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ARMOUR RESEARCH FOUNDATION
of
ILLINOIS INSTITUTE OF TECHNOLOGY
Technology Center
Chicago 16, Illinois

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Project No. 90-934 B
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PHASE DIAGRAMS OF ZIRCONIUM-BASE
BINARY ALLOYS

A Study of the Systems of Zirconium
with Tin, Molybdenum, Copper, Wolfram, Chromium,
Silicon, Aluminum, and Magnesium

Final Report
(C00-89)

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for

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PHASE DIAGRAMS OF ZIRCONIUM-BASE BINARY ALLOYS

A Study of the Systems of Zirconium with Tin, Molybdenum, Copper, Wolfram, Chromium, Silicon, Aluminum, and Magnesium

ABSTRACT

High-purity alloys of the various systems were arc melted, annealed, and subjected to thermal analysis under special protective conditions. Phase diagrams were determined for all of the systems except zirconium-magnesium.

1. Zirconium-Tin: Three intermediate phases, designated Zr_4Sn (24.55% Sn), Zr_5Sn_3 (43.84% Sn), and $ZrSn$ (56.55% Sn) were found, of which Zr_5Sn_3 melts with an open maximum at 1985°C. Zr_4Sn is formed by the peritectoid reaction: $\beta + Zr_5Sn_3 \rightleftharpoons Zr_4Sn$ at 1325°C, while the peritectic $Zr_5Sn_3 + \text{melt (83% Sn)} \rightleftharpoons ZrSn$ occurs at 1140°C. Beta solid solution and Zr_5Sn_3 form a eutectic at 23.5% Sn and 1590°C. Beta dissolves a maximum of 21% Sn at this temperature. The peritectoid $\beta + Zr_4Sn \rightleftharpoons \alpha$ occurs at 980°C and 9% Sn. 6.5% Sn is soluble in beta zirconium at this temperature. The solubility of tin in alpha decreases to about 1.5% at 600°C. Tin displays no detectable solubility for zirconium. The eutectic or peritectic between tin and $ZrSn$ lies at higher tin content than 99.5%, and not more than 1°C above or below the melting point of tin.
2. Zirconium-Molybdenum: One intermediate phase, $ZrMo_2$ (67.78% Mo) exists. It is formed by the peritectic $Mo_{ss} + \text{melt (58% Mo)} \rightleftharpoons ZrMo_2$ at 1880°C. Beta solid solution and $ZrMo_2$ form a eutectic at 31% Mo and 1520°C. Beta dissolves 22% Mo at this temperature. The eutectoid $\beta \rightleftharpoons \alpha + ZrMo_2$ exists at 7.5% Mo and 780°C. Less than 0.18% Mo is soluble in alpha zirconium. Less than 10% zirconium is soluble in molybdenum.
3. Zirconium-Copper: Five intermediate phases, designated Zr_2Cu (25.83% Cu), $ZrCu$ (41.06% Cu), Zr_2Cu_3 (51.09% Cu), Zr_2Cu_5 (63.52% Cu), and $ZrCu_3$ (67.63% Cu) were found. Of these, Zr_2Cu , $ZrCu$, Zr_2Cu_3 , and $ZrCu_3$ melt with open maxima at 1000°, 935°, 895°, and 1100°C, respectively. Zr_2Cu_5 results from a peritectic reaction between $ZrCu_3$ and melt (61% Cu) at 1070°C. Five eutectics are formed: β - Zr_2Cu at 21% Cu and 995°C, Zr_2Cu - $ZrCu$ at 37% Cu and 928°C, $ZrCu$ - Zr_2Cu_3 at 47% Cu and 890°C, Zr_2Cu_3 - Zr_2Cu_5 at 53% Cu and 885°C, and $ZrCu_3$ -Cu at 91% Cu and 965°C. Beta dissolves 3.8% Cu at 995°C. The eutectoid $\beta \rightleftharpoons \alpha + Zr_2Cu$ exists at 1.6% Cu and 822°C. Less than 0.18% Cu is soluble in alpha zirconium. The solubility of zirconium in copper appears to be less than 1%.

4. Zirconium-Wolfram: One intermediate phase, ZrW_2 (80.13% W) occurs. It is formed by the peritectic reaction: $\text{W}_{\text{ss}} + \text{melt}(50\% \text{ W}) \rightleftharpoons \text{ZrW}_2$ at approximately 2175°C . Beta solid solution and ZrW_2 form a eutectic at 18% W and 1650°C . Beta dissolves 8% W at this temperature. The eutectoid $\beta \rightleftharpoons \alpha + \text{ZrW}_2$ exists at 0.5% W and 850°C . Less than 0.5% W is soluble in alpha. Less than 10% Zr is soluble in wolfram.
5. Zirconium-Chromium: One intermediate phase, ZrCr_2 (53.28% Cr) melts with an open maximum at 1700°C . Two eutectics are formed: $\beta\text{-ZrCr}_2$ at 18% Cr and 1280°C , and $\text{ZrCr}_2\text{-Cr}_{\text{ss}}$ at 70% Cr and 1635°C . Beta dissolves up to 4.5% Cr at 1280°C . The eutectoid $\beta \rightleftharpoons \alpha + \text{ZrCr}_2$ occurs at 1% Cr and 835°C . Less than 0.28% Cr is soluble in alpha zirconium. Less than 10% Zr is soluble in chromium.
6. Zirconium-Silicon: Seven intermediate phases designated Zr_4Si (7.14% Si), Zr_2Si (13.33% Si), Zr_3Si_2 (17.02% Si), Zr_4Si_3 (18.74% Si), Zr_6Si_5 (20.40% Si), ZrSi (23.53% Si), and ZrSi_2 (38.09% Si) were found. Only Zr_6Si_5 melts with an open maximum at 2250°C ; the remainder are formed peritectically. The peritectic temperatures and compositions of the reacting melts are: for Zr_4Si , 1630°C and 4.5% Si; for Zr_2Si , 2110°C and 9% Si; for Zr_3Si_2 , 2210°C and 14.4% Si; for Zr_4Si_3 , 2225°C and 18% Si; for ZrSi , 2095°C and 24.2% Si; and for ZrSi_2 , 1520°C and 46% Si. Two eutectics are formed: $\beta\text{-Zr}_4\text{Si}$ at 2.9% Si and 1610°C , and $\text{ZrSi}_2\text{-Si}$ at 75% Si and 1355°C . The solubility of silicon in beta zirconium is less than 0.2%, and is less than 0.1% in alpha. The effect of silicon on the allotropic transformation of zirconium is undetermined, but proved to be very slight. Less than 5% zirconium is soluble in silicon.
7. Zirconium-Aluminum: Nine intermediate phases exist. These were designated Zr_3Al (8.80% Al), Zr_2Al (12.88% Al), Zr_5Al_3 (15.07% Al), Zr_3Al_2 (16.46% Al), Zr_4Al_3 (18.15% Al), ZrAl (22.82% Al), Zr_2Al_3 (30.72% Al), ZrAl_2 (37.16% Al), and ZrAl_3 (47.00% Al). Three of these, Zr_4Al_3 , ZrAl_2 , and ZrAl_3 , melt with open maxima at 1530° , 1645° , and 1580°C , respectively. Zr_5Al_3 , Zr_3Al_2 and Zr_2Al_3 are formed peritectically; the temperatures and compositions of reacting liquids are, for Zr_5Al_3 , 1395°C and 15% Al; for Zr_3Al_2 , 1480°C and 16% Al; and for Zr_2Al_3 , 1595°C and 30% Al. Zr_3Al , Zr_2Al , and ZrAl are formed in the solid state by peritectoid reactions at 975° , 1250° , and 1250°C , respectively. Three eutectics are formed; $\beta\text{-Zr}_5\text{Al}_3$ at 11% Al and 1350°C , $\text{Zr}_4\text{Al}_3\text{-Zr}_2\text{Al}_3$ at 22% Al and 1480°C , and $\text{ZrAl}_2\text{-ZrAl}_3$ at 45% Al and 1490°C . Beta dissolves 9.5% Al at 1350°C . The peritectoid reaction $\beta + \text{Zr}_3\text{Al} \rightleftharpoons \alpha$ occurs at 940°C and 3.5% Al. The solubility of aluminum in alpha decreases to 0.5% at 700°C . Zr_5Al_3 undergoes a reaction in the solid state, probably decomposing eutectoidally. The solid solution of zirconium in aluminum is very limited. Prior work is accepted in this high-aluminum range.
8. Zirconium-Magnesium: Since only very limited and uncontrolled alloying of these two metals could be obtained, no phase diagram studies were possible. The special experimental techniques applied are described.

PHASE DIAGRAMS OF ZIRCONIUM-BASE BINARY ALLOYS

A Study of the Systems of Zirconium with Tin, Molybdenum, Copper, Wolfram, Chromium, Silicon, Aluminum, and Magnesium

I. INTRODUCTION

This report constitutes a summary of investigations conducted under Contract No. AT(11-1)-149 toward determination of the phase diagrams of the following zirconium binary systems:

Priority	System	Contracted Range of Alloy	
		Atomic %	Weight %
1	Zirconium-Tin	0-100	0-100
2	Zirconium-Molybdenum	0- 50	0- 51.26
3	Zirconium-Copper	0- 50	0- 41.06
4	Zirconium-Wolfram	0- 50	0- 66.83
5	Zirconium-Chromium	0- 50	0- 36.31
6	Zirconium-Silicon	0- 50	0- 23.53
7	Zirconium-Aluminum	0-100	0-100
8	Zirconium-Magnesium	0- 50	0- 21.05

The investigation of each system except zirconium-magnesium was begun by preparing a set of arc-cast alloys covering the complete range of binary composition. This was deemed advisable in order that a clear picture of the phases participating in equilibrium at the highest alloy compositions called for by the contract be known. In general, then, the complete diagram of each system was determined to a degree of accuracy more or less depending upon the individual system. In the case of a system involving relatively complicated phase relationships in the region beyond the contracted alloy range, experimentation in this region was limited to achieve a fair degree of accuracy because unwarranted time and expense would otherwise be involved.

Work was then concentrated to achieve the highest degree of accuracy in the contracted alloy range of each system. Here again judgment was exercised in determining the scope of the work. As a general rule, the precise investigation was carried on to include the next intermediate phase beyond the intended (generally 50 at.%) alloy range, thus providing a reasonably bounded partial diagram.

The temperature range investigated was from 600°C to the solidus, and in some cases the liquidus, temperatures. Due to the very low rate of obtaining equilibrium at temperatures of 600°C and below for most of the zirconium binary systems, it was decided not to carry the investigation to lower temperature levels.

Although not specified contractually, the crystal structure of intermediate phases was investigated in a number of cases. This phase of the work was carried as far as the time and expense involved seemed to warrant.

The principal tool in determination of the diagrams was metallographic examination of specimens quenched after isothermal annealing. It was felt that most solid state thermal analysis techniques and dilatometry would be subject to error in certain of the systems, due to the very low diffusion rates of these alloys in the transformation range. X-ray diffraction analysis also suffers limitations in phase boundary determinations for most zirconium-rich alloys because, in certain composition-temperature areas, the decomposition of the body centered cubic phase into acicular alpha (hexagonal close packed) phase cannot be suppressed, no matter how drastic the quenching. X-ray diffraction techniques cannot differentiate between isothermally formed alpha and this acicular transformation alpha, and therefore is not useful in the identification of phases coexisting in these ranges.

This report is arranged to cover first the materials, equipment, and experimental techniques employed in the investigation. The data and results for the individual binary systems are then presented, and are summarized in the final section of the report.

II. MATERIALS

A. Zirconium

Zirconium crystal bar, produced by the deposition of the metal on a hot filament by decomposition of a volatile iodide, was used for all of these studies. This was also "low-hafnium" grade material. Initially, thirty pounds of Westinghouse "Grade 3" crystal bar and one pound of Foote "Grade 1" material, for comparison, were obtained from the Atomic Energy Commission. Normally the "Grade 1" zirconium would be purer and possess better properties than "Grade 3" metal from the same producer. In the case of the materials available for this work, however, preliminary tests showed that the as-received Westinghouse "Grade 3" bar was softer, cleaner microstructurally, and more amenable to cold working than the single bar of Foote "Grade 1" zirconium. Accordingly, the overall program was based on alloys prepared from "Grade 3" zirconium. This has some bearing on the experimental results, and will be discussed in detail in a later section.

Late in the program, small quantities of Westinghouse "Grade 1" crystal bar were obtained for the purpose of rechecking certain questionable phase boundaries, and this will be discussed under the results for the appropriate systems.

Cross sectional hardness values for five random "Grade 3" crystal bars and the "Grade 1" bar originally received are tabulated in Table I.

TABLE I
HARDNESS OF ZIRCONIUM CRYSTAL BAR, AS RECEIVED

Bar No.	Grade	Avg DPH*	Max & Min DPH	
A-4	3	62.5	67.0	57.5
A-25	3	62.7	71.9	56.5
A-46	3	67.9	78.8	54.7
A-72	3	63.1	66.8	57.9
A-91	3	60.7	64.3	56.9
A-15	1	94.4	96.7	92.0

*Vickers Diamond Pyramid Hardness, 10 kg Load

No manufacturer's analysis could be obtained on the lots of zirconium employed. A number of spectrographic checks were run on the "Grade 3" zirconium, which indicated slight variations from bar to bar. A representative analysis is listed below:

TABLE II
SPECTROCHEMICAL ANALYSIS* OF WESTINGHOUSE "GRADE 3" ZIRCONIUM
CRYSTAL BAR, AS-RECEIVED

Element	Concentration, %
Al	0.007
Cr	0.002
Fe	0.03
Hf	<0.05
Mg	0.0001
Ni	0.007
Ti	0.013
N	0.0087 (volumetric)
O	0.01 (gravimetric)
C	<0.01 (gravimetric)

*Obtained from the Argonne National Laboratory, Chicago, Illinois.

A supply of Bureau of Mines magnesium-reduced zirconium was obtained for some preliminary melting work, manufacture of heat treating cans, and miscellaneous experiments. None of the alloys for the phase diagram program were prepared from this material.

B. Preparation of Zirconium Melting Stock

The zirconium crystal bar, as received, was coated with corrosion product from the standard autoclave test by which its Grade designation is determined. This was cleaned at Argonne National Laboratory by a sand-blasting and HF-HNO₃ pickling technique developed by the Atomic Energy Commission.

The cleaned bars were cold rolled to approximately 1/32 in. sheet strip. The rolled strip was cut to 10 in. lengths and given a brief pickling treatment in 50-50 H₂SO₄ (for iron removal), followed by washing in acetone. The strips were then sheared to approximately 1/4 in. squares, bottled, given a final acetone rinse, dried, and stored for arc furnace charging.

C. Alloying Additions

An effort was made to procure the purest possible supplies of the eight alloy addition metals. A summary of these materials is listed in Table III. Representative or Lot analyses of the metals are tabulated in Table IV.

TABLE III
FORM, SUPPLIER, AND PURITY OF ALLOYING ADDITIONS

Element	Form	Supplier	Nominal Purity, %
Tin	Hemispherical ingots	Vulcan Detinning Co.	99.99
Molybdenum	Sheet	Fansteel Metallurgical Corp.	99.9
Copper	Rod, Cathodes	American Smelting & Refining Co.	99.99
Wolfram	Wire, Rod	Fansteel Metallurgical Corp.	99.9
Chromium	Ingot	National Research Corp.	99.5
	Electrolytic plates	Johnson-Matthey & Co.	99.9
Silicon	Pyrolytic crystals	DuPont; Johnson-Matthey Co.	99.99
	Powder	Electro Metallurgical Co.	99.9
Aluminum	Sheet	Aluminum Company of America	99.99
Magnesium	Distilled crystals	Dow Chemical Co.	99.99

TABLE IV
REPRESENTATIVE OR LOT ANALYSES OF ALLOYING ADDITIONS

Tin (Lot 52)		Molybdenum		Copper	
Fe	0.0020%	Mo	99.9+%	Fe	0.0009%
Sb	0.0002	Fe	0.005 max	Sb	0.0001
Pb	nil	Co	0.003 max	Pb	0.0002
Cu	nil	O	0.045 max	Sn	0.0001
				Ni	0.0001
				Bi	0.00001
				As	0.0001
				Te	0.0001

Wolfram		Chromium (NRC)		Chromium (J-M)	
W	99.9+%	C	0.05%	Metallic	<0.005%
R ₂ O ₃	0.02 max	O	0.045	O	0.005-0.015
		N	0.0026	N	0.020-0.035

Silicon (DuPont)		Silicon (Electro Met)	
Ca	0.005%	Ca	Trace to 0.010%
Na	0.005	Fe	0.005-0.015
Cu	0.001	Al	0.02-0.03
Mg	0.001	Mn	0.0005-0.0015
Mn	0.001	Cr	Trace to 0.009
Al	nil	C	0.02-0.04
Fe	0.03	P	0.005-0.010
P	nil	Co + Ni	Trace to 0.004
B	nil	Ti + Zr	0.002-0.005
		O	0.03-0.08

Aluminum		Magnesium	
Si	0.0006%	Al	<0.0001%
Fe	0.0005	Cu	<0.0005
Cu	0.0022	Fe	<0.0004
Mg	0.0003	Mn	<0.0002
Ca	<0.0006	Ni	<0.0004
Na	<0.0005	Pb	<0.001
		Si	<0.001
		Sn	<0.001
		Zn	<0.001
		Ba	<0.0001
		Ca	0.0013
		K	0.010
		Na	0.0037
		Sr	<0.0005

D. Preparation of Alloy Melting Stock

Molybdenum, as 0.003 in., and aluminum, as 0.040 in. sheet, were sheared to pieces approximately $1/4$ in. square, cleaned by several acetone rinses, and bottled for storage prior to arc melting. Tin, as hemispherical ingots, and copper, as $3/8$ in. rod or electrolytic electrodes, were cut in sections, cold rolled to approximately $1/32$ in. sheet strip, then sheared, cleaned, and stored as above. Wolfram, in the form of 0.001 to 0.005 in. wire, was cut to approximately $1/2$ in. lengths, cleaned, and stored. Wolfram charge was also prepared from $1/2$ in. diameter rod by crushing short lengths of the rod to granular form in a hydraulic press, treating for iron removal, rinsing in acetone, and drying. The ingot form of chromium metal was crushed to granular form, as received. When necessary, it was further sized by crushing, treated for iron removal, cleaned in acetone, and stored. The electrolytic chromium flake was sized to about $1/8$ in. granules by crushing in a mortar and pestle. This was then cleaned with acetone prior to storing as charge metal. The acicular silicon crystals were appropriate for arc furnace charge as received. This material was only rinsed with acetone and stored. The other supply of silicon was in the form of 80-mesh powder, which could not be used as such in the arc furnace. The powder was therefore consolidated by pre-melting in an atomic hydrogen arc, and the resulting pieces were crushed to minus- $1/4$ in. granules for charging stock. Magnesium metal, in the form of massive crystals, was put through the rolling mill and crushed, thereby, to approximately $1/4$ in. granular charging stock, which was cleaned, dried, and stored similarly to the other alloy additions.

Special charging forms and techniques, which were necessary in certain cases, are described later in the report under the systems to which they apply.

III. EQUIPMENT AND EXPERIMENTAL TECHNIQUES

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A. Melting of Alloys

1. Arc Melting Furnace

With only a few exceptions, which will be noted in later sections, all of the alloys were arc melted in a nonconsumable electrode furnace. This type of furnace has been used by a number of investigators for titanium alloy preparation (1,2,3,4).

A view of two small arc furnaces and accessory equipment is presented in Fig. 1. Figure 2 is a view of the furnace exploded to show interior features. Figure 3 shows the same furnace assembled and ready for melting. A cross-sectional drawing of the furnace is presented in Fig. 4.

Basically, the furnace consists of three separate parts: the electrode rod, the furnace head, and the furnace base, which contains a spun-copper melting crucible. Each is provided with a circulatory water cooling system. The furnace head and electrode rod are at the same electrical potential above that of the furnace base and crucible, which serve as the other electrode. The leads from the power source are connected to the furnace base and the electrode rod.

The electrode rod is composed of a replaceable 1/2 in. diameter wolfram tip brazed into a copper insert, which in turn is soft soldered into a 7/8 in. diameter copper tube. This tube contains a smaller concentric tube which directs inlet water onto the wolfram tip. The water then exits between the two concentric tubes and out the outlet tube.

The electrode rod enters the furnace head through a flexible metal bellows. This allows both lateral and vertical freedom of motion for the electrode, and provides a hermetic seal for the furnace. The furnace head contains a sight tube, an entry for an ingot turn-over rod, and a light source tube. On the sides are a water inlet and outlet for the cooling jacket and a combined passage for evacuation of the furnace and inlet of helium gas.

The base of the furnace is attached to the furnace table, and contains the spun copper crucible in which ingots are melted. Water is continuously circulated between the two during melting. In assembly, the furnace head is separated from the base by an insulating ring and two Neoprene O-rings, for electrical isolation, and an air-tight seal. Three spring clamps, fastened to the table, fit over the head and hold the entire unit firmly assembled.

A mechanical vacuum pump is used to evacuate the furnace, and high purity helium is released within to replace air and provide an inert and arc-stabilizing melting atmosphere.

Fig. 1

General View of Non-Consumable Electrode Arc Melting
Furnace

18

Fig. 1

Fig. 1
9

19

GUARDIAN BOND
C-McE
FAG-CONTENT U.S.A.

Fig. 2

Arc Melting Furnace Exploded to Show Interior Features

Fig. 2
10

Fig. 3

Arc Melting Furnace Assembled for Melting

Fig. 3
11

1. POWER LEADS
2. WATER-COOLED ELECTRODE
3. WATER INLETS AND OUTLETS
4. METAL BELLOWS
5. RUBBER VACUUM SEALS
6. SIGHT GLASS
7. INGOT TURNOVER ROD
8. ELECTRODE GUIDE NUT
9. CLAMPS (3 AT 120°)
10. WATER-COOLED BRASS HEAD
11. FIBRE INSULATOR
12. VACUUM INLET
13. ARGON INLET
14. SPONGE RUBBER GASKET
15. TRANSITE TABLE TOP
16. WATER-COOLED BRASS BASE
17. TUNGSTEN ELECTRODE TIP
18. SPUN COPPER CRUCIBLE
19. COPPER MELTING BLOCK
20. INGOT

0 1 2 3 4 5
SCALE: INCHES

FIG 4 - NON-CONSUMABLE ELECTRODE ARC FURNACE

Two sizes of furnace were available. One employs an SAE 400 Lincoln Arc Welding DC generator as a power source, and the other an SAE 900 Lincoln Arc Welding DC generator. In general, the smaller furnace was adequate for most of the melting, but in applications where larger ingots were desired or higher melting alloys were encountered, the larger furnace was used.

2. General Melting Practice

Various sizes and shapes of spun copper crucibles were available for the melting program. A copper block, machined to fit snugly in a flat-bottomed crucible, was most universally used. The charge material was melted in a hemispherical cavity in the block. Adjacent to the cavity, a 3/8 in. wolfram stud was provided for striking the arc. With this feature, the arc could be transferred to the charge in the melting cavity without contacting it directly, which obviated a possible source of alloy contamination. The size of ingot prepared varied, but in most cases a 20 gram button was made. The type of crucible, the form, size, and shape of charge material, and the melting conditions were developed by experience with each alloy system.

The steps in the general melting procedure were as follows:

- a. Insert the charge material in the melting cavity and assemble the furnace.
- b. Evacuate the furnace with a mechanical vacuum pump; then flush with Bureau of Mines, 99.99% purity, helium. Circulate hot water during the evacuation period to more rapidly degas the system.
- c. Evacuate again and flush a second time with helium. Set a static atmosphere of helium at about one inch of mercury above atmospheric pressure.
- d. Adjust cold water for proper cooling. Strike the arc on the wolfram stud and transfer the arc to the melting cavity. The power level and melting time vary considerably with the alloy system and composition.
- e. Invert ingot with the turn-over rod and remelt similarly. This is done successively a number of times predetermined for each system and composition range by experiment. Four to eight remelts represent average practice.
- f. Allow ingot to cool to room temperature. Turn off the cold water and circulate hot water to prevent moisture condensation when the furnace is opened. Turn off the hot water and helium and remove the ingot.

Since deviations from the standard melting practice were sometimes necessary, a discussion of the special techniques developed will be included under the sections devoted to the appropriate systems.

B. Heat Treatment

1. Precision Heat Treating Furnaces

Figures 5 and 6 show the majority of furnaces used in the heat treatment phase of the work. Nichrome wound furnaces, both vertical and horizontal type, were used at temperatures up to 950°C. Two Hevi-Duty "Alloy 10" wound furnaces were used for treatments between 1000° and 1250°C. Treatments above 1250°C were made in a small Globar tube furnace. Homogenization treatments, for which accuracy of temperature control was not of prime importance, were carried out in a box-type Globar furnace. All furnaces, except the last mentioned Globar furnace, were tubular, employing a glazed porcelain furnace tube, and had a constant temperature zone at least two inches long.

