166°C melting had taken place and the quenched delta phase appeared as the $(\gamma + \delta)$ eutectic. The temperature of the $(\gamma + \delta)$ eutectic reaction is therefore taken to be $1160 \pm 6^\circ\text{C}$. From the appearance of beta dendrites in cast alloys containing up to 40 at. % silver and from the dominant proportion of delta in this eutectic (90 to 95%), the composition of the eutectic is placed roughly at 46% silver.

Very little is known about the liquidus and solidus boundaries of the Ag-Zr system, other than that provided by Raub and Engel,¹⁵ who used graphite crucibles and rather impure zirconium. The general nature of the diagram must, however, be of the approximate form shown in Fig. 100, in which the results of the present experiments have been combined with those of Raub and Engel. The temperature for the congruent melting of AgZr determined by Raub and Engel has been shifted upward on this diagram to allow a $(\gamma + \delta)$ eutectic temperature of 1160°C. Additional experiments on the gamma phase are planned. Some longer anneals of alloys in the range 31 to 34 at. % silver will be made. A new melting-point determination will be made of the $(\beta + \text{liquid} \rightleftharpoons \gamma)$ horizontal in

which a relatively thick layer of beta phase will be developed on the surface of the $(\beta + \gamma)$ specimens by diffusion before the experiments are started. The melting of the gamma phase in the interior will be used to determine the peritectic reaction temperature.

On Fig. 100 the $[\beta/(\beta + \gamma)]$ boundary has been extrapolated by a logarithmic plot of the solubility against reciprocal temperature, the results approximating a straight line, which gives the beta-phase solid solubility at 1175°C as about 17.4 at. % silver.

The In-Zr System

G. W. Boyd

J. O. Betterton, Jr.

The In-Zr system is of particular interest because the solute involved is an element from Group IIIB different from aluminum. Aluminum has heretofore been the only representative of this group used in a phase diagram with a Group IVA element. Aluminum has the effect of raising the α/β boundaries of both titanium and zirconium; therefore, over a limited temperature range, the solid solubility of aluminum in the close-packed hexagonal phase is greater than that in the body-centered-cubic phase. The atoms of indium and zirconium are about the same size, and it was expected that the In-Zr phase diagram would be similar to the Ti-Al and the Zr-Al diagrams.

The experimental procedure used in the present investigation was similar to that used for Ag-Zr. The alloys were made from indium of 99.99% purity, supplied by the American Smelting and Refining Company, and of grade A zirconium crystal bar made by the Foote Mineral Company. No difficulty was encountered in arc-casting alloys up to 26 at. % indium in spite of the large difference in melting points of indium and zirconium. Near this composition, indium losses in casting were appreciable, and some special techniques may be required to extend the work to higher indium contents.

The effect of indium on the α/β boundaries was found to be in agreement with the over-all trend for rising boundaries to occur after Group IIIB. The partial phase diagram is shown in Fig. 102. The alpha phase forms by the peritectoid reaction

at $1070 \pm 10^\circ\text{C}$, where the numbers in parentheses refer to the composition of the phase concerned in atomic per cent of indium.

¹⁵E. Raub and M. Engel, Z. Metallkunde 39, 172 (1948).

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Fig. 102. Partial Phase Diagram for the In-Zr System.

At temperatures above 1070°C, the beta phase is in equilibrium with the first intermediate phase, which has been called gamma. The solubility of the beta increases with increasing temperature from 10% indium at 1070°C to 16.5% indium at 1300°C, which is the maximum temperature investigated. The phase boundaries drawn above this temperature are purely hypothetical ones deduced only from the appearance of cast microstructures. As an example, the microstructure shown in Fig. 103 illustrates the eutectic in a hypereutectic alloy containing 23 at. % indium. This eutectic

structure is believed to result from a reaction between beta and gamma phases in the vicinity of 21 to 22% indium. On the basis of the directions of the boundaries $[\beta/(\beta + \gamma)]$ and $[\gamma/(\beta + \gamma)]$, which would intersect if extrapolated to 1500°C, the temperature of this reaction would be placed between 1300 and 1500°C.

The appearance of the quenched alloys in the beta-phase region varied widely, depending upon the indium content and the nature of the transformation in quenching. The following sequence of microstructures was observed with increasing

indium: (1) large serrated grains, (2) basket weave, (3) acicular, and (4) a nucleated, radial structure growing from the former beta grain boundaries. When alloys of the same composition as that of the beta solid solution are quenched from lower temperatures, isothermal alpha grains are observed in a matrix of transformed beta. The appearance of the isothermal alpha grains is shown in Fig. 104. On the basis of quenching results, the $[\beta/(\alpha + \beta)]$

Fig. 103. Microstructure of Cast In-Zr Alloy (23 at. % Indium) Showing $(\beta + \gamma)$ Eutectic in Primary Crystals of Gamma Phase. Etchant: 46% H_2O , 46% HNO_3 , 8% HF . 1500X. Reduced 31%.