Temperature control was accomplished with Wheelco Model 252P Capaciline instruments or Leeds & Northrup Micromax controllers, operated in conjunction with Claud S. Gordon Xactlines. Chromel/Alumel thermocouples were employed for temperature control up to 950°C, and platinum/platinum-10% rhodium control couples were used at higher temperatures. An additional thermocouple in each furnace permitted continuous recording of furnace temperature. This was useful in noting any temperature variation which may have occurred overnight or during week-ends. Actual measurement of furnace temperature for phase diagram purposes was made with calibrated couples. Thermocouples of chromel-alumel, and of platinum/platinum-10% rhodium, were calibrated against a platinum/platinum-10% rhodium thermocouple calibrated by the National Bureau of Standards. Temperatures were measured at least twice a day during long-time annealing runs, and at more frequent intervals during short-time anneals. A Leeds & Northrup Model 8662 Precision Potentiometer was employed for all temperature measurements. Temperature control was $\pm 3^\circ\text{C}$ in general, but many anneals were held to smaller temperature variations.

2. Sample Preparation and Annealing

Zirconium-rich alloy ingots were trimmed to provide opposing flat edges and cold pressed in order to work the structures. A homogenization treatment was then carried out in either Vycor or quartz tubes, depending upon the temperature of treatment. The alloys were then reduced by cold rolling as much as the composition permitted, prior to the isothermal equilibrium anneal. An ingot is shown in Fig. 7, after the melting and cold working operations.

Specimens of ductile alloys employed for isothermal anneals were usually about $1/4$ in. x $1/4$ in. x $1/8$ in. in size. Fragments of less ductile alloys having an equivalent volume were used. From two to twenty-five specimens of one system were sealed in a single Vycor or quartz bulb; alloys from different systems were never included in the same bulb. A pure zirconium control sample was included with every heat treatment.

Fig. 5

Banks of Horizontal Precision-Controlled Annealing Furnaces
Also Showing Quenching Tank

26

26

Fig. 5
15

Fig. 6

Bank of Vertical Precision-Controlled Annealing Furnaces
Also Showing Precision Potentiometer

Fig. 6
16

Fig. 7

Steps in the Cold Working of a Zirconium Alloy Ingot
Prior to Heat Treatment

28

INGOT FROM
ARC FURNACE

INGOT WITH
PARALLEL FLATS

INGOT AFTER
COMPRESSION

INGOT AFTER
ROLLING

Fig. 7

Identification of samples was accomplished by stamping, if possible. When this was not feasible, a shadowgraph of the specimens was made by using an overhead light and specimens placed on photographic contact paper. The shadowgraph method of identification proved infallible, and no difficulty was ever encountered in identifying the samples after the annealing treatment and quench.

Samples were sealed in either Vycor or quartz bulbs for the isothermal anneals. Vycor was employed at temperatures up to 1100°C, and above this temperature quartz tubes were used. Liners of 0.003 in. molybdenum sheet were placed in bulbs scheduled for treatment above 1200°C. These liners served the dual purpose of providing specimen protection and physical support to the walls of the quartz tubes. The size of the bulb was dependent upon the size and number of specimens. They were usually from one to three in. long and 1/4 to 1 1/2 in. in diameter.

Treatments up to 950°C were carried out in bulbs sealed under vacuum. Since evacuated bulbs collapsed at higher temperatures, a partial pressure of argon was admitted into the bulbs for heat treatments above 950°C. This partial pressure was controlled to produce a pressure of one atmosphere at the temperature of treatment. A number of preliminary experiments proved argon to be the most satisfactory atmosphere to use in this operation.

Furnace temperatures were held for several hours at the desired level before bulbs were admitted to the furnaces. A maximum of three bulbs were placed in a furnace for an annealing run. At the conclusion of isothermal anneals, specimens were quenched directly from the furnace into quenching tanks (illustrated at the right of Fig. 5). A hinged paddle was used to break the specimen bulbs under water, thus insuring a rapid quench.

Annealing temperatures and times were varied according to the individual binary systems, and will be discussed in connection with each system separately.

C. Incipient Melting Studies

A high temperature vacuum induction furnace, similar to one described by Schramm, Gordon and Kaufmann (5), was used for the determination of solidus curves, eutectic and peritectic horizontals, and the melting points of metals and intermetallic compounds. Figure 8 is a drawing of this furnace, and Fig. 9 is a photograph of the assembled unit. The furnace contains a cylindrical tantalum heating chamber. Stabilized zirconia tubes provide an open passage from the top to a bottom chamber which can accommodate a Silicone or Apiezon oil quenching bath. The specimen is suspended within the heating zone by a 0.020 in. tungsten wire which is supported axially in the furnace by means of a fork attached to a horizontal off-center shaft. After the specimen is heated to any desired temperature, quenching is accomplished by revolving the shaft, allowing the wire to drop off the fork onto a cold bottom plate or into an oil bath.

1. PYREX SIGHT GLASS
2. SIGHT GLASS COVER MECHANISM
3. BRASS CAP; INTERRUPTED SCREW-THREAD
4. COOLING COILS
5. VACUUM OUTLET
6. SPECIMEN HOLDER MECHANISM
7. NEOPRENE GASKET SEAL
8. BRASS FURNACE TOP PLATE
9. ZIRCONIA TUBE
10. VYCOR FURNACE TUBE
11. LUCITE WATER JACKET TUBE
12. BRASS TIE RODS (4)
13. WATER JACKET OUTLET
14. ZIRCONIA POWDER INSULATION
15. SPECIMEN HOLDING WIRE; Mo OR W
16. SPECIMEN
17. HEATER UNIT; Ta OR W
18. ZIRCONIA TUBE AND COVER
19. INDUCTION COIL
20. Mo ROD SUPPORTS FOR HEATER UNIT (3)
21. ZIRCONIA TUBES
22. INSULATING BRICK BASE
23. WATER JACKET INLET
24. WAX SEAL
25. COOLING COILS
26. BRASS FURNACE BOTTOM PLATE
27. ATMOSPHERE INLET
28. FURNACE MOUNTING BLOCKS (4)
29. TRANSITE TABLE
30. QUENCHING JAR
31. SCREW CLAMP DEVICE FOR BOTTOM CAP
32. BRASS BOTTOM CAP

0 1 2 3 4 5
SCALE: INCHES

FIG. 8 -VACUUM INDUCTION FURNACE

Fig. 9

Vacuum Induction Furnace for Incipient Melting Studies

Fig. 9

The furnace is evacuated by a Distillation Products MC-275 oil diffusion pump with a Kinney Model 556 mechanical forepump. The source of power is a 15 KW General Electric high-frequency oscillator. The temperature limitations of the furnace are dictated only by the materials of construction. Temperatures in excess of 2500°C can be attained in a few minutes.

An atmosphere inlet in the lower chamber of the furnace permits rapid cooling of the interior after a heating run. High purity helium gas admitted through this opening will cool the furnace from above 2000°C to blackness in a few minutes.

An optical pyrometer was calibrated over the useful temperature range of the furnace by observing the melting of high-purity gold, copper, nickel, platinum, rhodium and iridium within the heating chamber. These data are summarized in Table V, and the calibration curve is presented in Fig. 10. This curve includes the corrections for the optical pyrometer and the Pyrex sight glass.

TABLE V
TEMPERATURE CALIBRATION FOR INCIPIENT MELTING EQUIPMENT

Metal	Accepted M.P., °C	Observed M.P., °C
Gold	1063.0±0.0	1064
Copper	1083.0±0.1	1088
Nickel	1455 ±1	1448
Platinum	1773.5±1	1720
Rhodium	1966 ±3	1902
Iridium	2454 ±3	2365

The observed figures are averaged from at least twelve trials for each metal. "Brightness" temperatures were reproducible within about ±5°C in these trials.

Separate tests proved that the furnace conditions very nearly approach those of a black-body. Alloys of unknown emissivity and different melting ranges (titanium- and silicon-base alloys) were wired adjacent to platinum and nickel, respectively. No apparent temperature differences between the adjacent specimens were detected up to the melting points of platinum or nickel. Several metals were wired within a small molybdenum cone; these yielded the same observed melting temperatures as those suspended without the cone background. Accordingly, no emissivity corrections have been necessary.

The technique employed for this work was to heat an alloy of given composition until visual signs of melting were observed, then to quench a series of specimens of the same composition from approximately 20°C intervals below the temperature of observed melting. These specimens were then examined microscopically for evidence of incipient melting.

FIG. 10 -TEMPERATURE CALIBRATION CURVE
FOR INCIPIENT MELTING FURNACE.

The accuracy of the method is dependent upon four factors: (1) the human error in optical readings; (2) reliance upon literature values for the melting points of the calibration metals; (3) the approach of the furnace to black-body conditions; and (4) the magnitude of the temperature increments used for quenched specimens. The latter increments probably exceeded temperature errors introduced by the first three factors. The estimated accuracy of determinations up to 2450°C is $\pm 15^{\circ}\text{C}$, providing sufficiently small temperature increments could be used.

D. Thermal Analysis

Thermal analysis studies were carried out in a sealed silica tube induction furnace using platinum/platinum-10% rhodium thermocouples in connection with a Brown Electronik recording potentiometer. The power for melting was supplied by a 35 KW Ajax Induction Heating Unit. A view of the assembled equipment is presented in Fig. 11.

The furnace tube is 3 in. I.D. x 18 in. long, sealed at one end. The rounded bottom of the furnace is filled with bubble alumina, which serves as a base support. A 2 in. I.D. Alundum tube, 6 1/2 in. long, serves as an insulating sleeve. Within this sleeve, and centered with respect to the exterior induction coil, a National Carbon Company Grade AGR graphite crucible is placed. The crucible dimensions are 1 15/16 in. O.D. x 4 in. long, with a melting cavity 7/8 in. diameter and 3 in. deep.

A water cooled brass furnace head is attached to the top of the furnace tube with sealing wax. A removable brass cap contains a sight glass, a water-cooled vacuum-seal entry for a thermocouple tube, and an atmosphere inlet tube. A Neoprene O-ring provides the hermetic seal between the furnace head and cap.

Platinum/platinum-10% rhodium thermocouples were used for all determinations. A stainless steel tube, bearing the insulated thermocouple wires, enters the furnace through the vacuum seal in the cap. At the lower end of the stainless tube, a machined graphite protection tube is attached by means of set screws. Double protection is provided by fine tubes of either quartz or high-fired alumina within the graphite tube. The inner tubes are sealed at the couple bead to provide a second barrier in case any of the melt should penetrate the graphite. Also, any tendency for graphite to contaminate the couple at the operating temperatures is obviated by this precaution.

The whole thermocouple assembly could be moved up and down through the vacuum seal, allowing the couple to be immersed or withdrawn from the molten bath at the appropriate times.

The procedure for a complete thermal analysis run is as follows:

Fig. 11

Assembled Thermal Analysis Unit

Fig. 11
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1. After the alloy has been charged and the furnace assembled, the system is evacuated. When the evacuation is complete, the furnace is flushed with Bureau of Mines Grade A helium. This step is repeated at least twice.
2. A helium atmosphere of 3 in. of mercury above atmosphere is maintained in the furnace. The thermocouple leads are attached to the recording instrument and the thermocouple is fixed in the up position.
3. The induction heating unit is then energized and the charge is rapidly melted. This can be detected visually through the sight glass. The bath temperature is measured with an optical pyrometer before the thermocouple is immersed, so that the safe operating temperature for platinum/platinum-10% rhodium is not exceeded.
4. When the proper temperature has been reached, the recording instrument is turned on and the thermocouple assembly is lowered into the melt.
5. At least two heating and cooling curves are obtained for each alloy. The rates of temperature change are controlled by varying the input power.
6. When the last heating curve is complete, the thermocouple is raised out of the bath and the induction unit turned off. The alloy is allowed to cool to room temperature under a helium atmosphere.

The thermal arrests are automatically recorded by the electronic recorder which plots one point per second. Conversion to corrected temperature is accomplished after each run by impressing the voltage necessary to match the arrest on the chart with a Leeds & Northrup Precision Potentiometer.

All of the alloys for thermal analysis were previously melted in the non-consumable electrode arc melting furnace to insure homogeneity. Normally, 50 to 100 gram melts (depending upon their specific gravity) were employed to yield a fairly standard bath volume.

Graphite contamination of the alloys was quite low due to the short time required for two heating and cooling cycles. Chemical analyses were made after thermal analysis of selected alloys in the various binary systems. Carbon contents averaged about 0.05%. This level of carbon contamination had little effect on the melting temperatures determined; very close checks with temperature values determined for the same alloys in the incipient melting furnace (which employs no carbon) corroborate this fact.

E. Metallographic Procedure

by C. A. Johnson

The metallographic procedure for the preparation of zirconium and zirconium-base alloys has been somewhat standardized.

An abrasive belt, 120 grit silicon carbide, was used to prepare the preliminary flat surface. Silicon carbide papers (280, 320, 400, 600 grits) produced the best results on samples containing gross amounts of intermetallic compound. The alundum papers had a tendency to crumble these hard and brittle phases. Silicon carbide papers were used for rough polishing samples of all compositions in the zirconium-wolfram, zirconium-chromium, and zirconium-silicon systems. Alundum papers (1, 1/0, 2/0, 3/0) proved satisfactory for samples of the other binary alloys.

Two steps were used in the final stage of polishing. Diamond compound (5-8 microns) was used on the first wheel, with airplane silk as a covering, and kerosene as the lubricant. When any deep scratches resulted from the use of this wheel, it was necessary to use a billiard cloth covered wheel charged with diamond. It was observed that these softer cloths had a tendency to relief polish, whereas the hard cloth backing minimized this.

Synthetic sapphire, gamma phase, was employed as the polishing medium on the final wheel. This abrasive, known by the name Linde B, is manufactured by the Linde Air Products Company. Adolph Buehler Microcloth was used as the wheel covering, and water as a lubricant.

The etchant which proved most generally useful was 60 cc glycerine, 20 cc HNO_3 , 20 cc HF. The reaction rate could be increased by heating the sample in a stream of hot water, or decreased by chilling the specimen. The etchant composition was also varied at times to obtain the desired control. Table VI summarizes general etching procedures for the zirconium binary alloys.

F. Analytical Procedures

by W. A. Dupraw

The determination of a phase diagram can be, at best, only as precise as the precision of its coordinates, temperature and composition. Chemical analysis must therefore be obtained with the greatest care. Since the determination of other elements alloyed with zirconium is a fairly new field, it seems advisable to summarize the analytical techniques employed for the eight binary systems of this investigation. These analytical procedures have been checked with metallic increments added to and recovered from high purity zirconium.

Dissolution of zirconium and zirconium alloys is not easy. Both zirconium and alloyed zirconium respond slowly to attack by aqua regia and very rapidly to an attack by equal parts of nitric and hydrofluoric acids. Following either acid attack the solution must be evaporated to copious fumes of sulfuric anhydride to effect complete removal of all fluorides and nitrates. Neither zirconium nor any of the zirconium alloys respond to fusion attack regardless of the flux selected.

TABLE VI
ETCHANTS EMPLOYED FOR ZIRCONIUM BINARY ALLOYS

System	60 $\text{C}_3\text{H}_3\text{O}_3$ + 20 HNO_3 + 20 HF	95 H_2O + 3 HNO_3 + 2 HF	$\text{K}_3\text{Fe}(\text{CN})_6$ + KOH + H_2O
Zirconium-Tin	All compositions. Use general Sn etchants for Sn-rich solid solutions.		
Zirconium-Molybdenum	β ; $\alpha + \beta$	$\text{L} + \beta$ $\text{L} + \text{ZrMo}_2$	$\beta + \text{ZrMo}_2$ $\alpha + \text{ZrMo}_2$
Zirconium-Copper	All compositions. Film formed by etching may be removed by rinse in 50 H_2O -50 NH_4OH -25 H_2O_2 .		
Zirconium-Wolfram	All compositions. Dilute etchant if necessary.		
Zirconium-Chromium	β ; $\alpha + \beta$	Used electrolytically. $\text{L} + \text{ZrCr}_2$; $\beta + \text{ZrCr}_2$; $\alpha + \text{ZrCr}_2$; $\gamma + \text{ZrCr}_2$.	
Zirconium-Silicon	All compositions. Some dilution may be necessary if reaction is too fast.		
Zirconium-Aluminum	All compositions. Some dilution may be necessary if reaction is too fast.		
Zirconium-Magnesium	Zr-rich material.		

The alloyed samples submitted for analysis were usually in solid form. Because of the hardness of the samples, they could not be "fined" by conventional sampling techniques; i.e., drilling, filing, sawing, or milling. The silicon series of alloys with a silicon content greater than 10% could be "fined" by crushing the sample in a stellite mortar. Because of the solid form of the submitted samples dissolution of the sample was in many cases a slow process.

The zirconium-wolfram alloys responded readily and rapidly to attack by equal parts of nitric and hydrofluoric acids, in platinum. Fluorides were removed by evaporation with sulfuric acid to copious fumes of sulfuric anhydride before transferring the solution to glassware.

The reaction of zirconium with PO_4^{+++} in 5 to 10% sulfuric acid and the reaction of zirconium with cupferron are separations that proved useful in analyzing some of the zirconium alloys.

1. Tin

Weigh a sample containing not more than 200 mg of Sn into a 500 ml Erlenmeyer flask. Add 15 ml of HBF_4 and 50 ml of 20% H_2SO_4 . Heat gently to dissolve sample. Dilute to 150 ml and add 60 ml of HCl .

Add 2-3 gms of iron powder to reduce Sn^{++++} to Sn^{++} . Titrate Sn^{++} with standard N/10 iodine, protecting from oxidation by conventional means. Standardize N/10 iodine with metallic Sn or preferably against a synthetic Zr-Sn standard.

2. Molybdenum

Dissolve a sample containing not more than 100 mg of Mo in aqua regia. Add 20 ml 1-1 H_2SO_4 and fume to remove chlorides and nitrates. Dilute to 200 ml and precipitate Mo with H_2S as MoS_3 . Filter and ignite at 500°C to MoO_3 .

3. Copper

Weigh a sample containing not more than 250 mg of copper into a 400 ml beaker. Dissolve in 15 ml HBF_4 and 50 ml of 20% H_2SO_4 with gentle heat. Most of the copper will remain insoluble, but all zirconium will dissolve. Proceed with one of the following according to personal preference:

a. Dilute to 300 ml and displace all soluble copper with aluminum. Filter off Cu^0 . Dissolve in HNO_3 .

b. Dilute to 250 ml. Precipitate Cu_2S with $\text{Na}_2\text{S}_2\text{O}_3$ and boil for 15 min. Filter off Cu_2S and ignite to CuO . Dissolve in HNO_3 .

c. Add HNO_3 dropwise to dissolve Cu^0 . Add 50 ml of water and 2-5 gms of tartaric acid to prevent zirconium from hydrolyzing. Boil out NO_2 . Cool.

d. Add 15 ml of 1-1 HNO_3 to dissolve Cu^0 . Add 5 gms of tartaric acid to prevent zirconium from hydrolyzing. Dilute to 100 ml and boil to remove all NO_2 . Cool and electrolyze.

Methods a, b, and c determine copper by the conventional iodide method. Methods a, b, and c were checked with synthetic zirconium-copper samples over an extended copper range.

4. Wolfram

Sample containing not more than 70-80 mg is dissolved in platinum with 5 ml HNO_3 and 5 ml HF , covered immediately, for reaction is very energetic. Add 15 ml 1-1 H_2SO_4 and fume to remove fluorides and nitrates. Precipitate W with α benzoinoxime (6,7). Filter and ignite to WO_3 at temperature not exceeding 700°C . Weigh, "proof out" WO_3 with NH_4OH , correcting for any ZrO_2 .

5. Chromium

Dissolve sample containing 40-70 mg Cr in a 400 ml beaker with 15 ml HBF_4 , 50 ml 20% H_2SO_4 . Heat gently to completely dissolve the sample. Proceed with standard $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-AgNO}_3\text{-KMnO}_4$ method for chromium. HBF_4 offers no interference.

at 130°C

Note: Attention is called to $\text{HBF}_4 \rightarrow \text{BF}_3 + \text{HF}$. Therefore keep heat low. Add H_3BO_3 if necessary to partly control this reaction.

6. Silicon

Dissolve in aqua regia; this is slow and may have to be repeated a few times. Add 20 ml perchloric acid and evaporate to strong fumes. Filter, ignite and fuse with Na_2CO_3 . Extract melt with HCl and fume with 20 ml perchloric acid. Ignite and weigh SiO_2 . "Proof out" with $\text{HF-H}_2\text{SO}_4$, obtaining true silica.

7. Aluminum

Dissolve sample in aqua regia. Add H_2SO_4 and fume thoroughly. Separate zirconium with cupferron, 10% H_2SO_4 , extracting with chloroform. Evaporate aqueous phase, which contains all aluminum, to strong SO_3 fumes, adding HNO_3 to destroy cupferron. Dilute and precipitate aluminum with NH_4OH . Ignite to Al_2O_3 and weigh.

8. Magnesium

Dissolve sample in aqua regia. Add H_2SO_4 and evaporate to strong SO_3 fumes. Separate zirconium with cupferron, 10% H_2SO_4 , and extract with chloroform. Evaporate aqueous phase, which contains all magnesium, to strong SO_3 fumes, adding HNO_3 to destroy cupferron. Dilute and add $(\text{NH}_4)_2\text{HPO}_4$. If any precipitate appears filter off ZrPO_4 , for cupferron separation was improperly made and Zr not quantitatively removed. Precipitate magnesium with NH_4OH . Ignite to $\text{Mg}_2\text{P}_2\text{O}_7$ and weigh.

G. X-Ray Diffraction

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by W. Rostoker

For reasons explained in the Introduction, X-ray diffraction analysis was confined to the investigation of a few intermediate phases in this work.

For the most part, the materials exposed were brittle enough to be very easily powdered with a mortar and pestle. Samples were prepared from those alloys possessing some malleability by filing, with subsequent magnetic removal of any iron particles and annealing to remove cold work. Powdered samples screened to -200 mesh were generally satisfactory. These were mounted in Pyrex capillaries and exposed to CuK_α (nickel-filtered) characteristic radiation for four to eight hours in a 7.18 cm Debye-Scherrer camera.

Films were measured twice and the patterns were indexed with the aid of a specially prepared set of Hull-Davey charts. Lattice parameters were calculated by means of a least squares solution of equations for the interplanar spacings of a number of high angle lines. As a final check of the accuracy of indexing and calculation of parameters, the interplanar spacings were calculated from the deduced lattice parameters and compared with observed values.

IV. PRELIMINARY INVESTIGATIONS AND GENERAL CONSIDERATIONS FOR THE PHASE DIAGRAM PROGRAM

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A. Transformation Study of Unalloyed Zirconium

According to the literature, zirconium undergoes an allotropic transformation, $\alpha(\text{h.c.p.}) \rightleftharpoons \beta(\text{b.c.c.})$ at $862 \pm 5^\circ\text{C}$ (8). It was desired to obtain a rough check on the transformation characteristics of the "Grade 3" crystal bar to be used for the phase diagram program. Five random samples of the "Grade 3" bar and one sample of the Foote "Grade 1" bar were selected. Specimens from the as-received bars, after surface cleaning, were cold pressed about 50%, heated to 1000°C in Vycor bulbs containing a reduced pressure of argon, and water quenched, then reduced an additional 50% by cold rolling. Specimens of each of these six-bar samples were sealed in evacuated Vycor bulbs, annealed for 7 hours at five temperatures between 850° and 890°C , and water quenched. Results of the microscopic examination of these specimens are shown in Table VII.

TABLE VII
TRANSITION DATA FOR ZIRCONIUM METAL

Bar No.	Grade	Quenching Temperature, $^\circ\text{C}$				
		886	878	868	856	851
A-4	3	β	β	β	$\alpha + \beta$	$\alpha + \beta$
A-25	3	β	β	β	$\alpha + \beta$	$\alpha + \beta$
A-46	3	β	β	β	β	$\alpha + \beta$
A-72	3	β	β	β	β	$\alpha + \beta$
A-91	3	β	β	β	$\alpha + \beta$	$\alpha + \beta$
A-15	1	β	β	$\alpha + \beta$	$\alpha + \beta$	$\alpha + \beta$

The beta structure referred to in the table was, of course, seen as transformed beta (acicular alpha) in the quenched specimens. The nature of this transformation product varied from a coarse acicular alpha, in specimens quenched from 886°C , to a coarse-grained "serrated" alpha, resulting from lower quenching temperatures. Alpha, in the table, denotes equiaxed isothermally formed alpha grains.