Fig. 104. Microstructure of an $(\alpha + \beta)$ Alloy (9.34 at. % Indium) in the In-Zr System Annealed for Five Days at $1060^\circ C$. Etchant: 46% H_2O , 46% HNO_3 , 8% HF . Polarized light. 100X. Reduced 30%.

phase boundary has been drawn in the phase diagram. The upper boundary of the $(\alpha + \beta)$ region is now reasonably well established, but the lower boundary has not been consistent throughout. The difficulty has now been related to a particular batch of crystal-bar zirconium, previously identified as No. 4, whose iron content is believed to be variable.

In the diagram, the $[\alpha/(\alpha + \beta)]$ boundary has been drawn, ignoring the results of the alloys made from this particular batch of zirconium. At the present time new castings have not yet been prepared to verify this boundary, and it has therefore been drawn as a dashed line to indicate its approximate nature.

The microstructures in the $(\alpha + \gamma)$ region were of interest because they resemble in some ways the eutectoid structures; this resemblance caused confusion at the beginning of the work. Figure 105 illustrates the appearance of one of these alloys. The structure is a Widmanstätten pattern of gamma-phase platelets in an alpha-phase matrix. The $(\alpha + \gamma)$ boundary decreases in solubility with temperature and in the diagram has been drawn by means of a relation of the type

$$\ln [In] = \frac{\Delta H}{RT} + \text{a constant},$$

where $[In]$ represents composition in atomic per cent indium. The curve has been dashed, since the results are not yet complete and the actual metallographic specimens have not been analyzed for indium content. The appearance of the gamma phase in the alpha matrix changes to that shown in Fig. 106 as the $(\alpha + \gamma)$ phase boundary is approached. The dark particles in the alpha-phase boundaries are presumed to be gamma, and since the amount of this phase and the location in the boundaries agree with what might be expected of gamma, alloys of this type have been placed in the $(\alpha + \gamma)$ region.

The gamma phase has been investigated by x-ray diffraction, and its crystal structure was found to be face-centered cubic with a lattice spacing of $4.45 \text{ \AA}$ and an x-ray density of 7.3 g/cc . Examination of the two-phase alloys in the $(\alpha + \gamma)$ region revealed no other phases than cp hexagonal zirconium solid solution and the face-centered-cubic gamma phase.

Fig. 105. Microstructure of In-Zr Alloy (9.4 at. % Indium) Showing Needle-like Gamma Phase in Alpha Matrix. (a) 38 days at 695°C. (b) 41 days at 600°C. Etchant: 46% H₂O, 46% HNO₃, 8% HF. 1300X. Reduced 31%.

The Pb-Zr System

G. D. Kneip, Jr. J. O. Betterton, Jr.

Technique. Alloys in the range of 0 to 10 at. % lead were successfully cast by the same arc-melting scheme as that used for previous phase-diagram work. It was found that remelting the ingots 10 to 12 times produced ingots with a negligible amount of segregation. The ingots were rolled to foil and cut up half way through the casting step to ensure thorough mixing.

The hardness of the cast alloys extrapolated to approximately 85 Vickers hardness, indicating very little contamination during casting.

Fig. 106. Microstructure of In-Zr Alloy (2 at. % Indium) Illustrating Appearance of Small Amounts of Gamma Phase in Boundaries of Alpha Grains. Annealed for 37 days at 553°C. Etchant: 46% H₂O, 46% HNO₃, 8% HF. 500X. Reduced 33%.

The ingots were cold-worked by rolling to $\frac{1}{4}$ - to $\frac{3}{8}$ -in.-dia rods and vacuum-annealing for 1 hr at 1000°C to remove contaminating gases prior to the 1100°C homogenizing anneal.

All alloys were cold-worked by hammering and degassed by vacuum-annealing for 15 to 20 min at the same temperatures as those used for the isothermal annealing treatments before they were sealed off in capsules. When several alloys were to be given the same annealing treatment, they were wrapped separately in zirconium foil (molybdenum for temperatures above 1000°C) and sealed into one capsule. No interaction between alloys was found when this was done. The minimum annealing times used at various temperatures, listed below, were found to produce regular isothermal structures in all cases.

Annealing Temperature (°C)	Annealing Time (days)
1100	7
1000	6
950	10
900	12
850	14

A reagent consisting of 48% nitric acid, 48% water, and 4% hydrofluoric acid was found to be a suitable etchant for the metallographic work.

The Phase Diagram. A tentative phase diagram for the $\alpha \rightarrow \beta$ transition region of the Pb-Zr system is presented in Fig. 107. The points in this diagram are based on the calculated compositions of the alloys and may differ slightly when the chemical analyses are completed.