The coexistence of alpha and beta phases in these structures either indicates lack of equilibrium or means that an equilibrium two-phase field does exist in this zirconium metal due to impurities. To check the former possibility, a series of specimens, pretreated as outlined earlier, was quenched after an increased holding time of 24 hours at 852°C . Examination of these structures showed less beta than was present in the series held for seven hours at 851°C . Apparently, then, the formation of isothermal alpha phase from zirconium pretreated in the beta field is a more time-consuming process than would be expected. However, the evidence is also strong that a narrow $\alpha + \beta$ field in the region of the ideal transition point actually does exist for this zirconium, possibly due to oxygen and/or nitrogen content.

The data in Table VII also indicate that the temperature (or range of temperatures) for allotropic transformation in iodide zirconium varies from bar to bar of the metal. Since the experimental values obtained here fall reasonably close to the accepted literature value of $862 \pm 5^\circ\text{C}$, this figure was used to standardize construction of the phase diagrams.

B. The Melting Point of Zirconium

According to Zwikker, quoted by de Boer (9), the melting point of high purity zirconium is 1857°C . Cubicciotti (10) determined an average value of 1865°C . In order to check the value for the zirconium metal used in this work, about a dozen melting point checks were performed in the incipient melting furnace. An average value of 1852°C was obtained. The maximum variation between individual runs was $\pm 10^\circ\text{C}$. This figure compares favorably with those previously reported, and was adopted in construction of the diagrams as representative of the Westinghouse "Grade 3" crystal bar employed.

C. Melting Practice

More than 20 unalloyed zirconium ingots were melted at the beginning of the program in order to determine optimum conditions for handling this metal. Ingots were melted at least twice without opening the furnace. The "Grade 3" material yielded hardness values in the range 85 to 100 Diamond Pyramid Hardness. (Rockwell B measurements, taken for comparison with the literature, were in the range 35 to $42 R_B$.) The Foote "Grade 1" metal ingots gave hardness values from 98 to 105 DPH. The small increase in hardness of this grade (see Table I, Section II, p. 3) upon melting, compared to the relatively large increase (25 to 40 DPH) for the "Grade 3" metal, may be due to the difference in the as-deposited state of aggregation of the two types of crystal bar. That the increase in hardness for "Grade 3" ingots was not due to contamination in melting was proved by replacing ingots in the furnace and remelting repeatedly without further hardness increase. Spectrographic checks were made on zirconium samples: (1) as-received; (2) as sand blasted and pickled; (3) as rolled and cleaned; (4) as arc melted. No pickup of silicon, iron, copper, or wolfram, which might be sources of contamination during the processing, was detected. Small control melts of unalloyed zirconium were interspersed throughout the entire melting program. Unless hardness checks on these control samples were within the 85 to 100 DPH range, alloys prepared subsequent to the previous acceptable control sample were rejected from the program. Occasional spectrographic checks were also made on the control samples.

D. Comments on the Placement of Phase Boundaries in Zirconium-Rich Alloys

Although iodide crystal bar zirconium is the purest supply of the metal existent, it was the observation of most investigators up to the time this work was undertaken that single phase zirconium was almost never encountered. There is always present some general distribution of small, dark, irregularly shaped particles, seemingly having no crystallographic relation to the matrix zirconium.

In addition, relatively high contents of oxygen and nitrogen can be held in solid solution in zirconium. Certainly the latter elements, and possibly the above mentioned impurity phase, can play a profound rôle in displacing phase boundaries and transformations in the pure metal and dilute alloys.

Some indication of the pickup of gaseous and other impurities by zirconium and its alloys during melting and heat treating operations can be obtained by hardness checks on control samples. Hardness is quite sensitive to such additions. A reasonable policy, then, was simply the rejection of melted or heat treated specimens whose unalloyed control samples showed appreciable hardness increase.

There remained, however, the impurities in the as-received material, which apparently are sufficient to produce frequent anomalous structures after certain treatments. This is evident from the wide transformation range of magnesium-reduced zirconium in comparison with that of iodide metal. As stated earlier, even various iodide bars yield appreciably different transformation ranges and all the evidence points to the existence of a two-phase $\alpha + \beta$ field near the ideal transformation point of this metal because of its impurities.

It was not surprising, then, that certain distortions of phase boundaries, and even anomalous structures in the dilute alloy regions of zirconium binary systems, were encountered. The diagram features affected by these factors were $\beta/\alpha + \beta$ and $\alpha/\alpha + \beta$ boundaries, the eutectoid or peritectoid compositions, and temperatures which occur at dilute alloy concentrations, and in some cases, $\alpha/\alpha + c$ boundaries, where c is the first intermediate phase. In every case, these effects were critically evaluated and careful judgment was exercised in the final placement of the affected phase boundaries. Figure 12 illustrates the considerations schematically. The dashed boundaries delineate what might be the fields, including an apparent three phase field, obtained from the micrographic analysis of a series of isothermal anneals. The solid lines indicate the construction which would be employed to give the best approximation of true binary equilibrium. By holding the composition and annealing temperature increments small enough, a very reasonable approximation could be obtained. It should be remembered, however, that true binary equilibrium does not, in fact, generally apply in the very dilute alloy regions of "Grade 3" zirconium binary systems.

Since the inception of this investigation, the Atomic Energy Commission has developed increasingly higher-quality "Grade 1" zirconium crystal bar, some of which is substantially free of the contaminating particles mentioned earlier. Late in the present program, a small quantity of such zirconium was employed in the preparation of dilute tin alloys for rechecking certain phase boundaries. The effects discussed above were so minimized that the boundaries could be precisely and unhesitatingly located. It is recommended that only similar high-quality "Grade 1" crystal bar be used as the base metal for future phase diagram investigations.

The diagram is a phase diagram for the Fe-Ni-C system. The vertical axis is labeled 'TEMPERATURE' and the horizontal axis is labeled 'WEIGHT PERCENT "X"'. The horizontal axis has major tick marks at 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0. The diagram shows several phase regions separated by solid and dashed lines. The regions are labeled as follows:

- α : Ferrite, located at low temperatures and low weight percent 'X'.
- β : Austenite, located at high temperatures and low weight percent 'X'.
- $\alpha + \beta$: Two-phase region between ferrite and austenite.
- $\alpha + \beta + c$: Three-phase region at low temperatures and low weight percent 'X'.
- $\alpha + c$: Two-phase region between ferrite and cementite at low temperatures and higher weight percent 'X'.
- $\beta + c$: Two-phase region between austenite and cementite at higher temperatures and higher weight percent 'X'.

The diagram includes data points represented by open circles, open squares, and solid circles, which likely represent experimental data or calculated phase boundaries. The lines are a combination of solid and dashed, indicating different types of phase boundaries or experimental vs. calculated results.

The diagram is a phase diagram for the Fe-Ni system. The vertical axis is labeled 'TEMPERATURE' and the horizontal axis is labeled 'WEIGHT PERCENT "X"'. The horizontal axis has major tick marks at 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0. The diagram shows several phase regions: 'a' (ferrite) on the left, 'β' (austenite) in the upper central region, 'α+β' (two-phase region) on the left, 'β+c' (two-phase region) on the right, and 'α+c' (two-phase region) at the bottom. The diagram is populated with various symbols: open circles, filled circles, open squares, and crosses, representing different experimental data points or phase boundaries. A solid line represents the phase boundary between 'a' and 'β', and another solid line represents the phase boundary between 'β' and 'β+c'. A horizontal line at the bottom represents the phase boundary between 'α' and 'α+c'.

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E. The Designation of Intermediate Phases
in the Alloy Systems

A considerable number of intermediate phases were found to exist in certain of the binary systems investigated, particularly the copper, silicon, and aluminum systems with zirconium. It was quite beyond the scope of the present work to obtain X-ray structure determinations of all of these phases, so that positive formulae assignments could be made. Only a few of these intermediate phases with zirconium have been detected or investigated in the previous literature.

In general, when a single phase alloy could be obtained, either in the cast or the heat-treated state, X-ray diffraction patterns were made. Some of these could be indexed and the structure determined with some assurance. Others yielded patterns so complicated that either more than one phase was present, or the single phase structure was too complex to warrant extended investigation in the present work.

Intermediate phases formed peritectically always appeared in the normal three phase as-cast configuration. In nearly all cases, it was found impossible or impractical (due to slow diffusion rates) to bring these reactions to completion and obtain a single phase by heat treatment. Therefore, X-ray diffraction exposure of these intermediate phases was not undertaken.

It was felt that designation of the many intermediate phases by the Greek letter system would not yield as much immediate information about the systems to those interested in the phase diagrams as would the assignment of stoichiometric formulae. Accordingly, careful judgment was exercised, taking into account all the available data, in assigning formulae to the intermediate phases. The simplest combining ratios, at or very near the observed occurrence of the phases, were selected in every case. Obviously this system is not infallible, and future investigations may show slight adjustments in the stoichiometric formulae representing some of these intermediate phases to be necessary. In the presentation of the diagrams, the following rules have been followed in regard to the intermediate phases:

1. Solid lines are used when the composition of the phase is felt to be firmly established.
2. Dashed lines are used when some displacement of the phase from the composition shown is deemed possible.
3. The phase formula is followed by a question mark when there is another simple stoichiometric formula that might alternatively be selected.

V. RESULTS AND DISCUSSION

A. The System Zirconium-Tin

1. Special Techniques

It was found that only alloys in the 0-35% tin composition range could be satisfactorily melted in copper block inserts according to the standard practice described earlier. Ingot stickage and high tin losses characterized higher tin content alloys melted in this way. A loose charge of tin-rich alloy melted in conical-bottomed copper crucibles did not stick, but still yielded high tin losses. It was found that by compacting the charge materials into cylindrical slugs prior to melting, alloys in the 35-100% tin range could be arc cast with a minimum of tin losses.

During the course of the work, certain tin-rich alloys were induction melted in graphite crucibles so that slower cooling rates could be utilized. A few alloys in the 95-100% tin range were melted in porcelain crucibles open to the air.

2. The Phase Diagram

Figure 13 presents the phase diagram of the zirconium-rich portion of this system. A large number of data points have been omitted for the sake of clarity. The phase diagram for the entire system is shown in Fig. 14.

The diagrams are based on the analyzed compositions listed in Table VIII. A large number of unanalyzed alloys gave supporting evidence to the phase relationships shown.

A preliminary study was made with specimens containing 5, 10, and 15% tin, annealed for three different lengths of time at each of the temperatures 700°, 800°, and 900°C, in order to determine the length of annealing time necessary for equilibrium. This study indicated that there was no detectable change in the relative amounts of the phases present after 200 hours at 700°C, 100 hours at 800°C, and 30 hours at 900°C. The isothermal annealing times were therefore selected on the basis of this information. A tabulation of pretreatment and annealing data for the zirconium-tin alloys is included in Tables IX and X.

The examination of as-cast alloys and alloys slowly cooled through certain regions was also quite instrumental in the determination of phase relationships.

The principal features of the zirconium-tin system may be summarized as follows:

a. Three intermediate phases exist; these are Zr_4Sn (24.55% Sn), which is formed by the peritectoid reaction: $\beta + Zr_5Sn_3 \rightarrow Zr_4Sn$ at $1325 \pm 20^\circ C$; Zr_5Sn_3 (tentative; 43.84% Sn), which melts with an open maximum at $1985 \pm 25^\circ C$; and $ZrSn$ (tentative; 56.55% Sn), formed by a peritectic reaction between Zr_5Sn_3 and a melt containing about 83% tin at $1140 \pm 15^\circ C$.

FIG.13-PARTIAL DIAGRAM OF THE ZIRCONIUM-TIN SYSTEM

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FIG.14- THE ZIRCONIUM - TIN SYSTEM

TABLE VIII
ANALYSES OF ZIRCONIUM-TIN ALLOYS

Alloy No.	Tin, Weight %	Alloy No.	Tin, Weight %
ZT 0.5-161	0.49	ZT 21-189	22.3
ZT 1-162	0.85	ZT 22-191	23.5
ZT 2-168	1.9	ZT 23-192	23.1
ZT 2-803	2.1	ZT 24-196	24.2
ZT 3-169	3.1	ZT 25-123	25.9
ZT 4-170	3.9	ZT 30-124	29.4
ZT 4-804	4.3	ZT 35-125	30.6
ZT 5-171	4.7	ZT 40-126	37.0
ZT 6-172	5.8	ZT 45-128	40.2
ZT 6-805	6.3	ZT 50-129	40.7
ZT 7-173	7.3	ZT 43-208	42.1
ZT 8-806	7.9	ZT 45-157	44.1
ZT 8-174	8.5	ZT 47-202	46.7
ZT 9-449	9.0	ZT 50-158	48.5
ZT 10-807	9.8	ZT 52-207	50.5
ZT 10-177	10.5	ZT 55-152	52.6
ZT 11-178	11.3	ZT 56-209	55.5
ZT 12-808	11.8	ZT 58-210	57.2
ZT 12-179	12.2	ZT 60-153	58.5
ZT 13-180	12.9	ZT 65-148	64.9
ZT 14-182	14.1	ZT 70-154	65.6
ZT 15-183	15.5	ZT 75-155	73.3
ZT 16-184	15.9	ZT 80-156	79.5
ZT 17-185	17.5	ZT 85-147	87.1
ZT 18-194	20.2	ZT 90-149	92.6
ZT 19-187	20.7	ZT 95-151	95.5
ZT 20-122	21.2		

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TABLE IX

PRETREATMENT AND ANNEALING OF ZIRCONIUM-TIN ALLOYS

Alloy	Cold Pressed, %*	Homogenized 1000°C, 5 hr*	Cold Rolled, %*	1472°C 20 min	1460°C 30 min	1400°C 2 hr
ZO-109(Zr)	55	x	77	x	x	x
ZT 0.5-161	26	x	81			x
ZT 1-162	17	x	78			x
ZT 2-168	31	x	82			x
ZT 3-169	27	x	85			x
ZT 4-170	24	x	85			x
ZT 5-171	20	x	82			x
ZT 6-172	24	x	76			x
ZT 7-173	23	x	74			x
ZT 8-174	16	x	63			x
ZT 9-174	12	x	53			x
ZT 10-177	11	x	37			x
ZT 11-178	12	x	38			x
ZT 12-179	10	x	26			x
ZT 13-180	10	x	21			x
ZT 14-182	6	x	19			x
ZT 15-183	7	x	6			x
ZT 16-184	6	x	5		x	x
ZT 17-185	8	x	4	x	x	x
ZT 18-194	3	x	-	x	x	x
ZT 19-187	2	x	-	x	x	x
ZT 20-122	2	x	-	x	x	x
ZT 21-189	7	x	-	x	x	x
ZT 22-191	1	x	-	x	x	x
ZT 23-192	-	x	-			x
ZT 24-196	1	x	-			x
ZT 25-123	-		-			x
ZT 30-124	-		-			x
ZT 35-125	-		-			x
ZT 40-126	-		-			x

*The pretreatment (i.e., cold pressing, homogenization, and cold rolling) corresponding to each alloy composition is the same for all annealing treatments, and is not repeated in subsequent columns.

TABLE IX (Cont.)

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Alloy	1350°C 2 hr	1300°C 5 hr	1247°C 5 hr	1200°C 7 hr	1153°C 16 hr	1098°C 20 hr	1048°C 20 hr
ZO-109(Zr)	x	x	x	x	x	x	x
ZT 0.5-161	x	x	x	x	x	x	x
ZT 1-162	x	x	x	x	x	x	x
ZT 2-168	x	x	x	x	x	x	x
ZT 3-169	x	x	x	x	x	x	x
ZT 4-170	x	x	x	x	x	x	x
ZT 5-171	x	x	x	x	x	x	x
ZT 6-172	x	x	x	x	x	x	x
ZT 7-173	x	x	x	x	x	x	x
ZT 8-174	x	x	x	x	x	x	x
ZT 9-179	x	x	x	x	x	x	x
ZT 10-177	x	x	x	x	x	x	x
ZT 11-178	x	x	x	x	x	x	x
ZT 12-179	x	x	x	x	x	x	x
ZT 13-180	x	x	x	x	x	x	x
ZT 14-182	x	x	x	x	x	x	x
ZT 15-183	x	x	x	x	x	x	x
ZT 16-184	x	x	x	x	x	x	x
ZT 17-185	x	x	x	x	x	x	x
ZT 18-194	x	x	x	x	x	x	x
ZT 19-187	x	x	x	x	x	x	x
ZT 20-122	x	x	x	x	x	x	x
ZT 21-189	x	x	x	x	x	x	x
ZT 22-191	x	x	x	x	x	x	x
ZT 23-192	x	x	x	x	x	x	x
ZT 24-196	x	x	x	x	x	x	x
ZT 25-123	x	x	x	x	x	x	x
ZT 30-124	x	x	x	x	x	x	x
ZT 35-125	x	x	x	x	x	x	x
ZT 40-126	x	x	x	x	x	x	x

TABLE IX (Cont.)

Alloy	997°C 20 hr	947°C 28 hr	902°C 30 hr	851°C 50 hr	750°C 150 hr	652°C 247 hr	548°C 400 hr
ZO-109(Zr)	x	x	x	x	x	x	x
ZT 0.5-161	x	x	x	x			
ZT 1-162	x	x	x	x			
ZT 2-168	x	x	x	x	x	x	x
ZT 3-169	x	x	x	x			
ZT 4-170	x	x	x	x	x	x	x
ZT 5-171	x	x	x	x		x	
ZT 6-172	x	x	x	x	x	x	x
ZT 7-173	x	x	x	x	x	x	
ZT 8-174	x	x	x	x	x	x	x
ZT 9-149	x	x	x	x	x	x	
ZT 10-177	x	x	x	x	x	x	x
ZT 11-178	x	x	x	x			
ZT 12-179	x	x	x	x	x	x	x
ZT 13-180	x	x	x	x			
ZT 14-182	x	x	x	x	x	x	
ZT 15-183	x	x	x	x			
ZT 16-184	x	x	x		x	x	
ZT 17-185	x	x	x	x			
ZT 18-194	x	x	x		x	x	
ZT 19-187	x	x	x	x			
ZT 20-122	x	x	x		x	x	
ZT 21-189	x	x	x	x			
ZT 22-191	x	x	x		x	x	
ZT 23-192	x	x	x	x			
ZT 24-196	x	x	x		x	x	
ZT 25-123	x	x	x	x			
ZT 30-124	x	x	x	x	x	x	
ZT 35-125	x	x	x	x	x	x	
ZT 40-126	x	x	x	x	x	x	

TABLE X

PRETREATMENT AND ANNEALING OF SPECIAL* ZIRCONIUM-TIN ALLOYS

Alloy	Cold Pressed, %**	Homogenized 1100°C-5 hr**	Cold Rolled, %**	1100°C 20 hr	1054°C 16 hr	1006°C 45 hr
ZO-802 (Zr)	57	x	65	x	x	x
ZT 2-803	58	x	54	x	x	x
ZT 4-804	56	x	57	x	x	x
ZT 6-805	59	x	54	x	x	x
ZT 8-806	56	x	47	x	x	x
ZT 10-807	52	x	47	x	x	x
ZT 12-808	41	x	49	x	x	x
ZO-841 (Zr)	47	x	70	x	x	x
ZT 1-842	30	x	79	x	x	x
ZT 2-843	31	x	78	x	x	x
ZT 4-844	32	x	79	x	x	x
ZT 6-845	32	x	78	x	x	x
ZT 8-846	33	x	72	x	x	x
ZT 9-847	18	x	74	x	x	x
ZT 10-848	25	x	75	x	x	x
ZT 11-849	14	x	54	x	x	x
ZT 12-850	20	x	37	x	x	x
ZT 13-851	21	x	25	x	x	x
ZT 14-852	21	x	19	x	x	x

* Alloys made with very high quality Westinghouse "Grade 1" crystal bar, from two separate lots.

** The pretreatment (i.e. cold pressing, homogenization, and cold rolling) corresponding to each alloy composition is the same for all annealing treatments, and is not repeated in subsequent columns.

TABLE X (Cont.)

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Alloy	957°C 70 hr	905°C 74 hr	853°C 120 hr	801°C 165 hr	748°C 280 hr	702°C 355 hr	656°C 400 hr	604°C 445 hr
ZO-802(Zr)	x	x	x	x	x	x		
ZT 2-803	x	x	x	x	x	x		
ZT 4-804	x	x	x	x	x	x		
ZT 6-805	x	x	x	x	x	x		
ZT 8-806	x	x	x	x	x	x		
ZT 10-807	x	x	x	x	x	x		
ZT 12-808	x	x	x	x	x	x		
ZO-841(Zr)	x	x	x	x	x	x	x	x
ZT 1-842	x	x	x	x	x	x	x	x
ZT 2-843	x	x	x	x	x	x	x	x
ZT 4-844	x	x	x	x	x	x	x	x
ZT 6-845	x	x	x	x	x	x	x	x
ZT 8-846	x	x	x	x	x	x	x	x
ZT 9-847	x	x	x	x	x	x	x	x
ZT 10-848	x	x	x	x	x	x	x	x
ZT 11-849	x	x	x	x	x	x	x	x
ZT 12-850	x	x	x	x	x	x	x	x
ZT 13-851	x	x	x	x	x	x	x	x
ZT 14-852	x	x	x	x	x	x	x	x

- b. Zirconium and Zr_5Sn_3 give rise to a eutectic at 23.5% tin and $1590 \pm 15^\circ C$.
- c. The solubility of tin in beta zirconium is approximately 21% at the eutectic temperature, 15% at $1325^\circ C$, and 6.5% at $980^\circ C$.
- d. Tin raises the $\alpha \rightleftharpoons \beta$ transformation temperature of zirconium, which results in the peritectoid: $\beta + Zr_4Sn \rightarrow \alpha$ at $980 \pm 20^\circ C$.
- e. The solubility of tin in alpha zirconium decreases from 9% at $980^\circ C$ to about 1.5% at $600^\circ C$.
- f. Tin displays no detectable solid solubility for zirconium. The eutectic or peritectic (undetermined) between tin and $ZrSn$ lies at higher tin content than 99.5%, and not more than $1^\circ C$ above or below the melting point of tin.

3. Zirconium-Rich Alloys

The position of the eutectic at 23.5% tin and $1590 \pm 15^\circ C$ is supported by considerable evidence. Figures 15 and 16 show alloys which bracket the eutectic composition quite accurately. The eutectic temperature was confirmed independently by the microscopic evaluation of specimens quenched in the incipient melting furnace and by thermal analysis. Figure 17, showing the microstructure of a 30.6% tin alloy, is typical of the Zr_5Sn_3 + eutectic structures obtained in arc cast alloys in the 24-46% tin composition range.

The highest temperature level at which the $\beta/\beta + Zr_5Sn_3$ phase boundary was experimentally located was $1472^\circ C$. Figures 18 and 19 show 17.5 and 20.2% tin alloys, respectively, quenched after an anneal at this temperature. The extrapolation of this phase boundary to the eutectic temperature indicates a maximum solubility of tin in beta zirconium of approximately 21%.

The sequence of as-cast zirconium-tin microstructures gave no clue as to the existence of a zirconium-rich intermediate phase; however, anneals in the solid state clearly proved that Zr_4Sn , having a singular composition at 24.55% tin, is formed by the peritectoid: $\beta + Zr_5Sn_3 \rightleftharpoons Zr_4Sn$ at about $1325^\circ C$. Figures 20 and 21 are the microstructures of a 23.5% tin alloy, quenched after annealing at 1350° and $1300^\circ C$, respectively. The peritectoid nature of the compound formation is better illustrated in the sequence of structures in Figs. 22 and 23. This alloy containing, nominally, 24% tin was induction melted in a graphite crucible. Figure 22 represents the as-cast structure, and Fig. 23 is the same alloy after an anneal at $1051^\circ C$. Since the reaction is not complete, the three-phase peritectoid arrangement is clear. The optimum amounts of Zr_4Sn were obtained by annealing a 24.2% tin arc melted alloy at various temperatures below $1300^\circ C$. Figure 24 shows the structure of this alloy after a 45 hour anneal at $951^\circ C$. Only small residual amounts of beta and Zr_5Sn_3 remain. The peritectoid temperature level was rechecked by reannealing specimens of this nearly 100% Zr_4Sn alloy at 1100° , 1200° , 1300° , and $1350^\circ C$ in order to reverse the reaction. Only the specimen annealed at $1350^\circ C$ transformed into beta and Zr_5Sn_3 phases.

Figure 25 represents the structure of a 29.4% tin alloy annealed at 1250°C, in the $Zr_4Sn + Zr_5Sn_3$ field. The reaction is nearly complete, but some unresorbed beta phase remains.

A sample of the 24.2% tin alloy containing nearly 100% Zr_4Sn was subjected to X-ray analysis. The specimen was prepared by filing. Iron particles were removed magnetically and the powders exposed to filtered, characteristic copper K_α radiation. The resulting pattern was indexed on a face-centered tetragonal Hull-Davy chart. The lattice parameters were: $a = 7.645 \text{ \AA}$, $c = 12.461 \text{ \AA}$, $c/a = 1.63$. A tabulation of the line values is included in the Appendix.