The principal feature of this portion of the diagram is the peritectoid reaction $\beta + \gamma \rightarrow \alpha$ at $900 \pm 25^\circ\text{C}$. The maximum solubility of lead in α -zirconium occurs at the peritectoid temperature and is 6 ± 1 at. %. The solubility of lead in β -zirconium is 4.5 ± 1 at. % at this temperature.

Since very few experimental points are available at present to establish the $\alpha/(\alpha + \gamma)$ boundary, the boundary shown was calculated from ideal solution theory by using a heat of reaction of 9140 cal/mole. This value was obtained by subtracting the heat of the zirconium $\alpha \rightarrow \beta$ transition from the heat of reaction at the $\beta/(\beta + \gamma)$ boundary.

The Sb-Zr System

W. M. Spicer J. O. Betterton, Jr.

The first investigation of Sb-Zr alloys was made by Russi and Wilhelm,¹⁶ who showed that the

¹⁶R. F. Russi, Jr. and H. A. Wilhelm, *Constitution Diagram of the Antimony-Zirconium Alloy System*, ISC-204 (Aug. 1951).

Fig. 107. Zirconium $\alpha \rightarrow \beta$ Transition Region of the Zr-Pb Phase Diagram.

temperature of the $\alpha \rightarrow \beta$ transition of zirconium was raised by additions of antimony. The general form of the zirconium-rich end of the system was shown to consist of a eutectic reaction between the first intermediate phase Zr_2Sb and β -zirconium solid solution of about 11 at. % antimony. The composition of this eutectic was found to be 17.5 at. % antimony, with a temperature of 1430°C . An interesting feature of the Sb-Zr system is the favorable aqueous corrosion resistance for low-antimony alloys reported by Peterson and Russi.¹⁷ This is in agreement with the corrosion theory of Chirigos and Thomas¹⁸ concerning the effects of different elements on the corrosion resistance of zirconium.

At Oak Ridge National Laboratory this system is part of a series of experiments in which B-subgroup elements of the same Long Period as zirconium are being added to zirconium. A study was made of the constitution of alloys with less than 5 at. % antimony between the temperatures 800 and 1300°C . The alloys were made by arc-casting antimony of 99.95% purity (supplied by Johnson, Matthey, and Co., Inc.) and grade 1 zirconium crystal bar. The same general techniques were used for these alloys as those for the previous ones with the exception that, whenever convenient, more than one alloy was sealed in the same capsule. The tendency to exchange alloying constituent was not observed either by weight changes or local segregation, and the method was satisfactory in this system. Care was taken, however, to ensure that all the alloys were in the zone of minimum thermal gradient in the furnace. Calibrated thermocouple measurements and furnaces whose temperature gradients were known to be small were used throughout the work.

After arc-casting, the alloys were homogenized for six days at 1100°C . The annealing times at other temperatures varied as follows: 1 hr, 1300°C ; 5 hr, 1260°C ; 2 days, 1200°C ; 14 days, 800 to 950°C . For low-antimony alloys the etching reagent 46% H_2O -46% HNO_3 -8% HF was found to be satisfactory, although the compound phase was darkened and etched unevenly. In critical cases when only a small amount of compound was to be

¹⁷D. Peterson and R. F. Russi, Jr., *Semi-Annual Progress Report in Metallurgy for Period April 1, 1951-September 30, 1951*, ISC-203, p 37.

¹⁸J. Chirigos and D. E. Thomas, *The Mechanism of Oxidation and Corrosion of Zirconium*, WAPD-53 (April 11, 1952).

METALLURGY PROGRESS REPORT

identified, use of a carefully hand-polished surface was found to be more satisfactory for determining the exact amount of compound present.

The new, partial equilibrium diagram for the zirconium-rich end of the system is given in Fig. 108. The peritectoid reaction $\beta + \text{Zr}_2\text{Sb} \rightleftharpoons \alpha$ was confirmed, although present work indicates that the temperature of this reaction is lower than that proposed by Russi and Wilhelm and that the solid solubility of antimony in zirconium is quite restricted. The temperature of the peritectic reaction is thought to be close to 870°C for the following reason. The critical anneal which was used to establish this temperature was run, first, for six days at 871°C and then for seven days at 869°C. Alloys 0.3 and 0.4 (the numbers refer to the antimony content expressed in atomic percentage) were of $(\alpha + \beta)$ microstructure but apparently the small variation in temperature was sufficient to put them in the $(\beta + \gamma)$ region for part of the time. Small traces of gamma phase were also observed in these alloys.