The alpha solid solution enters into a peritectoid reaction: $\beta + Zr_4Sn \rightleftharpoons \alpha$, at approximately 980°C and 9% tin in this system. The photomicrographs of Figs. 26 and 27 show the best evidence for the peritectoid temperature level. Both figures represent a 7.9% tin alloy; the former, annealed at 1006°C, consists of $\beta + Zr_4Sn$, while the latter, annealed at 957°C, contains $\alpha + \beta$. This peritectoid level was finally placed by the examination of several series of annealed alloys prepared with extremely clean Westinghouse "Grade 1" zirconium crystal bar, obtained from cooperating AEC laboratories. Considerable difficulty had been experienced earlier in interpreting the structures obtained in "Grade 3" zirconium alloys.

The sequence of structures in Figs. 28 through 31 present excellent evidence of the phase relationships in this region of the diagram. This series of alloys was annealed at 905°C; Fig. 28, a 1.0% tin alloy, is transformed beta, Fig. 29, a 2.1% tin alloy, contains $\alpha + \beta$, Fig. 30, a 6.3% tin alloy, falls in the alpha solid solution field, and Fig. 31, a 7.9% tin alloy, represents an $\alpha + Zr_4Sn$ structure.

The alpha solid solution field extends to about 9% at the peritectoid temperature, 980°C. The solid solubility of tin in alpha decreases rather sharply with falling temperature, as indicated by Figs. 32 and 33, representing alloys annealed at 801°C, and Figs. 34 and 35, of alloys annealed at 604°C. In this case, again, alloy structures based on "Grade 3" zirconium crystal bar were exceedingly difficult to interpret. The large quantity of impurity particles made it nearly impossible to detect the initial appearance of the Zr_4Sn phase, which also precipitates as a very fine dispersion of particles in the lower temperature ranges. Use of the special "Grade 1" zirconium-base alloys, which yielded alpha structures relatively free of impurities, made it possible to locate the $\alpha/\alpha + Zr_4Sn$ phase boundary with considerable accuracy.

4. The Intermediate Phase at 47% Tin

The intermediate phase which forms a eutectic with zirconium presented unusual experimental difficulties. Figures 36 through 38 represent as-cast 40.2, 44.1, and 46.7% tin alloys, respectively. Some residual eutectic is present in both the former alloys, whereas the last represents nearly 100% this phase. Melting point determinations on the 46.7% alloy showed that this phase melts with an open maximum at 1985±25°C. The phase is exceedingly unstable

toward air and/or moisture; a freshly polished surface will begin to discolor in a matter of minutes, and whole ingots disintegrate to powder in a few weeks. Alloys for the investigation of this region of the diagram had to be freshly prepared periodically because of this fact. Storage of freshly melted specimens in a vacuum dessicator prolonged their usefulness appreciably. Alloys containing 30-45% tin showed less tendency to completely disintegrate than the alloys in the 45-75% tin range.

The formula in closest agreement with the observed single phase composition is Zr_3Sn_2 (46.45% Sn); however, Dr. Paul Pietrokowsky, in an investigation of this zirconium-tin phase, has reported (11) that the structure is Zr_5Sn_3 (hexagonal, Mn_5Si_3 type), so this formula has been tentatively adopted in the present work. Zr_5Sn_3 corresponds to the composition 43.84% tin, which is about 3% lower in tin than the observed single phase alloys. In the diagram, the phase is placed at the experimentally determined, rather than the ideal, Zr_5Sn_3 composition. This shift may not be too surprising, in view of the relative size independence of the Mn_5Si_3 type of structure, in which atom substitutions might rather easily occur. A similar shift from stoichiometric ratio has been noted in the case of the phase Ti_5Si_3 (4). Attempts to index the Debye-Scherrer X-ray patterns of many as-cast and heat treated alloys in this composition area were unsuccessful at this laboratory. Several needles of the intermetallic compound were isolated from the top of an as-cast nominal 50% tin alloy and transmitted to Dr. F. Laves, University of Chicago, for a series of single crystal precession pictures. Using unfiltered copper radiation and small precession angles, Dr. Laves obtained a perfect hexagonal pattern, with indications of a relatively small unit cell. When such crystals remained in the camera overnight, they broke up or branched out into several pieces. Subsequent X-ray photograms gave intensity changes pointing to a rhombic, pseudo-hexagonal symmetry. Further work, with needles sealed in capillary tubes for protection against the atmosphere, is in progress, but no positive structure analysis of the phase was available at the termination of this project.

The general instability of these alloys made efforts to determine whether this intermediate phase exists over a range of composition fruitless. Tentatively, it should be considered to have a singular composition.

5. Tin-Rich Alloys

The two types of structures which occur in alloys containing more than 47% tin are illustrated in Figs. 39 and 40. The former is a 65.6% tin alloy, showing a typical three phase peritectic arrangement: primary Zr_5Sn_3 crystals, a peritectic wall of a new intermediate phase, and a matrix of tin. The latter is a nominal 95% tin alloy which contains only primary dendrites of the new phase in a matrix of tin. Only the tin-rich alloys which were nearly free of Zr_5Sn_3 crystals showed any stability in normal atmosphere; others tended to decompose rapidly after preparation. This fact, and the coexistence of phases melting at 1985° and 231°C in the alloys, made heat treatments to develop the peritectically formed intermediate phase virtually impossible. A series of thermal

analyses indicated that the peritectic temperature was located at $1140 \pm 15^\circ\text{C}$. The only other heating and cooling arrest was obtained at $231 \pm 1^\circ\text{C}$. The position of the peritectic melt, deduced from the disappearance of Zr_5Sn_3 as a primary phase in arc cast alloys, was roughly located between 80 and 87% tin. A special series of alloys in the composition range 75-95% tin were prepared to check this more accurately. These alloys were placed in carbon cups inside sealed quartz capsules and held for 20 hours at 1152°C , just above the peritectic temperature. Alloys containing 85% or more tin were completely molten, while alloys containing 80% or less tin contained liquid plus solid phases at this temperature. Accordingly, the peritectic melt can be placed at $83 \pm 3\%$ tin.

Identification of the intermediate phase formed by the peritectic reaction at 1140°C between Zr_5Sn_3 and the melt containing 83% tin once again required rather unusual techniques. Several two phase alloys containing primary crystals of this intermediate phase were subjected to anodic dissolution in a 10% NaOH electrolytic bath, stainless steel plates serving as cathodes. The tin matrix was taken into solution and small deposits of the primary phase were collected. Two samples from separate alloys were adequate for semi-micro analysis. The tin contents proved to be 53.3 and 51.2% in the two tests. The most likely stoichiometric composition in this vicinity is ZrSn (56.55% tin), and since the analytical accuracy on such samples cannot be considered too high, this formula is tentatively adopted for the intermediate phase, although the evidence is not entirely satisfactory. Certainly the analytical evidence seems to refute the existence of a phase located nearer the end of the peritectic horizontal, such as ZrSn_2 (72.33% Sn).

Some of the material collected from the electrolytic baths was subjected to X-ray analysis. A Debye-Scherrer pattern was taken, using filtered, characteristic copper K_α radiation. A complex pattern was obtained which has tentatively been indexed as orthorhombic, with the following parameters: $a = 7.43 \text{ \AA}$, $b = 5.82 \text{ \AA}$, $c = 5.16 \text{ \AA}$; $a:b:c = 1.28:1:0.885$. The lines obtained in this pattern are included in the Appendix.

By the rules of phase equilibria, tin must enter into either a eutectic or a peritectic reaction with ZrSn . In order to check this point, alloys with 95, 97, 99, and 99.5 nominal per cent tin were examined metallographically, and subjected to very careful thermal analysis. Arrests in all alloys were not distinguishable from that of pure tin within $\pm 1^\circ\text{C}$. The alloy most dilute in zirconium, 99.5% tin, still showed primary ZrSn crystals in a tin matrix. Accordingly, the eutectic or peritectic must occur between 99.5 and 100% tin and at $231 \pm 1^\circ\text{C}$.

6. Melting Range Determinations

The incipient melting techniques described earlier were employed for solidus, eutectic, and intermetallic compound melting determinations in the 0-47% tin range, but were inapplicable at higher tin contents, because of the presence of free tin in all of these alloys. Thermal analysis was employed

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for zirconium-rich alloys melting within the useful temperature range of platinum/platinum-10% rhodium thermocouples and in all tin-rich alloys. The data are summarized in Table XI.

TABLE XI
MELTING RANGE DETERMINATIONS FOR THE ZIRCONIUM-TIN SYSTEM

Alloy No.	Weight % Sn	Thermal Analysis		Incipient Melting	
		Arrests, °C	Comments	Melting Observed, °C	No Melting, °C
YZT 5-171	4.7			1710	1675
YZT 10-177	10.5			1635	1600
XZT 20-442	20 nom.	1592>1604	Sloping		
YZT 20-122	21.2			1610	1575
YZT 24-196	24.2			1575	1555
XZT 24-600	24 nom.	1590			
YZT 35-125	30.6			1585	--
YZT 40-126	37.0			1905	--
YZT 47-202	46.7			1985	--
YZT 52-207	50.5			1875	--
XZT 60-437	60 nom.	1121			
XZT 62-445	62 nom.	1144	Sharp, level		
XZT 70-154	70 nom.	1140...230	" "		
XZT 75-447	75 nom.	1165			
XZT 85-147	85 nom.	1173...230			
XZT 95	95 nom.	231	Iron-Constantan		
XZT 97	97 nom.	231	" "		
XZT 99	99 nom.	231+	" "		
XZT 99.5	99.5 nom.	231	" "		
XZT 100	100	231+	" "		

7. General Comments on Zirconium-Tin Alloys

Considerable safety precaution has been found necessary in the handling and storage of zirconium-tin alloys, particularly those containing 45-65% tin. On one occasion, a freshly prepared alloy within this composition range burst into flames spontaneously in a sample envelope, causing a small fire among similarly stored specimens. Alloys in the eutectic composition (24% tin) range also tend to spark brilliantly on cutting, and burn if in finely divided form, although there is no danger of spontaneous combustion in this composition range.

In view of the general phase relationships, as well as the instability of tin-rich zirconium-tin alloys, they are considered to be devoid of possible utility, and of academic interest only.

Fig. 15

Neg. No. 3791
ZT 23-192-C

X750

20% HF, 20% HNO₃ in glycerine

A 23.1% tin alloy, as cast. Predominantly β -Zr₅Sn₃ eutectic with some residual primaries of β solid solution.

Fig. 16

Neg. No. 3790
ZT 24-196-C

X750

20% HF, 20% HNO₃ in glycerine

a 24.2% tin alloy, as cast. Predominantly eutectic with a few primary crystals of Zr₅Sn₃.

Fig. 17

Neg. No. 3333
ZT 35-125-C

X100

Unetched

A 30.6% tin alloy, as cast. Primary crystals of Zr₅Sn₃ in a matrix of β -Zr₅Sn₃ eutectic.

Fig. 18

Neg. No. 3792

X150

ZT 17-185; P8-H1000-5; XR4-Q1472-1/4

20% HF, 20% HNO₃ in glycerine

A 17.5% tin alloy, quenched after annealing 1/4 hour at 1472°C. Transformed β structure.

Fig. 19

Neg. No. 3793

X150

ZT 18-194; P3-H1000-5; Q1472-1/4

20% HF, 20% HNO₃ in glycerine

A 20.2% tin alloy, quenched after annealing 1/4 hour at 1472°C. Transformed β + Zr₅Sn₃ crystals.

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Fig. 15

Fig. 16

Fig. 17

Fig. 18

Fig. 19

Fig. 20

Neg. No. 3794 X150
 ZT 22-191;P1-H1000-5;Q1350-2
 20% HF, 20% HNO₃ in glycerine

A 23.5% tin alloy, quenched after annealing 2 hours at 1350°C. Transformed β + Zr₅Sn₃ crystals.

Fig. 21

Neg. No. 3795 X150
 ZT 22-191;P1-H1000-5;Q1300-5
 20% HF, 20% HNO₃ in glycerine

A 23.5% tin alloy, quenched after annealing 5 hours at 1300°C. Original structure of β and Zr₅Sn₃ (small dark-stained crystals) reacting peritectoidally to form Zr₄Sn phase (gray).

Fig. 22

Neg. No. 3802 X150
 XZT 24-TA-C
 Unetched

A nominal 24% tin alloy, induction melted in graphite and slowly cooled. Some primary Zr₅Sn₃ in a matrix of divorced β -Zr₅Sn₃ eutectic.

Fig. 23

Neg. No. 3803 X150
 XZT 24-TA-Q1051-20
 20% HF, 20% HNO₃ in glycerine

A nominal 24% tin alloy (induction melted), quenched after annealing 20 hours at 1051°C. Peritectoid formation of Zr₄Sn from the reaction between β and Zr₅Sn₃.

Fig. 24

Neg. No. 3796 X150
 ZT 24-196;P1-H1000-5;Q951-45
 20% HF, 20% HNO₃ in glycerine

A 24.2% tin alloy, quenched after annealing 45 hours at 951°C. Nearly single phase Zr₄Sn. Small amounts of unreacted β and Zr₅Sn₃ remain.

Fig. 25

Neg. No. 3591 X150
 ZT 30-124;Q1247-5
 20% HF, 20% HNO₃ in glycerine

A 29.4% tin alloy, quenched after annealing 5 hours at 1247°C. Annealed in the Zr₄Sn + Zr₅Sn₃ field. Small amounts of unresorbed β phase remain (white).

Fig. 20

Fig. 21

Fig. 22

Fig. 23

Fig. 24

Fig. 25

Fig. 26

Neg. No. 4049 X150
 ZT 8-806;P56-H1100-5;XR47-Q1006-45
 20% HF, 20% HNO₃ in glycerine

A 7.9% tin alloy, quenched after annealing 45 hours at 1006°C. Transformed β and Zr₄Sn phases are in equilibrium.

Fig. 27

Neg. No. 4048 X150
 ZT8-806;P56-H1100-5;XR47-Q957-70
 20% HF, 20% HNO₃ in glycerine

A 7.9% tin alloy, quenched after annealing 70 hours at 957°C. Isothermal α and transformed β (serrated α) phases are present, indicating an anneal in the $\alpha + \beta$ field.

Fig. 28

Neg. No. 4034 X150
 ZT 1-842;P30-H1100-5;XR79-Q905-74
 20% HF, 20% HNO₃ in glycerine

A 1.0% tin alloy, quenched after annealing 74 hours at 905°C. "Serrated" α transformation product, indicating that the specimen was annealed in the β field.

Fig. 29

Neg. No. 4035 X150
 ZT 2-843;P31-H1100-5;XR78-Q905-74
 20% HF, 20% HNO₃ in glycerine

A 2.1% tin alloy, quenched after annealing 74 hours at 905°C. Equiaxed isothermal $\alpha +$ serrated α transformation product formed on quenching. This alloy was annealed in the $\alpha + \beta$ field.

Fig. 30

Neg. No. 4036 X150
 ZT 6-845;P32-H1100-5;XR78-Q905-74
 20% HF, 20% HNO₃ in glycerine

A 6.3% tin alloy, quenched after annealing 74 hours at 905°C. 100% equiaxed α , formed isothermally.

Fig. 31

Neg. No. 4037 X150
 ZT 8-846;P33-H1100-5;XR72-Q905-74
 20% HF, 20% HNO₃ in glycerine

A 7.9% tin alloy, quenched after annealing 74 hours at 905°C. $\alpha +$ fine precipitation of Zr₄Sn particles. Annealed just into the $\alpha +$ Zr₄Sn field.

Fig. 26

Fig. 27

Fig. 28

Fig. 29

Fig. 30

Fig. 31

Fig. 32

Neg. No. 4039 X150
 ZT 2-843;P31-H1100-5;XR78-Q801-145
 Unetched, Polarized light

A 2.1% tin alloy, quenched after annealing 145 hours at 801°C. 100% equiaxed α .

Fig. 33

Neg. No. 4041 X150
 ZT 4-844;P32-H1100-5;XR79-Q801-145
 Unetched, Polarized light

A 4.3% tin alloy, quenched after annealing 145 hours at 801°C. $\alpha + \text{Zr}_{14}\text{Sn}$ particles, principally in the grain boundaries. Note the decrease in grain size upon crossing the $\alpha/\alpha + \text{Zr}_{14}\text{Sn}$ boundary (compare with Fig. 32).

Fig. 34

Neg. No. 4042 X150
 ZT 1-842;P30-H1100-5;XR79-Q604-445
 Unetched, polarized light

A 1.0% tin alloy, quenched after annealing 445 hours at 604°C. 100% equiaxed α .

Fig. 35

Neg. No. 4043 X150
 ZT 2-843;P31-H1100-5;XR78-Q604-445
 Unetched, polarized light

A 2.1% tin alloy, quenched after annealing 445 hours at 604°C. $\alpha + \text{Zr}_{14}\text{Sn}$ particles. Note again the decrease in grain size on crossing the $\alpha/\alpha + \text{Zr}_{14}\text{Sn}$ boundary (compare with Fig. 34).

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Fig. 32

Fig. 33

Fig. 34

Fig. 35

Fig. 36
Neg. No. 3800
ZT 45-157 C
X150
Unetched

A 40.2% tin alloy, as cast. Primary crystals of Zr_5Sn_3 in a matrix of β - Zr_5Sn_3 eutectic.

Fig. 37
Neg. No. 3799
ZT 45-128 C
X150
Unetched

A 44.1% tin alloy, as cast. Cracked Zr_5Sn_3 primaries and a small amount of residual eutectic.

Fig. 38
Neg. No. 3801
ZT 50-129 C
X150
Unetched

A 46.7% tin alloy, as cast. Nearly 100% primary Zr_5Sn_3 crystals.

Fig. 39
Neg. No. 3483
ZT 70-154 C
X250
Unetched

A 65.6% tin alloy, as cast. Primary crystals of Zr_5Sn_3 , peritectic rims of $ZrSn$, and a matrix of tin. This specimen was allowed to stand 15 minutes after polishing before photographing. The Zr_5Sn_3 darkens rapidly in air and contrasts sharply with the peritectic phase.

Fig. 40
Neg. No. 4032
ZT 95-TA-C
X150
20% HF, 20% HNO_3 in glycerine

A nominal 95% tin alloy, melted in a porcelain crucible for thermal analysis. Primary $ZrSn$ crystals in a matrix of tin.

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Fig. 36

Fig. 37

Fig. 38

Fig. 39

Fig. 40

B. The System Zirconium-Molybdenum

by R. F. Domagala

1. Special Techniques

This system, along with wolfram, provided the only opportunity to use electrode tips of the same metal as the alloying addition. One-half inch diameter molybdenum tips were employed for all zirconium-molybdenum melts, so that the possibility of wolfram contamination was precluded. All of these alloys were melted in a copper block insert to the spun copper crucible, and were inverted and remelted four to six times. No special charging techniques were necessary. The general experimental techniques described earlier were applicable for this system.

2. The Phase Diagram

The phase relationships in the 0-50 atomic per cent molybdenum region of this diagram are presented in Fig. 41, and the entire diagram is presented in Fig. 42. Figure 41 includes most of the experimental points necessary for the construction of the diagram; some points were omitted for greater clarity. Important temperature levels and compositions are noted in both diagrams. Thermal analysis data, as well as the results of incipient melting work, have been shown in the first figure. The zirconium-rich solid solubility limits were outlined by metallographic inspection of isothermally annealed specimens. A preliminary study of specimens containing 3, 9, and 16% molybdenum, annealed for three different times at each of the temperatures 700°, 800°, and 900°C, was made in order to determine the favorable times at temperature for achieving equilibrium. No changes in the relative amounts of phases present were detected after 50 hours at 900°C, 150 hours at 800°C, and 250 hours at 700°C. Isothermal treatments were accordingly based on these preliminary data. The complete tabulation of pretreatment and annealing data for zirconium-molybdenum alloys is included in Tables XII and XIII. Many of the alloys were also examined in the as-cast condition to aid in construction of the diagram.

Chemical analyses of the alloys used in this study are presented in Table XIV. The diagram is based on these analyzed compositions.

Salient features of the zirconium-molybdenum diagram are as follows:

- a. Only one intermediate phase exists in this system. It is peritectically formed at $1880 \pm 20^\circ\text{C}$ by the reaction: Melt + molybdenum solid solution $\rightarrow \text{ZrMo}_2$. ZrMo_2 exists, ideally, at 67.78% molybdenum.
- b. A eutectic between beta solid solution and ZrMo_2 occurs at 31% molybdenum and $1520 \pm 15^\circ\text{C}$.
- c. The limit of solubility of molybdenum in beta zirconium is about 22% at the eutectic temperature.

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FIG. 41 — PARTIAL DIAGRAM OF THE ZIRCONIUM-MOLYBDENUM SYSTEM

FIG. 42 — THE ZIRCONIUM — MOLYBDENUM SYSTEM

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TABLE XII
PRETREATMENT AND ANNEALING OF ZIRCONIUM-MOLYBDENUM ALLOYS

Alloy	Cold Pressed, %*	Homogenized 1150°C-70 hr*	Cold Rolled, %*	1480°C 10 min**	1390°C 1 hr	1300°C 2 hr
ZO-285(Zr)	50	x	74	x	x	x
ZO-286(Zr)	51	x	71			
ZM 0.5-260	37	x	64			
ZM 1-240	3	x	44			
ZM 2-243	7	x	34			
ZM 3-242	2	x	17			
ZM 4-244	1	x	34			
ZM 5-245	2	x	68		x	x
ZM 6-246	1	x	75			
ZM 7-247	7	x	75		x	x
ZM 8-239	2	x	76			
ZM 9-237	4	x	75		x	x
ZM 10-235	4	x	72		x	x
ZM 12-315	3	x	72		x	x
ZM 14-322	3	x	41		x	x
ZM 16-321	4	x	21	x	x	x
ZM 18-320	2	x	25	x	x	x
ZM 20-319	2	x	20	x	x	x
ZM 22-318	3	x	5	x	x	x
ZM 24-314	0	x	11	x	x	x
ZM 26-317	7	x	-	x	x	x
ZM 28-316	1	x	5		x	x
ZM 30-323	-		-		x	x
ZM 35-324	-		-			
ZM 40-325	-		-			
ZM 45-328	-		-			
ZM 50-335	-		-		x	
ZM 55-330	-		-		x	
ZM 60-221	-		-	x	x	
ZM 62-331	-		-	x	x	
ZM 64-332	-		-	x	x	
ZM 66-333	-		-			
ZM 68-334	-		-		x	

*The pretreatment (i.e., cold pressing, homogenization, and cold rolling) corresponding to each alloy composition is the same for all annealing treatments, and is not repeated in subsequent columns.

**Took two hours to heat to temperature indicated, then held 14°C for 10 minutes.

TABLE XII (Cont.)

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Alloy	1204°C 8 hr	1100°C 20 hr	1000°C 40 hr	900°C 48 hr	840°C 240 hr	815°C 200 hr	800°C 150 hr	790°C* 610 hr
ZO-286(Zr)					x	x		x
ZO-285(Zr)	x	x	x	x			x	
ZM 0.5-260							x	
ZM 1-240				x	x	x	x	
ZM 2-243			x	x	x	x	x	
ZM 3-242				x	x	x	x	
ZM 4-244			x	x	x	x	x	
ZM 5-245	x	x		x	x	x	x	x
ZM 6-246		x	x	x	x	x	x	x
ZM 7-247	x	x		x	x	x	x	x
ZM 8-239		x	x	x	x	x	x	x
ZM 9-237	x	x		x	x	x	x	x
ZM 10-235	x	x	x	x	x	x	x	x
ZM 12-315	x	x	x	x	x	x	x	x
ZM 14-322	x	x	x	x			x	x
ZM 16-321	x	x	x	x			x	x
ZM 18-320	x	x	x					x
ZM 20-319	x	x	x	x			x	
ZM 22-318	x	x						
ZM 24-314	x							
ZM 26-317	x							
ZM 28-316	x							
ZM 30-323	x		x					
ZM 35-324								
ZM 40-325			x				x	
ZM 45-328								
ZM 50-335	x		x				x	
ZM 55-330	x							
ZM 60-221	x		x					
ZM 62-331	x						x	
ZM 64-332	x		x					
ZM 66-333								
ZM 68-334	x							

*Held at 900°C for 16 hours, slow cool to temp. indicated and held at temp. for times indicated.

TABLE XII (Cont.)

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Alloy	775°C* 380 hr	760°C* 380 hr	750°C 208 hr	740°C* 610 hr	700°C 256 hr	650°C 400 hr	600°C 475 hr	550°C 620 hr
ZO-286(Zr)	x	x		x				
ZO-285(Zr)			x		x	x	x	x
ZM 0.5-260			x		x	x	x	x
ZM 1-240			x		x	x	x	x
ZM 2-243			x		x	x	x	x
ZM 3-242			x		x	x	x	x
ZM 4-244			x		x	x	x	x
ZM 5-245	x	x	x	x	x	x	x	x
ZM 6-246	x	x	x	x	x	x	x	x
ZM 7-247	x	x	x	x	x	x	x	x
ZM 8-239	x	x	x	x	x	x	x	x
ZM 9-237	x	x	x	x	x	x	x	x
ZM 10-235	x	x	x	x	x	x	x	x
ZM 12-315	x	x	x	x	x			
ZM 14-322	x	x	x	x	x	x	x	x
ZM 16-321	x	x	x	x	x			
ZM 18-320	x	x	x	x	x	x	x	
ZM 20-319			x		x		x	
ZM 22-318			x		x	x		
ZM 24-314			x		x			
ZM 26-317								
ZM 28-316								
ZM 30-323					x		x	
ZM 35-324								
ZM 40-325					x		x	
ZM 45-328								
ZM 50-335					x		x	
ZM 55-330								
ZM 60-221					x		x	
ZM 62-331								
ZM 64-332					x		x	
ZM 66-333								
ZM 68-334								

*Held at 900°C for 16 hours, slow cool to temp. indicated and held at temp. for times indicated.

TABLE XIII
ALLOYS AND PRETREATMENT FOR DETERMINATION OF ALPHA SOLUBILITY
IN ZIRCONIUM-MOLYBDENUM ALLOYS

Alloy:	ZM 0.2-727	ZM 0.4-724	ZM 0.6-725	ZM 0.8-726
Cold Pressed (%)	54	50	17	17
Homogenized 1150°C - 65 hours	x	x	x	x
Cold Rolled (%)	61	62	73	64
830°C - 240 hours	x	x	x	x
800°C - 240 hours	x	x	x	x
775°C - 240 hours	x	x	x	x
750°C - 240 hours	x	x	x	x
700°C - 335 hours	x	x	x	x

TABLE XIV
ANALYSES OF ZIRCONIUM-MOLYBDENUM ALLOYS

Alloy No.	Molybdenum, Weight %
ZM 0.2-727	0.18
ZM 0.4-724	0.35
ZM 0.5-260	0.60
ZM 0.6-725	0.64
ZM 0.8-726	0.77
ZM 1-240	1.2
ZM 2-243	2.2
ZM 3-242	3.1
ZM 4-244	4.3
ZM 5-245	4.7
ZM 6-246	6.2
ZM 7-247	7.1
ZM 8-239	8.3
ZM 9-237	8.9
ZM 10-235	9.6
ZM 12-315	11.9
ZM 14-322	14.5
ZM 16-321	15.7
ZM 18-320	18.5
ZM 20-319	20.7
ZM 22-318	22.1
ZM 24-314	24.0
ZM 26-317	25.3
ZM 28-316	27.9
ZM 29-628	28.7
ZM 30-323	30.0
ZM 31-629	30.7
ZM 32-630	31.3
ZM 33-631	33.1
ZM 34-632	33.8
ZM 35-324	35.4
ZM 40-325	40.6
ZM 45-328	44.8
ZM 50-335	50.9
ZM 55-330	55.7
ZM 60-221	57.8
ZM 62-331	59.0
ZM 64-332	63.5
ZM 66-333	65.4
ZM 68-334	65.4
ZM 70-220	64.4*
ZM 80-219	79.4*
ZM 90-222	89.3*

*Analyzed for zirconium, molybdenum by difference.

- d. A sluggish eutectoid decomposition of beta into $\alpha + \text{ZrMo}_2$ occurs at $7.5 \pm 1\%$ molybdenum and $780 \pm 5^\circ\text{C}$.
- e. The limit of solubility of molybdenum in alpha zirconium is less than 0.18% at all temperatures.
- f. The limit of solubility of zirconium in molybdenum is probably less than 10% .

3. Zirconium-Rich Alloys

The eutectic occurring at 31% molybdenum and $1520 \pm 15^\circ\text{C}$ was located by the examination of several as-cast, incipient melting, and thermal analysis specimens in this region. The position of the eutectic composition is accurate to $\pm 1\%$. The temperature level was fixed as a result of several cooling and heating curves for the eutectic composition, as well as incipient melting work. Arc-cast alloys in the region of the eutectic always exhibited a very fine distribution of phases due to the rapid rate of cooling. However, Fig. 43 shows a 30.7% molybdenum alloy, quenched from 1535°C in the course of the incipient melting program, which clearly manifests the eutectic structure.

Examination of isothermally annealed specimens showed the solubility of molybdenum in beta zirconium to decrease from 22% at the eutectic level to $7.5 \pm 1\%$ at the eutectoid temperature. This is illustrated in Figs. 44 through 47. Figure 44 is a 20.7% molybdenum alloy quenched from 1480°C ; a typical beta structure is evident. A 22.1% molybdenum alloy, also quenched from 1480°C after 10 minutes at temperature, is shown in Fig. 45. Here a $\beta + \text{ZrMo}_2$ structure is present. A 9.6% and an 11.9% molybdenum alloy quenched from 900°C after 48 hours are shown in Figs. 46 and 47, respectively. The 9.6% alloy is 100% beta, while the 11.9% alloy is $\beta + \text{ZrMo}_2$.

The eutectoid decomposition: $\beta \rightarrow \alpha + \text{ZrMo}_2$ proceeds very slowly in this system. Anneals below the eutectoid temperature for as long as 400 hours have failed to cause more than a small percentage of beta to decompose. The eutectoid level was determined by examination of hypereutectoid alloys annealed at temperature increments of 15°C . The eutectoid temperature level and the sluggishness of the decomposition are illustrated in Figs. 48 and 49. The former, a 14.5% molybdenum alloy quenched from 790°C after 610 hours at temperature, shows ZrMo_2 in a retained beta matrix. Eutectoid decomposition in a 15.7% molybdenum alloy, quenched from 775°C after 380 hours, is seen adjacent to the large proeutectoid ZrMo_2 crystals. The amount of beta which has decomposed is observed to be small. The metastability of beta made accurate positioning of the eutectoid composition difficult, but the figure given, 7.5% , represents the best compromise possible, and is undoubtedly within $\pm 1\%$ of the equilibrium value. Eutectoid decomposition in hypoeutectoid alloys was never observed.

The solubility of molybdenum in alpha zirconium was determined by annealing specimens containing 0.2 , 0.4 , 0.6 , and 0.8 nominal per cent molybdenum at six temperature levels between 700° and 830°C , as shown in Table XIII. The

results of this work indicate the maximum solubility to be less than 0.18% at all temperatures. Figure 50 shows an 0.18% molybdenum alloy quenched from 775°C after 240 hours. A typical $\alpha + \beta$ structure is evident. The metastability of beta at this temperature explains the absence of eutectoid decomposition.

4. Intermediate Phase

The existence of the single intermediate phase in this system has been cited by Duwez (12), who reports the phase to be ZrMo_2 (stoichiometrically, 67.78% Mo), isomorphous with ZrW_2 . This was confirmed in the present work. ZrMo_2 is formed by the peritectic reaction: Melt + molybdenum-rich solid solution $\rightarrow \text{ZrMo}_2$. The peritectic formation and the composition of the liquid at the peritectic level are illustrated in Figs. 51 and 52. A 57.8% molybdenum arc melted alloy is shown in the former figure. Only two phases, ZrMo_2 and beta, are present. The latter figure, a 59.0% molybdenum arc melted alloy, illustrates the appearance of the third phase, molybdenum rich solid solution, as primary dendrites. This places the composition of the liquid at the peritectic level between 57.8 and 59.0% molybdenum.

Accurate positioning of the composition of the intermediate phase was difficult because normal annealing treatments failed to bring the peritectic reaction to completion. However, Fig. 53 shows a 65.4% molybdenum alloy quenched from 1870°C in the course of the incipient melting program. Here the reaction has apparently gone to completion, and only beta and intermediate phase remain. The composition of the phase therefore is further to the molybdenum side of the diagram than the composition of this alloy--supporting the designation of this phase as ZrMo_2 .

Zn X-ray pattern of -325 mesh powder from a 57.8% molybdenum alloy was made, using CuK_α radiation. Interpretation of the pattern indicated that the intermediate phase has a cubic lattice Cl_5 , MgCu_2 type, with $a = 7.59 \text{ \AA}$. The data are tabulated in the Appendix. This is in agreement with Duwez (12), who reports ZrMo_2 to be of the same lattice type, with $a = 7.58 \text{ \AA}$.

5. Molybdenum-Rich Alloys

A limited amount of work was done with molybdenum-rich alloys to help outline that portion of the system. Examination of as-cast alloys containing 70, 80, 90, and 100 nominal per cent molybdenum show the maximum solubility of zirconium in molybdenum to be less than 10%.

6. Melting Range Determination

An incipient melting program was carried out to determine the solidus curves and the peritectic level in this system. Specimens from the same alloy ingots used for isothermal anneals were employed, and the experimental methods are described in an earlier section of this report. Table XV lists the alloys used and the temperatures from which they were quenched. The results of this work were included in the construction of the diagram.

TABLE XV
MELTING RANGE DETERMINATIONS FOR THE ZIRCONIUM-MOLYBDENUM SYSTEM

Alloy No.	Wt. % Mo	Thermal Analysis Arrests, °C	Incipient Melting	
			Melting Observed, °C	No Melting, °C
YZM 10-235	9.6	1520	1640	1590
YZM 20-319	20.7		1560	--
YZM 31-629	30.7		1535	1500
YZM 31-791	30.8			
YZM 40-325	40.6		1550	1505
YZM 60-221	57.8		1965	1855
YZM 62-331	59.0		1900	1870
YZM 66-333	65.4		1900	1870

A eutectic alloy, melted (1535°C) and recrystallized, was shown in Fig. 43. The same alloy quenched from 1500°C is shown in Fig. 54. A fine distribution of phases characteristic of an annealed eutectic is evident. As a result of this and other incipient melting data, the eutectic level was placed at 1520°C. Similar incipient melting data placed the peritectic temperature at 1880°C. A 65.4% molybdenum alloy quenched from 1870°C was presented in Fig. 53, showing the disappearance of molybdenum solid solution upon the completion of the peritectic reaction.

Thermal analysis was limited in this system by the temperature levels involved. It was possible to obtain several cooling curves for a eutectic alloy; the eutectic arrest was determined to be 1520±15°C—in excellent agreement with incipient melting data. The composition of the alloy used for thermal analysis was 30.8% molybdenum.

Fig. 43

Neg. No. 3990 X250
 YZM 31-629
 Electrolytic: $K_3Fe(CN)_6 + NaOH + H_2O$

A 30.7% molybdenum alloy quenched from 1535°C in the incipient melting furnace. β -ZrMo₂ eutectic.

Fig. 44

Neg. No. 3986 X250
 ZM 20-319; P2-H1150-70; XR20-Q1480-10 min
 20% HF, 20% HNO₃ in glycerine

A 20.7% molybdenum alloy quenched from 1480°C. The retained β solid solution structure indicates a solubility greater than 20.7% molybdenum at this temperature.

Fig. 45

Neg. No. 3987 X250
 ZM 22-318; P3-H1150-70; XR5-Q1480-10 min
 Electrolytic: $K_3Fe(CN)_6 + NaOH + H_2O$

A 22.1% molybdenum alloy quenched from 1480°C. Retained β solid solution + ZrMo₂ crystals. At this temperature the $\beta/\beta + ZrMo_2$ boundary is therefore situated between 20.7 and 22.1% molybdenum.

Fig. 46

Neg. No. 3988 X250
 ZM 10-235; P4-H1150-70; XR72-Q900-48
 20% HF, 20% HNO₃ in glycerine

A 9.6% molybdenum alloy quenched from 900°C. Retained β solid solution.

Fig. 47

Neg. No. 3989 X500
 ZM 12-315; P3-H1150-70; XR72-Q900-48
 Electrolytic: $K_3Fe(CN)_6 + NaOH + H_2O$

A 11.9% molybdenum alloy quenched from 900°C. Retained $\beta +$ isothermal ZrMo₂ crystals. Comparison with Fig. 46 places the $\beta/\beta + ZrMo_2$ boundary between 9.6 and 11.9% molybdenum at 900°C.

Fig. 48

Neg. No. 3815 X750
 ZM 14-322; P3-H1150-70; XR41-Q790-610
 Electrolytic: $K_3Fe(CN)_6 + NaOH + H_2O$

A 14.5% molybdenum alloy quenched after annealing for 610 hours at 790°C. The retained $\beta + ZrMo_2$ structure indicates the alloy was annealed above the eutectoid temperature.

83

Fig. 43

Fig. 44

Fig. 45

Fig. 46

Fig. 47

Fig. 48

Fig. 49

Neg. No. 3609 X750
 ZM 16-321; P4-H1150-70; XR21-Q775-380
 Electrolytic: $K_3Fe(CN)_6 + NaOH + H_2O$

A 15.7% molybdenum alloy quenched from 775°C. A small amount of β adjacent to the proeutectoid $ZrMo_2$ crystals has decomposed eutectoidally into $\alpha + ZrMo_2$. This places the eutectoid level above 775°C.

Fig. 50

Neg. No. 3995 X500
 ZM 0.2-727; P54-H1150-65; XR61-Q775-240
 20% HF, 20% HNO_3 in glycerine

An 0.18% molybdenum alloy quenched after annealing at 775°C. The $\alpha +$ metastable β structure shows the limited solubility of molybdenum in α phase.

Fig. 51

Neg. No. 3992 X750
 ZM 60-221 C
 2% HF, 3% HNO_3 in water

A 57.8% molybdenum as-cast alloy. Primary $ZrMo_2$ crystals in a matrix of degenerated eutectic, β - $ZrMo_2$.

Fig. 52

Neg. No. 3993 X750
 ZM 62-331 C
 2% HF, 3% HNO_3 in water

A 59.0% molybdenum as-cast alloy. Primary molybdenum-rich solid solution, peritectic walls of $ZrMo_2$, and degenerated eutectic matrix. Comparing this with Fig. 51 shows the composition of the peritectic liquid must lie between 57.8 and 59% molybdenum.

Fig. 53

Neg. No. 3994 X750
 YZM 66-333; Q1870
 2% HF, 3% HNO_3 in water

A 65.4% molybdenum alloy quenched from 1870°C in the incipient melting furnace. The peritectic reaction apparently has gone to completion, and only $\beta + ZrMo_2$ remain after the high temperature anneal.

Fig. 54

Neg. No. 3991 X750
 YZM 31-629; Q1500
 Electrolytic: $K_3Fe(CN)_6 + NaOH + H_2O$

A 30.7% molybdenum alloy quenched from 1500°C in the incipient melting furnace. A fine distribution of phases characteristic of the annealed eutectic structure.

Fig. 49

Fig. 50

Fig. 51

Fig. 52

Fig. 53

Fig. 54

C. The System Zirconium-Copper

by C. E. Lundin

1. Special Techniques

All of the arc melted alloys were prepared in the manner described in the melting techniques section. No deviations from this practice were found necessary for zirconium-copper alloys.

Several of the intermediate phases and eutectics displayed nearly similar melting points. In order to detect the very small differences in the melting temperatures of these alloys, which neither thermal analysis nor the standard incipient melting techniques provided with an accuracy deemed necessary, another method was developed. The specimens were sealed in Vycor bulbs and annealed at various accurately controlled temperatures. Metallographic examination was then employed to reveal incipient melting points.

2. The Phase Diagram

The 0-50 atomic per cent region of the zirconium-copper diagram is presented in Fig. 55, plotted with weight per cent as the principal composition scale. The complete diagram from 0 to 100 atomic and weight per cent copper is presented in Fig. 56. An expanded view of the zirconium-rich portion of the diagram is shown in Fig. 57.

Table XVI lists the analyses of the alloys from which these diagrams have been derived.

The preliminary study to determine the times necessary to attain equilibrium at various annealing temperatures arbitrarily involved percentages of 1, 4, and 7% copper. Optimum times at temperature for 700°, 800°, and 900°C were 350, 150, and 75 hours, respectively. This was based on no detectable change in the relative amounts of phases present. Isothermal annealing times for all temperatures were selected on a basis of these data. A complete tabulation of the pretreatment and annealing data for the zirconium-copper alloys is given in Table XVII.

The principal features of the zirconium-copper system may be summarized as follows:

- a. The maximum solubility of copper in beta zirconium is 3.8% at the eutectic temperature. The solubility of copper in alpha zirconium is less than 0.18% at all temperatures. A eutectoid reaction occurs at 1.6% copper and $822 \pm 10^\circ\text{C}$.
- b. A eutectic exists at 21% copper and $995 \pm 10^\circ\text{C}$, between zirconium and Zr_2Cu (25.83% copper).

FIG.55-PARTIAL DIAGRAM OF ZIRCONIUM - COPPER SYSTEM.

FIG.56- THE ZIRCONIUM -COPPER SYSTEM.

TABLE XVI
ANALYSES OF ZIRCONIUM-COPPER ALLOYS

Alloy No.	Copper, Wt. %	Alloy No.	Copper, Wt. %
ZC 0.1-363	0.09	ZC 40-259	39.6
ZC 0.2-364	0.18	ZC 41-348	41.1
ZC 0.3-365	0.31	ZC 42-349	42.8
ZC 0.4-366	0.44	ZC 43-350	43.1
ZC 0.5-270	0.47	ZC 44-351	44.2
ZC 0.6-367	0.63	ZC 45-261	44.7
ZC 0.8-369	0.78	ZC 46-361	46.1
ZC 1-272	1.05	ZC 47-353	47.6
ZC 1.25-581	1.1	ZC 48-354	47.9
ZC 1.50-582	1.4	ZC 48.5-478	48.5
ZC 1.75-583	1.6	ZC 49-271	49.3
ZC 2-273	1.8	ZC 50-262	50.1
ZC 2.5-584	2.2	ZC 51-504	50.9
ZC 3-274	3.2	ZC 52-355	52.2
ZC 4-275	3.8	ZC 53-427	52.4
ZC 5-276	5.0	ZC 53-505	52.4
ZC 5-251	5.2	ZC 54-356	54.3
ZC 6-277	5.8	ZC 56-430	55.0
ZC 7-280	6.7	ZC 56-357	55.8
ZC 8-279	7.8	ZC 58-358	57.8
ZC 9-281	8.5	ZC 60-506	59.6
ZC 10-284	9.5	ZC 60-263	59.9
ZC 10-248	10.3	ZC 61-502	60.2
ZC 15-250	15.4	ZC 62-503	62.5
ZC 18-252	17.8	ZC 63-429	62.2
ZC 20-255	19.3	ZC 64-576	63.8
ZC 21-424	20.9	ZC 65-577	64.8
ZC 23-425	23.2	ZC 66-578	65.8
ZC 25-254	25.1	ZC 67.5-264	66.7
ZC 26-256	25.6	ZC 67.5-432	67.0
ZC 27-342	26.9	ZC 69-359	68.6
ZC 29-343	28.9	ZC 70-265	69.9
ZC 30-257	31.2	ZC 71-579	71.6
ZC 33-426	32.2	ZC 72-580	71.5
ZC 35-258	35.7	ZC 80-267	79.4
ZC 37-344	37.0	ZC 86-268	86.0
ZC 38-345	38.3	ZC 90-269	91.1
ZC 39-360	38.6	ZC 95-433	95.2*

*Analyzed for zirconium; copper by difference.

TABLE XVII
PRETREATMENT AND ANNEALING OF ZIRCONIUM-COPPER ALLOYS

Alloy No.	Cold Pressed,%*	Homogenized 900°C-7 hr*	Cold Rolled,%*	980°C 25 hr	950°C 50 hr	900°C 72 hr
ZO-283 (Zr)	55	x	89	x	x	x
ZC 0.1-363	46	x	72	x	x	x
ZC 0.2-364	50	x	80	x	x	x
ZC 0.3-365	54	x	67	x	x	x
ZC 0.4-366	53	x	64	x	x	x
ZC 0.5-270	52	x	80	x	x	x
ZC 0.6-367	58	x	65	x	x	x
ZC 0.8-369	57	x	66	x	x	x
ZC 1-272	49	x	75	x	x	x
ZC 1.25-581	24	x	77	x	x	x
ZC 1.50-582	12	x	74	x	x	x
ZC 1.75-583	15	x	70	x	x	x
ZC 2-273	28	x	48	x	x	x
ZC 2.50-584	17	x	20	x	x	x
ZC 3-274	17	x	44	x	x	x
ZC 4-275	10	x	34	x	x	x
ZC 5-276	11	x	53	x	x	x
ZC 6-277	13	x	13	x	x	x
ZC 7-280	13	x	35	x	x	x
ZC 8-279	14	x	33	x	x	x
ZC 9-281	11	x	27	x	x	x
ZC 10-284	8	x	19	x	x	x
ZC 15-211	-	x	-	x	x	x
ZC 20-255	-	x	-	x	x	x

*The pretreatment cycle (that is, the cold pressing, homogenization, and cold rolling) corresponding to each alloy composition is the same for all annealing treatments, and is not repeated in subsequent columns.

TABLE XVII. (Cont.)

Alloy No.	850°C 100 hr	830°C 100 hr	815°C 100 hr	800°C 150 hr	750°C 256 hr	700°C 400 hr	650°C 450 hr	600°C 648 hr
ZO-283 (Zr)	x	x	x	x	x	x	x	x
ZC 0.1-363	x	x	x	x	x	x	x	x
ZC 0.2-364	x	x	x	x	x	x	x	x
ZC 0.3-365	x	x	x	x	x	x	x	x
ZC 0.4-366	x	x	x	x	x	x	x	x
ZC 0.5-270	x	x	x	x	x	x	x	x
ZC 0.6-367	x	x	x	x	x	x	x	x
ZC 0.8-369	x	x	x	x	x	x	x	x
ZC 1-272	x	x	x	x	x	x	x	x
ZC 1.25-581	x	x	x	x	x			
ZC 1.50-582	x	x	x	x	x			
ZC 1.75-583	x	x	x	x	x			
ZC 2-273	x	x	x	x	x	x	x	x
ZC 2.50-584	x	x	x	x	x			
ZC 3-274	x	x	x	x	x	x	x	x
ZC 4-275	x	x	x	x	x	x	x	x
ZC 5-276	x	x	x	x	x	x	x	x
ZC 6-277	x	x	x	x				
ZC 7-280	x	x	x	x				
ZC 8-279	x	x	x	x				
ZC 9-281	x	x	x	x				
ZC 10-284	x		x	x				
ZC 15-211	x		x	x				
ZC 20-255	x		x	x				

- c. An intermediate phase is formed at about 27% copper and $1000 \pm 10^\circ\text{C}$, which probably corresponds to the formula Zr_2Cu (25.83% copper).
- d. A eutectic occurs at 37% copper and $928 \pm 10^\circ\text{C}$ between Zr_2Cu and ZrCu (41.06% copper).
- e. An intermetallic compound forms at 41% copper and $935 \pm 10^\circ\text{C}$, corresponding to the formula ZrCu (41.06% copper).
- f. A eutectic between ZrCu and Zr_2Cu_3 (51.09% copper) exists at 47% copper and $890 \pm 10^\circ\text{C}$.
- g. An intermetallic compound forms at 50% copper and $895 \pm 10^\circ\text{C}$, corresponding to the formula Zr_2Cu_3 (51.09% copper).
- h. A eutectic between Zr_2Cu_3 and Zr_2Cu_5 (tentative, 63.52% copper) occurs at 53% copper and $885 \pm 10^\circ\text{C}$.
- i. The intermediate phase designated Zr_2Cu_5 is formed peritectically by a reaction between the melt containing 61% copper and ZrCu_3 (tentative, 67.63% copper) at $1070 \pm 10^\circ\text{C}$.
- j. An intermediate phase exists at about 71.5% copper and melts at $1100 \pm 10^\circ\text{C}$. The formula ZrCu_3 (67.63% copper) has been tentatively accepted for this phase on a basis of previous literature.
- k. A eutectic between ZrCu_3 and copper exists at 91% copper and $965 \pm 10^\circ\text{C}$.
- l. The solubility of zirconium in copper is very limited. Previous investigators, although in disagreement on exact values, agree that the solubility is less than 1% zirconium.

3. Zirconium-Rich Alloys

The zirconium-rich portion of the diagram is given in Fig. 57. The phase boundaries were determined from the structures of isothermally annealed alloys scheduled in Table XVII.