It was found possible to draw the curves of the diagram by the following procedure, which was

advantageous because of the smallness of the $(\alpha + \beta)$ region and because only two temperatures were investigated on the $[\alpha/(\alpha + \text{Zr}_2\text{Sb})]$ boundary. An expression of the type

$$\ln [\text{Sb}] = \frac{\Delta H}{RT} + \text{a constant}$$

was fitted graphically to the experimental points of the $[\beta/(\beta + \text{Zr}_2\text{Sb})]$ boundary, and the composition of the beta phase at 870°C was read from this graph to be 0.11 at. % antimony. The ideal solution formula

$$\ln \frac{[\text{Zr}]_\beta}{[\text{Zr}]_\alpha} = \frac{L}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)$$

$$= \frac{710}{1.986} \left(\frac{1}{1138} - \frac{1}{1143} \right)$$

was used to estimate the composition of the alpha phase at the peritectoid horizontal. The result, 0.75 at. % antimony, agrees well with the experimental results, for example, the value obtained from studies of the microstructure of alloy 0.75 at 856°C. The $[\alpha/(\alpha + \text{Zr}_2\text{Sb})]$ boundary was then drawn by using a ΔH that was obtained by subtracting the heat of the transition in pure zirconium from the heat of solution (30,300 cal/mole) of the Zr_2Sb compound in the beta phase, even though the assumption that this heat of solution is constant with temperature is not strictly correct.

Typical microstructures of these alloys are shown in Figs. 109 and 110. In Fig. 109 is shown the alloy 0.3 after it was annealed at five different temperatures: 1100, 901, 869, 856, and 800°C. Figure 109a, a photomicrograph of the specimen annealed at 1100°C, shows the transformation structure quenched from the homogeneous beta region. The microstructure of this alloy at 901°C is largely beta, with a trace of Zr_2Sb phase particles, but at 869°C the alloy is in the $(\alpha + \beta)$ region. At 856°C, the microstructure shows a trace of beta phase in grain boundaries of the alpha grains. At 800°C the microstructure of this alloy shows traces of Zr_2Sb phase finely distributed in the larger, alpha-grain matrix. Figure 110 shows the microstructure of the alloy 1.6 annealed at the five different temperatures, 1200, 1100, 901, 856, and 800°C, in the phase regions homogeneous β , $\beta + \text{Zr}_2\text{Sb}$, $\beta + \text{Zr}_2\text{Sb}$, $\alpha + \text{Zr}_2\text{Sb}$, and $\alpha + \text{Zr}_2\text{Sb}$, respectively.

Fig. 108. Partial Phase Diagram of the Sb-Zr System.

PERIOD ENDING APRIL 10, 1954

Fig. 109. Typical Microstructures of an Sb-Zr Alloy (0.3 at. % Antimony). (a) Transformed beta, 1093°C, 500X. (b) Beta plus trace of Zr_2Sb , 901°C, 500X. (c) Alpha plus beta, 870°C, 500X. (d) Alpha plus trace of beta, 856°C, 500X. (e) Alpha plus trace of Zr_2Sb , 800°C, 1200X. Reduced 31.5%.

METALLURGY PROGRESS REPORT

Fig. 110. Typical Microstructures of an Sb-Zr Alloy (1.6 at. % Antimony). (a) Transformed beta, 1195°C, 500X. (b) Beta plus trace of Zr_2Sb , 1093°C, 500X. (c) Beta plus Zr_2Sb , 901°C, 500X. (d) Alpha plus Zr_2Sb , 856°C, 500X. (e) Alpha plus Zr_2Sb , cathodic vacuum etching, 800°C, 150X. Reduced 30%.

The Zr_2Sb particles in the $(\alpha + Zr_2Sb)$ region were so small and uneven in etching characteristic with chemical reagents that it was not easy to determine whether the smallest particles were really Zr_2Sb . The last photograph on Fig. 110 was taken by F. Cain, Jr., of Westinghouse Atomic Power Division, using the method of cathodic vacuum etching during which the surface is bombarded by gaseous ions in vacuum.¹⁹ It will be seen that this result was in good agreement with

the chemical-etching results in the $(\alpha + Zr_2Sb)$ region and that it supports the interpretation of the small particles as being Zr_2Sb .

It should be noted on Fig. 109 that the alloys 0.3 and 0.4, when annealed at 856°C (12°C below the $\alpha \rightarrow \beta$ transition in pure zirconium), still contain small amounts of the beta phase. This condition is believed to be a result of impurities in the zirconium crystal bar; the effects of these impurities will become more significant as the proportion of antimony is reduced. A new series of alloys made with a still better grade of zirconium is being cast, and it is hoped that these new alloys will correct this situation.

¹⁹T. R. Padden and F. Cain, Jr., *A Modified Cathodic Vacuum Etching Procedure with Versatile Metallographic Applications*, WAPD-83 (May 25, 1953).