The allotropic transformation temperature, $\alpha \rightleftharpoons \beta$, is decreased from 862° to 822°C by increasing amounts of copper. Thus, a eutectoid reaction, $\beta \rightleftharpoons \alpha + \text{Zr}_2\text{Cu}$, occurs at a composition of about 1.6% copper. The eutectoid level was determined to lie between the alloy series annealed at 815° and 830°C . The placement of this eutectoid temperature was based principally on the structures of hypereutectoid alloys. The hypereutectoid alloys in the $\beta + \text{Zr}_2\text{Cu}$ region displayed partial eutectoid decomposition during water quenching. This phenomenon is indicated in Fig. 58, a 3.2% copper alloy quenched from 830°C , in which decomposition, probably nucleated by proeutectoid Zr_2Cu crystals, is seen to progress out from the original beta grain boundaries. At 815°C

(Fig. 59), the structure consists of particles of Zr_2Cu in a matrix of isothermal alpha. Therefore, at the annealing temperatures of 830° and 815°C, the specimens were $\beta + Zr_2Cu$ and $\alpha + Zr_2Cu$, respectively. Partial eutectoid decomposition was also noted in other hypereutectoid alloys quenched from above 822°C.

The convergence of the beta solid solution field toward the eutectoid composition, 1.6% copper, is illustrated by Figs. 60 through 62, of alloys containing 1.05, 1.8, and 3.2% copper, respectively, annealed at 850°C. Structures containing $\alpha + \beta$, β , and $\beta + Zr_2Cu$ are evident.

The uppermost experimental placement (980°C) of the $\beta/\beta + Zr_2Cu$ boundary is illustrated in Figs. 63 and 64. The extrapolation of this boundary to the eutectic temperature, 995°C, indicates a maximum copper solubility in beta zirconium of about 3.8%.

The maximum extent of copper solubility in alpha zirconium is illustrated in Figs. 65 and 66, showing alloys annealed at 830°C. The former, a 0.09% copper alloy, consists of alpha solid solution. The latter, an 0.18% copper alloy, contains $\alpha + \beta$.

Within a restricted region near the eutectoid composition, anomalous three phase structures were often found. Departure from true binary equilibrium in this region did not seriously affect the placement of the eutectoid composition and temperature. This phenomenon is discussed in Section IV-D of this report.

4. Intermediate Phases

Although the scope of the work on the zirconium-copper system was to include alloys up to 50 atomic per cent copper (41.06 wt.%), alloys were made to obtain the major features of the diagram to 100% copper. Figure 56 represents the complete diagram on a weight and atomic per cent basis.

Surveying the system in the direction of increasing copper content, the structure in Fig. 63 is that of an alloy with 3.2% copper. The structure represents beta solid solution. Figure 67, an alloy with 10.3% copper, shows primary beta plus eutectic. At 20.9% copper, the first eutectic is encountered; this is depicted in Fig. 68. The compound Zr_2Cu exists at a theoretical weight per cent of 25.83. The alloy which most nearly approaches a single phase structure analyzes 26.9% copper. This is presented in Fig. 69. X-ray studies of this alloy were made, and the structure was determined to be face centered tetragonal. Lattice constants were determined as follows: $c = 3.716 \text{ \AA}$, $a = 4.536 \text{ \AA}$, and $c/a = 0.819$. The lines measured and indexed are presented in the Appendix.

Between the Zr_2Cu compound and the next intermediate phase, there exists a eutectic. It was best exhibited in a 37.0% copper alloy, shown in Fig. 70. From 37 to 41.1% copper, primary crystals of the new phase increase in amount, and a nearly single phase structure is obtained at 41.2%. This is shown in Fig. 71. The most probable formula for this phase is $ZrCu$ (41.06% copper). There is a pronounced acicularity present within the primary $ZrCu$ crystals, which may be

evidence of a transformation or reaction involving this phase in the solid state. Debye-Scherrer X-ray photograms were made of this alloy in the as-cast condition and as-annealed at 900° and 700°C. The lines were so numerous that no attempt was made to index the structure.

Progressing further toward the copper-rich end of the diagram, the next structural feature is a eutectic between ZrCu_3 and the next intermediate phase at 47.6% copper, shown in Fig. 72. An alloy containing 50.2% copper exhibits a nearly single phase structure, indicative of an intermediate phase (Fig. 73). The formula Zr_2Cu_3 (51.09% copper) was assigned to this phase. X-ray photograms were taken of as-cast and annealed (800°C) alloys; however, none were indexed because of the large number of lines present. An alloy containing 52.4% copper, Fig. 74, represents the next eutectic structure between Zr_2Cu_3 and a new intermediate phase. Between 52.4% and 60.2% copper, primary crystals of this new phase increase in relative amount.

Figure 75 shows a 60.2% copper alloy whose structure consists of primary compound crystals plus eutectic. In an alloy of 62.5% copper (Fig. 76), a new type of primary crystal (hexagonal habit) appears in small amounts and is surrounded by a rim of the phase which was primary in the 60.2% alloy. Thus, a peritectic reaction takes place between the melt at about 61% and primary hexagonal type crystals to form a peritectic phase. Figure 77 shows the 62.5% copper alloy after annealing. The peritectic reaction has proceeded considerably, but not to completion, since resorption of the hexagonal habit crystals is not complete. The peritectic phase is tentatively assigned the formula Zr_2Cu_5 (63.52% copper), although it might alternatively be ZrCu_3 (67.63% copper).

The next single phase alloy with an open maximum, Fig. 78, contains 71.5% copper. This is the copper-rich intermediate phase which has been called ZrCu_3 (67.63% copper), by previous investigators. This designation is tentatively adopted, although in the present work the single phase alloys lie closer to the theoretical formula ZrCu_4 (73.59% copper). X-ray photograms of the as-cast and annealed (900°C) 71.5% copper alloy contained too many lines to obtain reliable indexing.

An alloy containing 91.1% copper, Fig. 79, depicts the eutectic between ZrCu_3 and the copper solid solution.

No alloys were made to study the limited solid solubility of zirconium in copper. This has been treated in the literature.

5. Melting Point Determinations

The induction furnace incipient melting techniques described earlier in this report were not sufficiently precise to differentiate between certain temperature levels in this system. The approximate melting temperatures of intermediate phases and eutectics were, nevertheless, preliminarily determined by this technique. Thermal analysis was more generally useful, but again, more exacting work

was required to place some of the characteristic temperatures. A separate technique was employed in these cases which involved short-time, precision controlled, isothermal anneals. Specimens were sealed in Vycor bulbs and held at various small temperature increments in the vicinity of the roughly determined melting point. These were then quenched and examined microscopically for signs of incipient melting. This technique was applicable to the zirconium-copper system because the melting levels were, in general, considerably lower than those encountered in the other binary systems.

Table XVIII summarizes the melting data for this system.

Temperature values shown on the diagrams are all thermal analysis or bulb annealing figures, and were chosen on the basis of the best checks and the highest accuracy.

6. Discussion of the Literature

It was found, upon investigating the structures of a few alloys with more than 50 atomic per cent copper, that the phase relationships were in disagreement with those reported in previous work. Therefore, it was deemed advisable to make a rather thorough survey of the system to 100 atomic per cent copper. Allibone and Sykes (13), Pogodin and Shumova (14), and Raub and Engel (15) have contributed work on the copper-rich end of the zirconium-copper diagram. The latest and seemingly the most complete investigation was that of Raub and Engel, in which alloys up to 68.3% zirconium (31.7-100% Cu) were studied principally by thermal analysis and microscopic examination. These authors report a compound ZrCu_3 (1116°C m.p.) and two eutectics, one at 86.3% copper (977°C m.p.) and the other at 49% copper (877°C m.p.). They also found the solubility of zirconium in copper to be less than 0.1% at 940°C. In the area on the zirconium side of ZrCu_3 , Raub and Engel report only a eutectic between ZrCu_3 and an unidentified zirconium-rich phase. The present investigation has shown the existence of three intermediate phases, ZrCu , Zr_2Cu_3 , and Zr_2Cu_5 (?), the last being peritectically formed, and three eutectics in this same region. The melting points of the intermetallic compound ZrCu_3 and the eutectic ZrCu_3 -Cu agree favorably in the two investigations.

TABLE XVIII
MELTING RANGE DETERMINATIONS FOR THE ZIRCONIUM-COPPER SYSTEM

Alloy	Wt. % Cu	Thermal Analysis		Bulb Anneals*	
		Arrests, °C	Melting Observed, °C	No Melting, °C	
XZC 10-790	10.1	1505, 990			
XZC 21-730	21.1	995			
XZC 27-736	27.3	1000			
YZC 27-342	26.9		1006**		
ZC 27-342	26.9		1006		994
XZC 37-735	36.7	935			
YZC 37-344	37.0		930**		
ZC 37-344	37.0		930		925
XZC 41-734	41.3	935			
ZC 41-348	41.1		940		930
XZC 47-750	47.0	890			
XZC 50-732	49.8	895			
XZC 53-731	53.3	885			
XZC 65-747	64.7	1072, 885			
XZC 71-748	71.6	1100			
YZC 71-579	71.6		1121**		
XZC 90-749	89.5	965			

*Isothermal anneals of specimens sealed in glass bulbs and held in tube furnaces.

**Incipient melting data.

Fig. 58

Neg. No. 3694 X500
 ZC 3-274;P17-H900-7;XR44-Q830-100
 20% HF, 20% HNO₃ in glycerine

A 3.18% copper alloy, quenched after annealing 100 hours at 830°C. This structure consists of proeutectoid crystals of Zr₂Cu and a matrix of β transformation product, indicating that the specimen was quenched from above the eutectoid temperature.

Fig. 59

Neg. No. 3695 X500
 ZC 3-274;P17-H900-7;XR44-Q815-100
 20% HF, 20% HNO₃ in glycerine

A 3.18% copper alloy, quenched after annealing 100 hours at 815°C. Proeutectoid crystals of Zr₂Cu in a matrix of isothermal α . Note the two sizes of compound grains; the smaller particles undoubtedly result from the eutectoid reaction. This alloy was quenched from below the eutectoid temperature.

Fig. 60

Neg. No. 5025 X250
 ZC 1-272;P49-H900-7;XR75-Q850-100
 20% HF, 20% HNO₃ in glycerine

A 1.05% copper alloy, quenched after annealing 100 hours at 850°C. Grains of isothermally formed α in a matrix of transformed β . This alloy was annealed in the $\alpha + \beta$ field.

Fig. 61

Neg. No. 5026 X250
 ZC 2-273;P28-H900-7;XR48-Q850-100
 20% HF, 20% HNO₃ in glycerine

A 1.8% copper alloy, quenched after annealing 100 hours at 850°C. The structure consists of single phase transformed β . This alloy was annealed in the β field.

Fig. 62

Neg. No. 5027 X250
 ZC 3-274;P17-H900-7;XR44-Q850-100
 20% HF, 20% HNO₃ in glycerine

A 3.2% copper alloy, quenched after annealing 100 hours at 850°C. Proeutectoid crystals of Zr₂Cu in a matrix of transformed β . This alloy was annealed in the $\beta + \text{Zr}_2\text{Cu}$ field.

Fig. 58

Fig. 59

Fig. 60

Fig. 61

Fig. 62

Fig. 63

Neg. No. 5023 X250
 ZC 3-274;P17-H900-7;XR44-Q980-25
 20% HF, 20% HNO₃ in glycerine

A 3.2% copper alloy, quenched after annealing 25 hours at 980°C. Structure is single phase transformed β .

Fig. 64

Neg. No. 5024 X250
 ZC 4-275;P10-H900-7;XR34-Q850-100
 20% HF, 20% HNO₃ in glycerine

A 3.8% copper alloy, quenched after annealing 25 hours at 980°C. Structure consists of proeutectoid Zr₂Cu crystals in a matrix of transformed β .

Fig. 65

Neg. No. 5032 X500
 ZC 0.1-363;P46-H900-7;XR72-Q830-100
 20% HF, 20% HNO₃ in glycerine

A 0.09% copper alloy, quenched after annealing 100 hours at 830°C. Nearly single phase isothermal α , representing maximum solubility of copper.

Fig. 66

Neg. No. 5028 X250
 ZC 0.2-364;P50-H900-7;XR80-Q830-100
 20% HF, 20% HNO₃ in glycerine

An 0.18% copper alloy, quenched after annealing 100 hours at 830°C. The structure consists of a small amount of transformed beta at isothermal α grain boundaries. This composition is beyond the maximum solubility of copper in α phase.

Fig. 67

Neg. No. 5029 X500
 ZC 10-284 C
 20% HF, 20% HNO₃ in glycerine

A 9.5% copper alloy, as-cast. Primary dendrites of β solid solution in a matrix of eutectic Zr-Zr₂Cu.

Fig. 68

Neg. No. 5030 X750
 ZC 21-424 C
 20% HF, 20% HNO₃ in glycerine

A 20.9% copper alloy, as-cast. The very fine structure of the Zr-Zr₂Cu eutectic.

Fig. 63

Fig. 64

Fig. 65

Fig. 66

Fig. 67

Fig. 68

Fig. 69

Neg. No. 3475 XL00
 ZC 27-342 C
 20% HF, 20% HNO₃ in glycerine

A 26.9% copper alloy, as cast. This structure represents nearly 100% of the intermetallic compound Zr₂Cu.

Fig. 70

Neg. No. 3600 X750
 ZC 37-344 C
 20% HF, 20% HNO₃ in glycerine

A 37% copper alloy, as cast. Intimate phase mixture representing the structure of the eutectic Zr₂Cu-ZrCu.

Fig. 71

Neg. No. 3602 X 75
 ZC 41-348 C
 Unetched, polarized light

A 41.1% copper alloy, as cast. Virtually 100% primary crystals of the intermetallic compound ZrCu. Acicularity within the primaries is undoubtedly evidence that this phase undergoes a transformation in the solid state.

Fig. 72

Neg. No. 3603 X500
 ZC 47-353 C
 20% HF, 20% HNO₃ in glycerine

A 47.6% copper alloy, as cast. Intimate phase mixture representing the eutectic ZrCu-Zr₂Cu₃.

Fig. 73

Neg. No. 3604 XL50
 ZC 50-262 C
 20% HF, 20% HNO₃ in glycerine

A 50.1% copper alloy, as cast. Nearly single phase structure representing the intermediate phase Zr₂Cu₃.

Fig. 74

Neg. No. 3605 X500
 ZC 53-505 C
 20% HF, 20% HNO₃ in glycerine

A 52.4% copper alloy, as cast. The eutectic structure Zr₂Cu₃-Zr₂Cu₅.

Fig. 69

Fig. 70

Fig. 71

Fig. 72

Fig. 73

Fig. 74

Fig. 75

Neg. No. 5034
ZC 61-502 C

X250

20% HF, 20% HNO₃ in glycerine

A 60.2% copper alloy, as-cast. Primary crystals of the intermetallic compound Zr₂Cu₅ in a matrix of the degenerated Zr₂Cu₃-Zr₂Cu₅ eutectic.

Fig. 76

Neg. No. 3606
ZC 62-503 C

X250

20% HF, 20% HNO₃ in glycerine

A 62.5% copper alloy, as cast. A three phase structure giving evidence of the peritectic reaction: ZrCu₃ + melt → Zr₂Cu₅. The white primaries of ZrCu₃ are surrounded by serrated peritectic walls of Zr₂Cu₅ in a matrix of degenerated Zr₂Cu₃-Zr₂Cu₅ eutectic.

Fig. 77

Neg. No. 3696
ZC 62-503; Q700-350

X200

20% HF, 20% HNO₃ in glycerine

A 62.5% copper alloy, quenched after annealing 350 hours at 700°C. A three phase structure in which the peritectically formed Zr₂Cu₅ has grown at the expense of the primary ZrCu₃ crystals during the annealing treatment (compare with the cast structure, Fig. 76).

Fig. 78

Neg. No. 5035
ZC 72-580 C

X250

Unetched

A 71.5% copper alloy, as-cast. Virtually 100% of the intermetallic compound ZrCu₃.

Fig. 79

Neg. No. 5031
ZC 90-269 C

X750

20% HF, 20% HNO₃ in glycerine

A 91.1% copper alloy, as-cast. This structure represents the eutectic ZrCu₃-Cu.

Fig. 75

Fig. 76

Fig. 77

Fig. 78

Fig. 79

D. The System Zirconium-Wolfram

by R. F. Domagala

1. Special Techniques

In the zirconium-wolfram system, as in the zirconium-molybdenum system, ingots were arc melted using an electrode of the same material as the alloying metal. The wolfram-tipped electrodes precluded any introduction of a third metal in the melting process.

The preparation of homogeneous ingots containing no unmelted wolfram presented a difficult problem. Merely charging the two metals in the desired proportions for arc melting always resulted in the presence of unalloyed wolfram particles. After many trials, varying the charge form and melting techniques, a satisfactory procedure was evolved, which consisted of melting master alloy ingots and combining granules of the master alloy with pure zirconium to produce the required alloy. The preparation of a 50% master alloy followed the following pattern: A charge of pure wolfram in the form of -20 mesh granules was arc melted at high power levels (700-900 amperes). While holding this charge molten, an equivalent weight of zirconium was charged, very slowly, into the bath, yielding an approximately 50W-50Zr master alloy. To insure complete homogeneity, the master alloy was then crushed and divided into three parts. Each part was melted in the arc furnace and then crushed again. The three parts were again combined and melted. This master alloy was then crushed and served as melting stock for alloys of lower wolfram content.

Essentially, then, the problem of unmelted wolfram particles was obviated by starting with pure wolfram melts and adding zirconium to these. Master alloys containing 26, 50, 52, 70, and 90% wolfram served for the preparation of all other zirconium-wolfram compositions, in the following manner:

<u>Master, % W</u>	<u>Alloys, % W</u>
26	0.5, 1 to 10 by 1%, 10 to 26 by 2%
50	10 to 50 by 5%
52	46, 49, 52
70	55, 60, 65, 70
90	75, 80, 85, 90

Calculated amounts of zirconium were added to granules of the analyzed master alloys to yield the desired compositions. Alloys containing up to 50% wolfram were arc melted in a copper block insert, without opening the furnace, eight times, while alloys richer in wolfram were melted in a heavy-wall copper crucible ten times. However, regardless of the number of times high wolfram content ingots were remelted, there was a tendency for gravity segregation of the wolfram-rich phase to the bottom of the ingot. This segregation did not hinder the evaluation of the structural features of the system.

2. The Phase Diagram

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The phase relationships in the 0-50 weight per cent wolfram region are presented in Fig. 80, and the 0-50 atomic per cent wolfram region is shown in Fig. 81. Figure 82 presents the entire diagram on the basis of both weight and atomic per cent. Characteristic temperatures and compositions are noted in all drawings, but experimental points necessary for their determination have been included only in Fig. 80. To retain as much clarity as possible, some points have been omitted. The complete tabulation of annealing and pretreatment data is included in Tables XIX and XX. All the alloys were examined in the as-cast condition to aid in the construction of the diagram.

The diagrams are based on the chemical analyses of alloys, presented in Table XXI.

The salient features of the zirconium-wolfram system include:

- a. One intermediate phase exists in the system. It is peritectically formed at $2175 \pm 25^\circ\text{C}$ by the reaction: Melt + wolfram solid solution $\rightarrow \text{ZrW}_2$. ZrW_2 should exist, ideally, at 80.13% wolfram.
- b. A eutectic between beta solid solution and ZrW_2 occurs at $1650 \pm 15^\circ\text{C}$ and 18% wolfram.
- c. The limit of solubility of wolfram in beta zirconium is about 8% at the eutectic level.
- d. A eutectoid decomposition of beta into $\alpha + \text{ZrW}_2$ occurs at about 0.5% wolfram and $850 \pm 15^\circ\text{C}$.
- e. The solubility of wolfram in alpha zirconium is less than 0.5% at all temperature levels.
- f. A limited investigation of the wolfram-rich region showed that less than 10 weight per cent zirconium is soluble in wolfram.

3. Zirconium-Rich Alloys

The eutectic between beta and ZrW_2 at 1650°C and 18% wolfram was positioned after examining alloys containing 0.5 to 26 nominal per cent wolfram in the arc-cast condition. The eutectic composition is believed to be accurate to $\pm 2\%$ wolfram. Figure 83 shows a 21.1% wolfram alloy in the arc-cast condition, illustrating the very fine distribution of phases characteristic of the eutectic in this system. Although some primary ZrW_2 was present in this alloy, the eutectic structure was considered better for presentation than that of the 100% eutectic alloy containing 17.9% wolfram.

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FIG.80—PARTIAL DIAGRAM OF THE ZIRCONIUM—
WOLFRAM SYSTEM.

FIG.81 - PARTIAL DIAGRAM OF THE ZIRCONIUM-WOLFRAM SYSTEM.

FIG.82- THE ZIRCONIUM - WOLFRAM SYSTEM.

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TABLE XIX
PRETREATMENT AND ANNEALING DATA FOR ZIRCONIUM-WOLFRAM ALLOYS

Alloy No.	Cold Pressed,%*	Homogenized 1200°C*	Cold Rolled,%*	1460°C **	1400°C 1 hr
ZO 283 (Zr)	55	***	89	x	x
ZW 0.5-784	32	70 hr	80		
ZW 1-783	23	70 hr	74		x
ZW 2-782	3	70 hr	53	x	x
ZW 3-781	2	70 hr	40		x
ZW 4-780	2	70 hr	34	x	x
ZW 5-779	2	70 hr	36		x
ZW 6-778	-	70 hr	31	x	x
ZW 7-777	-	70 hr	25		x
ZW 8-768	-	70 hr	19	x	x
ZW 9-776	-	70 hr	15		x
ZW 10-775	-	70 hr	16	x	x
ZW 12-774	-	44 hr	23	x	x
ZW 14-773	-	44 hr	30	x	x
ZW 16-772	-	44 hr	18	x	x
ZW 18-771	-	44 hr	12	x	x
ZW 20-770	-	44 hr	14	x	x
ZW 22-769	-	44 hr	13	x	x
ZW 24-767	-	44 hr	8	x	x
ZW 26-766	-	44 hr	-	x	x
ZW 30-647				x	
ZW 35-648					
ZW 40-649				x	
ZW 45-650					
ZW 50-652				x	
ZW 55-801					

*The pretreatment (i.e. cold pressing, homogenization, cold rolling), corresponding to each alloy composition is the same for all annealing treatments, and is not repeated in subsequent columns.

**Specimens placed in furnace at 1400°C; temperature rose to 1460°C in 100 min. Specimens then quenched.

***Homogenized at 900°C for 7 hours.

TABLE XIX (Cont.)

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Alloy No.	1300°C 2 hr	1200°C 8 hr	1100°C 20 hr	1006°C 48 hr	950°C 50 hr	900°C 75 hr
ZO 283 (Zr)	x	x	x	x	x	x
ZW 0.5-784				x	x	x
ZW 1-783		x	x	x	x	x
ZW 2-782	x	x	x	x	x	x
ZW 3-781		x	x	x	x	x
ZW 4-780	x	x	x	x	x	x
ZW 5-779		x	x	x	x	x
ZW 6-778	x	x	x	x	x	x
ZW 7-777		x	x	x	x	x
ZW 8-768	x	x	x	x	x	x
ZW 9-776		x	x	x	x	x
ZW 10-775	x	x	x	x	x	x
ZW 12-774	x	x	x	x	x	x
ZW 14-773	x	x	x	x	x	x
ZW 16-772	x	x	x	x	x	x
ZW 18-771	x	x	x	x	x	x
ZW 20-770	x	x	x	x	x	x
ZW 22-769	x	x	x	x	x	x
ZW 24-767	x	x	x	x	x	x
ZW 26-766	x	x	x	x	x	x
ZW 30-647			x			
ZW 35-648	x					x
ZW 40-649			x			
ZW 45-650	x					x
ZW 50-652			x			
ZW 55-801	x					x

TABLE XIX (Cont.)

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Alloy No.	850°C 95 hr	800°C 170 hr	746°C 240 hr	700°C 335 hr	650°C 450 hr	600°C 500 hr
ZO 283 (Zr)	x	x	x	x	x	x
ZW 0.5-784	x	x	x	x	x	x
ZW 1-783	x	x	x	x	x	x
ZW 2-782	x	x	x	x	x	x
ZW 3-781	x	x	x	x	x	x
ZW 4-780	x	x	x	x	x	x
ZW 5-779	x	x	x	x	x	x
ZW 6-778	x	x	x	x	x	x
ZW 7-777	x	x	x	x	x	x
ZW 8-768	x	x	x	x	x	x
ZW 9-776	x	x	x	x	x	x
ZW 10-775	x	x	x	x	x	x
ZW 12-774	x	x	x			
ZW 14-773	x	x	x			
ZW 16-772	x	x	x			
ZW 18-771	x	x	x			
ZW 20-770	x	x	x	x		x
ZW 22-769	x	x	x			
ZW 24-767	x	x	x			
ZW 26-766	x	x	x			
ZW 30-647		x				x
ZW 35-648				x		
ZW 40-649		x				x
ZW 45-650				x		
ZW 50-652		x				x
ZW 55-801				x		

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TABLE XX
SPECIAL* HIGH TEMPERATURE ANNEALING TREATMENTS--
ZIRCONIUM-WOLFRAM SYSTEM

Alloy No.	1520°C 5 min	1590°C 5 min
ZO-283 (Zr)	x	x
ZW 5-179	x	x
ZW 6-178	x	x
ZW 7-777	x	x
ZW 8-768	x	x
ZW 9-776	x	x
ZW 10-775	x	x
ZW 12-774	x	x
ZW 14-773	x	x
ZW 16-772		x

*These treatments were carried out in small molybdenum canisters supported by wolfram wire in the incipient melting furnace.

TABLE XXI
ANALYSES OF ZIRCONIUM-WOLFRAM ALLOYS

Alloy No.	Wolfram, Wt.%	Alloy No.	Wolfram, Wt.%
ZW 0.5-784	0.49	ZW 22-769	21.1
ZW 1-783	1.3	ZW 24-767	22.2
ZW 2-782	2.2	ZW 25-646	23.5
ZW 3-781	2.9	ZW 26-766	24.0
ZW 4-780	3.6	ZW 30-647	30.4
ZW 5-642	5.0	ZW 35-648	34.9
ZW 5-779	4.7	ZW 40-649	38.5
ZW 6-778	5.3	ZW 45-650	42.6
ZW 7-777	6.1	ZW 46-783	46.6
ZW 8-768	7.2	ZW 49-782	48.5
ZW 9-776	8.2	ZW 50-652	57.6
ZW 10-643	10.3	ZW 52-781	52.3
ZW 10-775	9.3	ZW 55-801	55.4
ZW 12-774	11.3	ZW 60-800	61.3
ZW 14-773	14.0	ZW 65-799	65.5
ZW 15-644	15.2	ZW 70-798	71.3
ZW 16-772	14.5	ZW 75-796	77.9
ZW 18-771	17.5	ZW 80-795	82.8
ZW 20-645	20.1	ZW 85-794	87.6
ZW 20-770	17.9	ZW 90-765	91.2

Metallographic examination of isothermally annealed specimens indicates that the solubility of wolfram in beta zirconium decreases from a maximum of 8% at the eutectic temperature to about 0.5% at the eutectoid temperature. This is illustrated in Figs. 84-87. Figures 84 and 85 show 3.6 and 5.3% wolfram alloys, respectively, quenched from 1460°C. The former was 100% beta at the annealing temperature, while the latter contained ZrW_2 . The $\beta/\beta + ZrW_2$ boundary is further bracketed by Figs. 86 and 87. Figure 86 is a 0.49% wolfram alloy quenched from 950°C, showing an all-transformed beta structure, and Fig. 87, a 1.3% wolfram alloy given the same treatment, illustrates a $\beta + ZrW_2$ structure.

The decomposition of beta into $\alpha + ZrW_2$ was observed to occur at $850 \pm 15^\circ\text{C}$. The difficulty in accurately positioning the eutectoid temperature was amplified in this system, due to the low alloy content of the eutectoid composition and the fact that the eutectoid temperature is close to the transformation temperature of pure zirconium. Figure 88 shows a 1.3% chromium alloy quenched from 850°C, showing an $\alpha + \beta + ZrW_2$ structure characteristic of alloys quenched from this temperature, and indicating the proximity to the eutectoid temperature. The same alloy quenched from 900°C and an 0.49% chromium alloy quenched from 800°C are shown in Figs. 89 and 90, respectively. The former is clearly a transformed $\beta + ZrW_2$ structure, while the latter illustrates an $\alpha + ZrW_2$ structure. The limited solubility of wolfram in alpha zirconium is also indicated by the latter figure.

4. Intermediate Phase

A single intermediate phase, peritectically formed, was detected in the system. Claassen and Burgers (16) have reported this phase to be ZrW_2 , ideally located at 80.13% wolfram, and its crystal structure to be cubic (C-15 type), with the lattice parameter $a = 7.61 \text{ \AA}$. The peritectic formation of this phase and the composition of the liquid phase participating in the peritectic reaction are illustrated in Figs. 91 and 92. The former figure, a 48.5% wolfram alloy, as cast, illustrates a $ZrW_2 + \text{eutectic}$ structure, while the latter figure shows wolfram solid solution as the primary phase in a 52.3% wolfram alloy. Accordingly, the composition of the peritectic liquid has been placed at 50% wolfram.

Because of the considerable difference in wolfram content between the peritectic melt and the intermediate phase, and the difficulty in equilibrating the resultant three phase alloys, nearly single phase ZrW_2 structures were not obtained, and X-ray patterns were not made to check the structure of this phase. Since the phase exists in a region appreciably beyond the contracted scope of work for this system, the effort expended in this direction was limited and the work of Claassen and Burgers has been tentatively accepted as valid.

5. Wolfram-Rich Alloys

A limited amount of work in the wolfram-rich region of this system indicated a solubility of zirconium in wolfram of less than 10%. Earlier in this

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section of the report, mention was made of the gravity segregation of the wolfram-rich phase during arc melting. This segregation did not interfere with the qualitative delineation of phase fields in this region, but was another factor adding to the difficulty of obtaining any alloy suitable for an X-ray determination of the structure of the intermediate phase.

6. Melting Range Determinations

The incipient melting data employed for the construction of the zirconium-wolfram diagram are presented in Table XXII. The eutectic temperature, $1650 \pm 15^\circ\text{C}$, was determined by quenching alloys containing 14.5, 17.9, and 30.4% wolfram. Alloys containing 71.3 and 82.8% wolfram were useful in establishing the temperature of the peritectic reaction ($2175 \pm 25^\circ\text{C}$).

TABLE XXII
MELTING RANGE DETERMINATIONS FOR THE ZIRCONIUM-WOLFRAM SYSTEM

Alloy No.	Weight % W	Incipient Melting	
		Melting Observed, $^\circ\text{C}$	No Melting, $^\circ\text{C}$
YZW 5-779	4.7	1815	1775
YZW 16-772	14.5	1665	1605
YZW 20-770	17.9	1665	1635
YZW 30-647	30.4	1695	1645
YZW 70-798	71.3	2175	2070
YZW 80-795	82.8	2175	2075

Several attempts were made to check the eutectic temperature by thermal analysis. Thermocouple failures ended each trial, but optical pyrometer readings during the course of the thermal analysis work indicated that the figure determined by the incipient melting technique must be very nearly correct.

Fig. 83

Neg. No. 3824 X200
ZW 22-796 C
20% HF, 20% HNO₃ in glycerine

A 21.1% wolfram as-cast alloy. A fine distribution of phases characteristic of the β -ZrW₂ eutectic.

Fig. 84

Neg. No. 4084 X250
ZW 4-780; P2-H1200-70; XR34-Q11460
20% HF, 20% HNO₃ in glycerine

A 3.6% wolfram alloy quenched from 1460°C. Transformed β solid solution.

Fig. 85

Neg. No. 5019 X250
ZW 6-778; P0-H1200-70; XR31-Q11460
20% HF, 20% HNO₃ in glycerine

A 5.3% wolfram alloy quenched from 1460°C. Transformed β + isothermal ZrW₂ crystals.

Fig. 86

Neg. No. 4085 X250
ZW 0.5-784; P32-H1200-70; XR80-Q950-50
20% HF, 20% HNO₃ in glycerine

A 0.49% wolfram alloy quenched from 950°C. Transformed β solid solution.

Fig. 87

Neg. No. 4086 X250
ZW 1-783; P23-H1200-70; XR74-Q950-50
20% HF, 20% HNO₃ in glycerine

A 1.3% wolfram alloy quenched from 950°C. Transformed β + a small amount of isothermal ZrW₂ at the grain boundaries. This alloy is just into the β + ZrW₂ phase field at 950°C.

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Fig. 83

Fig. 84

Fig. 85

Fig. 86

Fig. 87

Fig. 88

Neg. No. 4088 X500
ZW 1-783;P23-H1200-70;XR74-Q850-95
20% HF, 20% HNO₃ in glycerine

A 1.3% wolfram alloy quenched from 850°C. An $\alpha + \beta + \text{ZrW}_2$ structure characteristic of alloys quenched from this temperature, indicating the proximity to the eutectoid level.

Fig. 89

Neg. No. 5099 X500
ZW 1-783;P23-H1200-70;XR74-Q900-75
20% HF, 20% HNO₃ in glycerine

A 1.3% wolfram alloy quenched from 900°C. Transformed $\beta +$ small crystals of isothermal ZrW_2 . Annealed above the eutectoid temperature.

Fig. 90

Neg. No. 4087 X500
ZW 0.5-784;P32-H1200-70;XR80-Q800-170
20% HF, 20% HNO₃ in glycerine

A 0.49% wolfram alloy quenched from 800°C. The $\alpha + \text{ZrW}_2$ structure places the eutectoid temperature above 800°C.

Fig. 91

Neg. No. 4082 X250
ZW 49-784 C
20% HF, 20% HNO₃ in glycerine

A 48.5% wolfram alloy, as-cast. Primary ZrW_2 crystals in a matrix of degenerated $\beta\text{-ZrW}_2$ eutectic.

Fig. 92

Neg. No. 4083 X500
ZW 52-781 C
20% HF, 20% HNO₃ in glycerine

A 52.3% wolfram alloy, as-cast. Primary wolfram-rich solid solution, peritectic walls of ZrW_2 and eutectic matrix. Comparing this with Fig. 91 shows that the composition of the peritectic liquid must lie between 48.5 and 52.3% wolfram.

Fig. 88

Fig. 89

Fig. 90

Fig. 91

Fig. 92

E. The System Zirconium-Chromium

by R. F. Domagala

1. Techniques

No special techniques were employed for this system. The experimental procedures outlined in earlier sections of this report were employed.

2. The Phase Diagram

Figures 93 through 96 show the phase relationships in the system zirconium-chromium. Figure 93 is a partial diagram up to ZrCr_2 , while Fig. 94 is restricted to the 0-50 atomic per cent chromium region. An expanded view of the zirconium-rich portion of the system is included in Fig. 95, while the final figure gives the complete diagram on a weight and atomic per cent basis (Fig. 96). Most data points necessary for the delineation of phase boundaries are included in Figs. 93 and 95.

The characteristic compositions and temperatures of the diagram are as follows:

- a. Maximum solubility of chromium in beta zirconium of 4.5%.
- b. A eutectic between β and ZrCr_2 at 18% chromium and $1280 \pm 10^\circ\text{C}$.
- c. A single intermediate phase at 53% chromium, corresponding to the formula ZrCr_2 . This phase melts at $1700 \pm 25^\circ\text{C}$.
- d. A eutectoid decomposition of beta into $\alpha + \text{ZrCr}_2$ at $835 \pm 10^\circ\text{C}$ and $1 \pm 0.25\%$ chromium.
- e. Solubility of chromium in alpha zirconium of less than 0.28%.
- f. A eutectic between ZrCr_2 and chromium-rich solid solution at 70% chromium and $1635 \pm 15^\circ\text{C}$.
- g. Maximum solubility of zirconium in chromium of less than 10%.

A study of specimens containing 0.48, 1.5, and 4.7% chromium, annealed for three different times at 700° , 800° , and 900°C , showed no changes in the relative amounts of phases present after 50 hours at 900°C , 150 hours at 800°C , and 250 hours at 700°C . Isothermal anneals were outlined, based on these preliminary data. Tables XXIII and XXIV list the alloys, their pretreatment, and the annealing schedule followed for the determination of the phase diagram. Chemical analyses of these alloys are included in Table XXV. The diagrams presented are based upon these analyzed compositions.

FIG.93-PARTIAL DIAGRAM OF THE ZIRCONIUM-CHROMIUM SYSTEM

FIG.94 — PARTIAL DIAGRAM OF THE ZIRCONIUM-CHROMIUM SYSTEM

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FIG. 95—EXPANDED DIAGRAM OF THE ZIRCONIUM-RICH REGION OF THE ZIRCONIUM-CHROMIUM SYSTEM

FIG.96 -THE ZIRCONIUM-CHROMIUM SYSTEM

TABLE XXIII
PRETREATMENT AND ANNEALING OF ZIRCONIUM-CHROMIUM ALLOYS

Alloy No.	Cold Pressed,%*	Homogenized 1200°C-75 hr*	Cold Rolled,%*	***		
				1350°C 2 hr	1300°C 2 hr	1200°C 6 hr
ZO-286 (Zr)	51	**	71	x	x	x
ZR 0.25-401	30	x	74			
ZR 0.50-402	54	x	69			
ZR 0.75-403	28	x	74			
ZR 1-408	22	x	73	x	x	x
ZR 2-404	14	x	7	x	x	x
ZR 3-405	13	x	2	x	x	x
ZR 4-406	11	x	5	x	x	x
ZR 5-407	8	x	6	x	x	x
ZR 7-596	6	x	22	x	x	x
ZR 9-597	7	x	12	x	x	x
ZR 10-388	10	x	10	x	x	x
ZR 15-389	4	x	2	x	x	
ZR 16-598	-	x	9			
ZR 17-599	-	x	20	x	x	x
ZR 18-601	-	x	24			
ZR 19-602	-	x	23	x	x	
ZR 20-390	4	x	-			
ZR 22-603	-	x	8			
ZR 25-392		x				
ZR 30-393		x		x		x
ZR 35-406		x				
ZR 40-394		x		x		x
ZR 48-604				x		
ZR 49-605						
ZR 50-396		x				
ZR 51-606						
ZR 52-607						
ZR 53-608				x	x	x
ZR 55-625				x	x	x
ZR 57-610				x		
ZR 59-626				x		
ZR 60-398		x				x
ZR 70-395				x		

*The pretreatment (i.e., cold pressing, homogenization, cold rolling) corresponding to each alloy composition is the same for all annealing treatments and is not repeated in subsequent columns.

**Homogenized at 1150°C for 70 hours.

***Specimens in region of eutectic composition melted.

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TABLE XXIII (Cont.)

Alloy No.	1100°C 20 hr	994°C 40 hr	950°C 40 hr	900°C 65 hr	860°C 140 hr	840°C 145 hr	830°C 145 hr
ZO-286 (Zr)	X	X	X	X	X	X	X
ZR 0.25-401			X	X	X	X	X
ZR 0.50-402			X	X	X	X	X
ZR 0.75-403			X	X	X	X	X
ZR 1-408	X	X	X	X	X	X	X
ZR 2-404	X	X	X	X	X	X	X
ZR 3-405	X	X	X	X	X	X	X
ZR 4-406	X	X	X	X	X	X	X
ZR 5-407	X	X	X	X	X	X	X
ZR 7-596	X	X	X	X		X	
ZR 9-597	X		X	X	X	X	X
ZR 10-388	X	X					
ZR 15-389							
ZR 16-598							
ZR 17-599				X		X	
ZR 18-601							
ZR 19-602		X	X		X		X
ZR 20-390	X						
ZR 22-603							
ZR 25-392							
ZR 30-393		X		X	X		X
ZR 35-406							
ZR 40-394	X	X				X	
ZR 48-604							
ZR 49-605							
ZR 50-396							
ZR 51-606		X		X	X		
ZR 52-607							
ZR 53-608	X	X		X		X	
ZR 55-625		X					
ZR 57-610							
ZR 59-626	X	X					
ZR 60-398				X			
ZR 70-395	X		X				

TABLE XXIII (Cont.)

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Alloy No.	820°C 150 hr	800°C 145 hr	750°C 215 hr	700°C 240 hr	650°C 310 hr	600°C 360 hr
ZO-286 (Zr)	x	x	x	x	x	x
ZR 0.25-401	x	x	x	x	x	x
ZR 0.50-402	x	x	x	x	x	x
ZR 0.75-403	x	x	x	x	x	x
ZR 1-408	x	x	x	x	x	x
ZR 2-404	x	x	x	x	x	x
ZR 3-405	x	x	x	x	x	x
ZR 4-406	x	x	x	x	x	x
ZR 5-407	x	x	x	x	x	x
ZR 7-596	x	x				
ZR 9-597	x	x	x		x	
ZR 10-388						
ZR 15-389						
ZR 16-598						
ZR 17-599	x	x				
ZR 18-601						
ZR 19-602						
ZR 20-390			x		x	
ZR 22-603						
ZR 25-392						
ZR 30-393			x	x	x	x
ZR 35-406						
ZR 40-394	x	x		x		x
ZR 48-604						
ZR 49-605						
ZR 50-396						
ZR 51-606		x	x	x		x
ZR 52-607	x					
ZR 53-608		x		x		x
ZR 55-625	x			x		x
ZR 57-610						
ZR 59-626						
ZR 60-398			x			
ZR 70-395						

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TABLE XXIV

SPECIAL ANNEALS* TO DETERMINE EUTECTOID TEMPERATURE
IN THE ZIRCONIUM-CHROMIUM SYSTEM

Alloy No.	780°C 360 hr	800°C 365 hr	820°C 360 hr	840°C 385 hr
ZO-286	x	x	x	x
ZR 0.25-401	x	x	x	x
ZR 0.50-402	x	x	x	x
ZR 0.75-403	x	x	x	x
ZR 1-408	x	x	x	x
ZR 2-404	x	x	x	x
ZR 3-405	x	x	x	x
ZR 4-406	x	x	x	x
ZR 5-407	x	x	x	x

*Specimens held at 900°C for 17 hours, slowly cooled to temperature and held for time indicated, followed by water quench.

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TABLE XXV
ANALYSES OF ZIRCONIUM-CHROMIUM ALLOYS

Alloy No.	Chromium, Wt. %
ZR 0.25-401	0.28
ZR 0.50-402	0.48
ZR 0.75-403	0.51
ZR 1-408	0.81
ZR 2-404	1.5
ZR 3-405	2.6
ZR 4-406	4.4
ZR 5-407	4.7
ZR 7-596	6.5
ZR 9-597	8.5
ZR 10-388*	10.0
ZR 15-389	15.2
ZR 16-598	15.6
ZR 17-599	16.8
ZR 18-601	17.6
ZR 19-602	18.9
ZR 20-390	19.2
ZR 22-603	21.9
ZR 25-392	25.0
ZR 30-393	29.7
ZR 35-406	34.7
ZR 40-394	37.6
ZR 48-604	48.6
ZR 49-605	49.3
ZR 50-396	50.7
ZR 51-606	51.3
ZR 52-607	52.4
ZR 53-608	53.1
ZR 55-625	55.4
ZR 57-610	56.6
ZR 59-626	59.8
ZR 60-398	58.5
ZR 70-395	68.3
ZR 80-391	76.8
ZR 90-397	84.9

*Johnson-Mathey Chromium.

Figures 97 through 101 are a series of photomicrographs of alloys over the entire system. Cored beta solid solution plus a fine eutectic are shown in the first figure, a 10.0% chromium arc-cast alloy. A eutectic structure is evident in Fig. 98, a 19.1% chromium alloy employed in the thermal analysis program for this system. The arc-cast alloys in the region of the eutectic displayed a very fine distribution of phases, difficult to resolve, and consequently the slowly-cooled thermal analysis alloy was chosen to best illustrate the eutectic structure. Figure 99 is a 34.7% chromium alloy, in the arc-cast condition, illustrating a ZrCr_2 plus eutectic structure. The intermediate phase is shown in Fig. 100. Here a 53.1% chromium alloy is seen to be nearly single phase. This substantiates the designation of the phase as ZrCr_2 , ideally located at 53.28% chromium. A 69.5% chromium alloy, also from the thermal analysis program, is shown in Fig. 101, illustrating the ZrCr_2 -chromium eutectic.

3. Zirconium-Rich Alloys

The phase relationships in the zirconium-rich portion of the system were outlined by metallographic examination of as-cast alloys and the isothermally annealed specimens listed in Tables XXIII and XXIV. The structure of the eutectic between ZrCr_2 and beta zirconium has already been illustrated in Fig. 98. Several arc-cast alloys were employed in locating the eutectic composition at 18% chromium. Figures 102 and 103 illustrate 4.4 and 4.7% chromium alloys, respectively, quenched after 2 hours at 1300°C. The former is a 100% retained beta structure, while the latter shows beta plus signs of incipient melting, placing it just into the $\beta + \text{liquid}$ field at the temperature of treatment. Thus, the maximum solubility of chromium in beta zirconium must lie between the two compositions and the eutectic temperature must be below 1300°C. Figures 104 and 105 further position the $\beta/\beta + \text{ZrCr}_2$ line. The former figure is an 0.81% chromium alloy quenched from 950°C after 40 hours; a transformed beta structure is seen. The latter figure, a 1.5% chromium alloy given the same annealing treatment, displays a $\beta + \text{ZrCr}_2$ structure.

Accurate positioning of the eutectoid composition and temperature was difficult because of the unsuppressible decomposition of beta into $\alpha + \text{ZrCr}_2$ on quenching, and due to the anomalous structures observed in this region of the diagram, as discussed in Section IV-D of this report. However, the composition value presented (1% chromium) is believed to be accurate to $\pm 0.25\%$ chromium. The eutectoid temperature, $835 \pm 10^\circ\text{C}$, was determined after examination of specimens annealed at 20°C intervals in this region. Figures 106 and 107 illustrate a 1.5% chromium alloy annealed at 840° and 830°C, respectively. The former figure illustrates a $\beta + \text{ZrCr}_2$ structure, while the latter figure shows $\alpha + \text{ZrCr}_2$ phases in equilibrium.

The maximum solubility of chromium in alpha zirconium was determined to be less than 0.28% at all temperatures. Figure 108 illustrates a 0.28% chromium alloy quenched after 360 hours at 820°C. ZrCr_2 particles are present in this structure.

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4. Intermediate Phase

A single intermediate phase having a maximum melting point was found in this system. The examination of cast structures placed this phase at 53% chromium, corresponding to the formula ZrCr_2 (stoichiometrically, 53.28% Cr). This is in agreement with Wallbaum (17), and Hayes, Roberson and Davies (18), who also report the existence of ZrCr_2 . An X-ray diffraction pattern of powder from a 53.1% chromium alloy was made using CuK_α characteristic filtered radiation. Interpretation of the pattern showed this phase to be hexagonal close packed, with the lattice parameters given below:

	<u>Observed</u>	<u>Calculated</u>
c	-	8.262 Å
a	-	5.079 Å
c/a	1.65	1.627

The tabulation of X-ray pattern data is given in the Appendix.

These values compare favorably with an axial ratio of 1.633, reported by Wallbaum, who classes ZrCr_2 as MgZn_2 type (C14). Hayes, et al., however, report the phase to be face centered cubic, of the MgCu_2 type, with $a = 7.21$ Å.

5. Chromium-Rich Alloys

Although determination of phase relationships in the region 50-100 atomic per cent chromium was beyond the scope of the contract, a limited amount of work was done. A eutectic between ZrCr_2 and chromium was established at about 70% chromium and $1635 \pm 15^\circ\text{C}$. The structure of this eutectic has been illustrated in Fig. 101. The solubility of zirconium in chromium was observed to be less than 10%.

6. Melting Range Determinations

Thermal analysis and incipient melting were used to determine solidus curves and eutectic horizontals. Table XXVI summarizes the data employed in construction of the diagram. The zirconium-rich eutectic was found to lie between 1295° and 1265°C , by the incipient melting technique, while the results of quenching a 1.5% chromium alloy aided in positioning the $\beta/\beta + \text{L}$ boundary. An average eutectic arrest at $1280 \pm 10^\circ\text{C}$ was found for 9.5, 19.1, and 34.3% chromium alloys--in excellent agreement with the incipient melting data. The melting point of the intermediate phase, ZrCr_2 , was determined to be $1700 \pm 25^\circ\text{C}$, while the chromium-rich eutectic was found to melt at $1635 \pm 15^\circ\text{C}$. It was possible to determine the liquidus arrest in the 34.3% chromium alloy as $1500 \pm 15^\circ\text{C}$.

TABLE XXVI

MELTING RANGE DETERMINATIONS FOR THE ZIRCONIUM-CHROMIUM SYSTEM

Alloy No.	Weight % Cr	Thermal Analysis		Incipient Melting	
		Arrests, °C		Melting Observed, °C	No Melting, °C
YZR 2-404	1.5			1603	1525
YZR 5-407	4.7			1610	---
XZR 10-742	9.5	1280			
YZR 18-601	17.6			1295	1265
XZR 18-743	19.1	1280			
XZR 35-744	34.3	1500...1280			
XZR 53-745	52.6	1700			
XZR 70-746	69.5	1635			

7. Discussion of the Literature

Phase diagrams of the zirconium-chromium system have been published by E. T. Hayes, et al. (18) and M. K. McQuillan (19). The former authors extended their investigation from zirconium to ZrCr_2 , while McQuillan presents the entire system. The general features of these two diagrams may be summarized as follows:

Hayes, et al.

1. Zr- ZrCr_2 eutectic at 18% Cr and 1380°C
2. Max. solubility of Cr in β -Zr: 6.2% at 1380°C
3. Eutectoid, $\beta \rightarrow \alpha + \text{ZrCr}_2$, at 1.8% Cr and 805°C
4. Negligible solubility of Cr in α -Zr
5. Intermediate phase, ZrCr_2 at 53% Cr, melting at 1525°C. Crystal structure: cubic, MgCu_2 type; $a = 7.21 \text{ \AA}$

McQuillan

1. Single intermediate phase at 48% Cr, formed by peritectic reaction $\beta + \text{L} \rightarrow \text{C}$ at 1650°C
2. Solubility of Cr in β -Zr decreasing sharply from about 48% at 1650°C to about 5% at 1350°C, then gradually to about 2% at 835°C
3. Eutectoid, $\beta \rightarrow \alpha + \text{C}$ at 2% Cr and 835°C
4. Very limited solubility of Cr in α -Zr
5. Compound- Cr_{53} eutectic at 70% Cr and about 1545°C
6. Limited solubility of Zr in Cr

Comparing the features tabulated above with those listed earlier in this section for the current work, it may be seen that Hayes et al. and the present authors are in agreement on the general constitution of the zirconium-rich

region, whereas McQuillan has determined a greatly different set of phase relationships. The present work, however, agrees with McQuillan that the intermediate phase and the chromium-rich solid solution form a eutectic. To a certain extent, differences in the results may be attributable to the use of different zirconium stock in the three programs. Hayes, et al. and McQuillan used magnesium-reduced zirconium metal, while the present work is based on alloys prepared with the higher purity iodide crystal bar.

Fig. 97

Neg. No. 3997 X150
 ZR 10-372;C
 Electrolytic: $K_3Fe(CN)_6 + NaOH + H_2O$
 A 10.0% chromium alloy, as-cast.
 Cored β solid solution in a matrix
 of $\beta-ZrCr_2$ eutectic.

Fig. 98

Neg. No. 3998 X500
 XZR 18-601;TA-C
 Electrolytic: $K_3Fe(CN)_6 + NaOH + H_2O$
 A 19.1% chromium alloy employed for
 thermal analysis. This slowly cooled
 alloy exhibits the $\beta-ZrCr_2$ eutectic
 structure.

Fig. 99

Neg. No. 3999 X500
 ZR 35-406;C
 Electrolytic: $K_3Fe(CN)_6 + NaOH + H_2O$
 A 34.7% chromium alloy, as-cast.
 Primary crystals of $ZrCr_2$ in a matrix
 of $\beta-ZrCr_2$ eutectic.

Fig. 100

Neg. No. 3704 X200
 ZR 53-608;C
 Electrolytic: $K_3Fe(CN)_6 + NaOH + H_2O$
 A 53.1% chromium alloy, as-cast.
 Nearly single phase structure repre-
 senting the intermediate phase $ZrCr_2$,
 located ideally at 53.23% Cr.

Fig. 101

Neg. No. 4007 X750
 XZR 70-746;TA-C
 Electrolytic: $K_3Fe(CN)_6 + NaOH + H_2O$
 A 69.5% chromium alloy used for ther-
 mal analysis. This slowly cooled
 alloy exhibits the $ZrCr_2$ -Cr eutectic.

Fig. 102

Neg. No. 3996 X150
 ZR 4-406;P11-H1200-75;XR5-Q1300-2
 20% HF, 20% HNO_3 in glycerine
 A 4.4% chromium alloy quenched after
 annealing at 1300°C. A retained β
 structure.

Fig. 97

Fig. 98

Fig. 99

Fig. 100

Fig. 101

Fig. 102

Fig. 103

Neg. No. 3820 X250
 ZR 5-407;P8-H1200-75;XR6-Q1300-2
 Electrolytic: $K_2Fe(CN)_6 + NaOH + H_2O$

A 4.7% chromium alloy quenched after annealing at 1300°C. Retained β + signs of incipient melting. At 1300°C this alloy was just into the $\beta + L$ field. Thus the eutectic temperature must be below 1300°C and the maximum β solubility less than 4.7% chromium.

Fig. 104

Neg. No. 4028 X500
 ZR 1-408;P22-H1200-75;XR73-Q950-40
 20% HF, 20% HNO_3 in glycerine

A 0.81% chromium alloy quenched from 950°C. Transformed β solid solution.

Fig. 105

Neg. No. 4029 X500
 ZR 2-404;P14-H1200-75;XR7-Q950-40
 20% HF, 20% HNO_3 in glycerine

A 1.5% chromium alloy quenched from 950°C. Transformed $\beta + ZrCr_2$ crystals. The $\beta/\beta + ZrCr_2$ boundary is therefore between 0.8 and 1.5% Cr at 950°C.

Fig. 106

Neg. No. 4031 X500
 ZR 2-404;P14-H1200-75;XR7-Q840-385
 20% HF, 20% HNO_3 in glycerine

A 1.5% chromium alloy quenched from 840°C. A transformed $\beta + ZrCr_2$ structure indicates this alloy was annealed above the eutectoid level.

Fig. 107

Neg. No. 4030 X500
 ZR 2-404;P14-H1200-75;XR7-Q830-145
 20% HF, 20% HNO_3 in glycerine

A 1.5% chromium alloy quenched from 830°C. The $\alpha + ZrCr_2$ structure indicates that the eutectoid level is above 830°C.

Fig. 108

Neg. No. 3819 X500
 ZR 0.25-401;P30-H1200-75;XR74-Q820-360
 20% HF, 20% HNO_3 in glycerine

A 0.28% chromium alloy quenched from 820°C. The $\alpha + ZrCr_2$ structure in this alloy demonstrates that the solubility of chromium in α is very small.

Fig. 103

Fig. 104

Fig. 105

Fig. 106

Fig. 107

Fig. 108

F. The System Zirconium-Silicon

by C. E. Lundin

1. Special Techniques

The melting of the zirconium-silicon alloys throughout the range of composition followed the standard methods outlined in the section on melting techniques. Also, pretreatment and annealing techniques were the same as described in the section on heat treatment.

The metallography of the zirconium-silicon alloys presented a problem in interpretation of structures due to the large number of phase fields within a small range of composition. The interpretation was greatly enhanced by the use of polarized light for the identification of phases. This will be discussed more thoroughly in the section on the intermediate phases.

2. The Phase Diagram

The addition of a small increment of silicon by weight to zirconium causes a rather large shift in the atomic percentage of silicon. This is more prominent in the zirconium-rich portion of the diagram, and manifests itself by a crowding of phase fields on a weight per cent diagram toward the zirconium end. Accordingly, it was necessary to prepare many alloys in small increments by weight to completely survey the phase fields. The scope of the work on this system was to determine the phase diagram up to 50 atomic per cent (23.53 wt.%) silicon. However, sufficient alloys were cast to survey the entire system.

Figures 109 and 110 represent the phase diagram up to 50 atomic and 25 weight per cent silicon, respectively. Figures 111 and 112 show the entire system on a basis of atomic and weight per cent, respectively. An expanded view of the zirconium-rich region is given in Fig. 113.

Analyses of the zirconium-silicon alloys are presented in Table XXVII.

A preliminary study was undertaken in order to determine the times necessary to attain equilibrium at several annealing temperatures. A 700°, 800°, and 900°C anneal was made on alloys containing 0.1, 1.0, and 3.0% silicon. The results indicated no detectable changes in the relative amounts of phases after annealing periods of 250, 100, and 50 hours at 700°, 800°, and 900°C, respectively. The remainder of the annealing series was scheduled from this preliminary work. A complete tabulation of pretreatment and annealing data is given in Table XXVIII.

A summary of the major features of the diagram, on a weight per cent basis, in the sequence of increasing silicon content, is as follows:

a. The maximum solubility of silicon in beta zirconium is less than 0.2% at 1610°C. The maximum solubility of silicon in alpha zirconium is less than 0.1% at 860°C.

FIG.109—PARTIAL DIAGRAM OF THE ZIRCONIUM-SILICON SYSTEM

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FIG. 110 - PARTIAL DIAGRAM OF THE ZIRCONIUM-SILICON SYSTEM

FIG. III - THE ZIRCONIUM-SILICON SYSTEM

FIG. 112 - THE ZIRCONIUM - SILICON SYSTEM

FIG. II3- PARTIAL DIAGRAM OF ZIRCONIUM-SILICON SYSTEM

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TABLE XXVII
ANALYSES OF ZIRCONIUM-SILICON ALLOYS

Alloy No.	Silicon, Wt. %	Alloy No.	Silicon, Wt. %
ZS 0.1-463	--	ZS 16-853	15.5
ZS 0.2-464	0.18	ZS 17-549	17.7
ZS 0.3-465	0.29	ZS 18-854	17.6
ZS 0.4-466	0.42	ZS 18.5-856	18.7
ZS 0.5-467	0.47	ZS 19-855	19.1
ZS 0.6-439	0.60	ZS 19.5-857	19.3
ZS 0.7-468	0.65	ZS 20-413	19.5
ZS 0.8-440	0.78	ZS 20.5-862	20.1
ZS 1-441	1.0	ZS 21-548	20.5
ZS 2-450	2.1	ZS 21.5-859	21.0
ZS 3-451	2.9	ZS 22-547	22.3
ZS 4-452	4.1	ZS 22.5-860	22.8
ZS 5-453	4.9	ZS 23-595	22.4
ZS 5-409	4.7	ZS 23.5-861	23.5
ZS 6-454	5.9	ZS 24-545	24.4
ZS 7-455	7.2	ZS 24.5-863	24.3
ZS 7-555	7.4	ZS 25-414	24.6
ZS 8-456	7.7	ZS 26-544	25.5
ZS 8-554	8.4	ZS 28-543	27.4
ZS 9-457	9.2	ZS 30-415	29.1
ZS 10-458	10.3	ZS 35-416	36.1
ZS 10-410	10.4	ZS 45-417	45.6
ZS 10-412	10.7	ZS 55-418	54.9
ZS 11-553	11.7	ZS 65-419	65.2
ZS 12-552	11.3	ZS 75-420	76.1
ZS 13-594	13.3	ZS 85-422	84.5
ZS 14-550	14.3	ZS 95-423	95.6
ZS 15-411	14.5		

TABLE XXVIII

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PRETREATMENT AND ANNEALING OF ZIRCONIUM-SILICON ALLOYS

Alloy No.	Cold Pressed,%*	Homogenized 1150°C-50 hr*	Cold Rolled,%*	1167°C 20 min	1100°C 30 min	1300°C 1 hr
ZO-283 (Zr)	55	x	89	x	x	x
ZS 0.1-433	33	x	75	x	x	x
ZS 0.2-464	37	x	78	x	x	x
ZS 0.3-465	32	x	82	x	x	x
ZS 0.4-466	28	x	78	x	x	x
ZS 0.5-467	35	x	80			
ZS 0.6-439	24	x	77			
ZS 0.7-468	26	x	73			
ZS 0.8-440	19	x	76			
ZS 1-441	17	x	73	x	x	x
ZS 2-450	16	x	41			
ZS 3-451	5	x	0			
ZS 4-452	3	x	12			
ZS 5-453	3	x	8	x	x	x
ZS 6-454	2	x	7			
ZS 7-455	1	x	-			
ZS 8-456	0	x	-			
ZS 9-457	0	x	-			
ZS 10-458	0	x	-	x	x	x
ZS 11-553	-	-	-			
ZS 12-552	-	-	-		x	
ZS 13-594	-	-	-			
ZS 15-411	-	-	-	x		x
ZS 17-549	-	-	-			
ZS 20-413	-	-	-	x		
ZS 21-548	-	-	-			
ZS 24-545	-	-	-		x	
ZS 30-415	-	-	-			
ZS 35-416	-	-	-	x		

*The pretreatment (i.e., cold pressing, homogenization, cold rolling) corresponding to each alloy composition is the same for all annealing treatments, and is not repeated in subsequent columns.

TABLE XXVIII (Cont.)

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Alloy No.	1200°C 6 hr	1100°C 16 hr	1000°C 24 hr	900°C 50 hr	875°C 100 hr	850°C 99 hr	820°C 95 hr	800°C 100 hr	700°C 240 hr
ZO-283 (Zr)	x	x	x	x	x	x	x	x	x
ZS 0.1-433	x	x	x	x	x	x	x	x	x
ZS 0.2-464	x	x	x	x	x	x	x	x	x
ZS 0.3-465	x	x	x	x	x	x	x	x	x
ZS 0.4-466	x	x	x	x	x	x	x	x	x
ZS 0.5-467	x	x	x	x	x	x	x	x	
ZS 0.6-439	x	x	x	x	x	x	x	x	x
ZS 0.7-468	x	x	x	x	x	x	x	x	
ZS 0.8-440	x	x	x	x	x	x	x	x	x
ZS 1-441	x	x	x	x	x	x	x	x	x
ZS 2-450	x	x	x	x	x	x	x	x	
ZS 3-451	x	x	x	x	x	x	x	x	
ZS 4-452	x	x	x	x	x	x	x	x	
ZS 5-453	x	x	x	x	x	x	x	x	x
ZS 6-454	x	x	x	x	x	x	x	x	
ZS 7-455	x	x	x	x	x	x	x	x	x
ZS 8-456	x	x	x	x	x	x	x	x	
ZS 9-457	x	x	x	x	x	x	x	x	
ZS 10-458	x	x	x	x	x	x	x	x	x
ZS 11-553	x	x	x	x	x	x	x	x	
ZS 12-552	x	x	x	x	x	x	x	x	
ZS 13-594	x	x	x	x	x	x	x	x	x
ZS 15-411	x		x	x				x	
ZS 17-549	x		x	x					
ZS 20-413				x				x	
ZS 21-548	x		x						
ZS 24-545			x	x				x	
ZS 30-415			x					x	
ZS 35-416			x					x	

- b. Zirconium forms a eutectic with Zr_4Si at 2.9% silicon and $1610 \pm 15^\circ C$.
- c. The intermediate phase Zr_4Si (7.14% Si) is formed by the peritectic reaction between Zr_2Si (tentative, 13.33% Si) and the melt containing 4.5% silicon at $1630 \pm 15^\circ C$.
- d. The phase Zr_2Si (tentative) is formed by the peritectic reaction between Zr_3Si_2 (17.02% Si) and the melt containing 9% silicon at $2110 \pm 25^\circ C$.
- e. The phase Zr_3Si_2 is formed by the peritectic reaction between Zr_4Si_3 (18.74% Si) and the melt containing 14.4% silicon at $2210 \pm 25^\circ C$.
- f. The intermediate phase Zr_4Si_3 is formed by the peritectic reaction between Zr_6Si_5 (20.40% Si) and the melt containing 18% silicon at $2225 \pm 25^\circ C$.
- g. The intermediate phase Zr_6Si_5 is formed at 20. % silicon and melts with an open maximum at $2250 \pm 25^\circ C$.
- h. The phase $ZrSi$ (23.53% Si) is formed by a peritectic reaction between Zr_6Si_5 and the melt containing 24.2% silicon at $2095 \pm 25^\circ C$.
- i. The phase $ZrSi_2$ (38.09% Si) is formed by a peritectic reaction between $ZrSi$ and the melt containing 46% silicon at $1520 \pm 15^\circ C$.
- j. A eutectic exists between $ZrSi_2$ and silicon at 75% silicon and $1355 \pm 15^\circ C$.
- k. The solubility of zirconium in silicon is considerably less than 5%, but no attempt was made to precisely determine the value.

3. Zirconium-Rich Alloys

The zirconium-rich region of the diagram is given in Fig. 113. The tabulation of pretreatment and annealing schedules is presented in Table XXVIII.

The effect of silicon additions on the allotropic transformation of zirconium could not be determined because of the extremely small solubility of this element in both zirconium modifications.

Since the structure of these very dilute alloys is affected by the non-equilibrium conditions discussed in Section IV-D of this report, it cannot be said whether a eutectoid or peritectoid reaction characterizes this system. The solubility of silicon in beta zirconium is less than 0.2%, even at high temperatures, as shown by Fig. 114. Transformed beta and Zr_4Si are present in a 0.18% silicon alloy quenched from $1467^\circ C$. The maximum solubility of silicon in alpha zirconium is indicated in Fig. 115, a 0.1% silicon alloy annealed at $820^\circ C$. Here an $\alpha + Zr_4Si$ structure is seen. Since the solubilities are so limited, the temperature of the eutectoid or peritectoid must lie very close to the allotropic transformation of pure zirconium ($862^\circ C$).

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Evidence corroborating this is shown in Figs. 116 and 117. The former is the $\beta + \text{Zr}_4\text{Si}$ structure of a 0.60% silicon alloy annealed at 875°C, while the latter shows $\alpha + \text{Zr}_4\text{Si}$ in the same alloy, quenched from 850°C. A number of the alloys in this temperature-composition region yielded three phase structures, as explained earlier. These were not, however, typical peritectoid structures.

4. Intermediate Phases

The alloy region beyond that specified in the contract was investigated with the preparation of a number of silicon-rich alloys. The phase relationships are shown in Fig. 111 on an atomic per cent basis, and in Fig. 112 on a weight per cent basis.

Due to the large number of intermediate phases within a limited range of composition, the interpretation of structures and microscopic identification of phases was exceedingly difficult under bright field illumination. The use of polarized light proved to be exceptionally helpful in this respect, because all of the intermediate phases yielded striking contrasts in color.

The eutectic between zirconium solid solution and Zr_4Si (7.14% Si) is shown in Fig. 118, the as-cast structure of a 2.9% silicon alloy. Figure 119, an arc cast 4.1% silicon alloy, depicts primary crystals of Zr_4Si in a matrix of eutectic. Figure 120 is a 4.9% silicon alloy, annealed at 1200°C. Approximately 75% Zr_4Si in a matrix of zirconium is present in this structure, which indicates a compound composition of about 7% silicon. The as-cast structure of a 4.9% silicon alloy shows primary crystals of a new phase, designated Zr_2Si (tentative, 13.33% Si), peritectic walls of Zr_4Si , and a matrix of the zirconium- Zr_4Si eutectic, as in Fig. 121. Accordingly, the peritectic melt must contain about 4.5% silicon.

Figure 122, an as-cast 9.2% silicon alloy, depicts another primary phase, designated Zr_3Si_2 (17.02% Si) and peritectic walls of Zr_2Si , indicating that another peritectic melt has been passed. Figure 123, a 14.3% silicon alloy, as cast, contains the same phases, but a decided increase in the amount of Zr_3Si_2 present. However, in the as-cast structure of a 14.5% silicon alloy (Fig. 124), another peritectic melt has been passed and new primary crystals, designated Zr_4Si_3 (18.74% Si), appear with peritectic rims of Zr_3Si_2 . This same configuration of phases, with an increase to nearly 100% Zr_4Si_3 , is seen in Fig. 125, a 17.6% silicon alloy. Figure 126, an as-cast 18.7% silicon alloy, discloses new primary crystals of the phase designated Zr_6Si_5 (20.40% silicon) surrounded by peritectic walls of Zr_4Si_3 . Zr_6Si_5 is the only intermediate phase in the zirconium-silicon system which melts with an open maximum. Figure 127, the as-cast structure of a 20.1% silicon alloy, shows a nearly single phase Zr_6Si_5 structure. In an alloy containing 22.3% silicon, Fig. 128, Zr_6Si_5 remains the primary phase, but is surrounded by new peritectic rims of a phase designated ZrSi (23.53% silicon).

Rosette-shaped primaries of Zr_6Si_5 are still seen in an alloy containing about 24% silicon, Fig. 129. However, in the as-cast structure of a 24.3%

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silicon alloy, Fig. 130, Zr_6Si_5 has disappeared; $ZrSi$ is the primary phase (nearly 100%) with a minor peritectic network of the phase designated $ZrSi_2$ (38.09% Si). Figure 131, the as-cast structure of a 36.1% silicon alloy, depicts primary $ZrSi$ crystals, peritectic walls of $ZrSi_2$, and a matrix of $ZrSi_2$ -silicon eutectic. The position of the peritectic melt which reacts with $ZrSi$ to form $ZrSi_2$ is very nearly approached in Fig. 132, an as-cast alloy containing 45.6% silicon. Very small amounts of $ZrSi$ primary crystals remain, surrounded by $ZrSi_2$ peritectic walls and a matrix of eutectic. $ZrSi_2$ is the primary phase in a eutectic matrix in Fig. 133, representing a 54.9% silicon alloy. The structure of the eutectic, $ZrSi_2$ -silicon, is shown in Fig. 134, a 76.2% silicon alloy. Figure 135, an as-cast 84.5% silicon alloy, contains about 50% primary silicon crystals in a matrix of eutectic.

The intermetallic compound Zr_2Si (13.33% Si) was tentatively placed at its theoretical composition in view of work done by Paul Pietrokowsky (11) and from the relative amounts of phases present in alloys made in this investigation. The alternative formula, Zr_3Si , 9.30% silicon, is a possibility, but is not likely from the previous considerations.

The formulae Zr_3Si_2 and Zr_4Si_3 were the most likely combinations possible for the two peritectically formed intermediate phases between 14.5 and 20.1% silicon. Two nearly single phase structures were observed at about 20.1 and 24.3% silicon, and conform to the ideal compositions of Zr_6Si_5 and $ZrSi$, respectively. The intermetallic compound $ZrSi_2$ has been identified by Naray-Szabo (20), who reported an orthorhombic structure with lattice constants: $a = 3.72 \text{ \AA}$, $b = 14.61 \text{ \AA}$, and $c = 3.67 \text{ \AA}$.

X-ray structure determination of the intermediate phases was not attempted in most cases where these phases were formed peritectically. Annealing to nearly one phase structures was virtually impossible because of the very slow rates of diffusion in the arc-cast alloys. The alloy containing 24.4% silicon and exhibiting a single phase $ZrSi$ structure was successfully indexed. It is based on a hexagonal lattice with the following lattice constants: $c = 12.772 \text{ \AA}$, $a = 7.005 \text{ \AA}$, $c/a = 1.823$. Data on the analysis of the structure are presented in the Appendix.

5. Melting Range Determinations

Thermal analysis of a large portion of the diagram was impossible due to the high temperatures involved. Only a few alloys could be studied by this method. Incipient melting techniques were relied upon to supply information concerning the high temperature features. This method, too, was more difficult to apply than was normally the case, because of the complexity of structures resulting from the many peritectic reactions. However, the results obtained correlated well with as-cast structural relationships. Table XXIX presents the data obtained from the thermal analysis and incipient melting studies.

TABLE XXIX

MELTING RANGE DETERMINATIONS FOR THE ZIRCONIUM-SILICON SYSTEM

Alloy	Weight % Si	Thermal Analysis	Incipient Melting	
		Arrests, °C	Melting Observed, °C	No Melting, °C
XZS 2-737	1.8	1585		
XZS 3-738	3.0	1610		
YZS 3-451	2.9		1615	1580
XZS 5-739	4.9	1630		
YZS 5-453	4.9		1630	1600
XZS 9-740	9.4	1630		
YZS 14-550	14.3		2130	2090
YZS 15-411	14.5		2225	2195
YZS 20-413	19.5		2225	--
YZS 20.5-862	20.1		2250	--
YZS 22-547	22.3		2095	--
XZS 45-884	44.2	1520, 1365		
YZS 45-417	45.6		1520	--
XZS 75-741	74.5	1350		

Fig. 114

Neg. No. 3829 X250
 ZS 0.2-464; P37-H1150-50; XR78-Q1467-1/3
 20% HF, 20% HNO₃ in glycerine

0.18% silicon alloy, water quenched after annealing 1/3 hour at 1467°C. Crystals of Zr₄Si in a matrix of decomposed β. Limited solubility of silicon in β zirconium evident.

Fig. 115

Neg. No. 5039 X250
 ZS 0.1-463; P33-H1150-50; XR75-Q820-95
 20% HF, 20% HNO₃ in glycerine

0.10% silicon alloy, water quenched after annealing 100 hours at 820°C. Crystals of Zr₄Si in a matrix of equiaxed α zirconium. Limited solubility of silicon in α zirconium evident.

Fig. 116

Neg. No. 5040 X500
 ZS 0.6-439; P24-H1150-50; XR77-Q875-100
 20% HF, 20% HNO₃ in glycerine

0.60% silicon alloy, water quenched after annealing 100 hours at 875°C. Zr₄Si crystals in a matrix of β zirconium. Some nonequilibrium α also present.

Fig. 117

Neg. No. 5041 X500
 ZS 0.6-439; P24-H1150-50; XR77-Q850-99
 20% HF, 20% HNO₃ in glycerine

0.60% silicon alloy, water quenched after annealing 99 hours at 850°C. Zr₄Si crystals in a matrix of isothermal α.

Fig. 118

Neg. No. 3697 X250
 ZS 3-451 C
 20% HF, 20% HNO₃ in glycerine

2.9% silicon alloy, as cast. Structure of the eutectic, Zr-Zr₄Si.

Fig. 119

Neg. No. 5043 X250
 ZS 4-452 C
 20% HF, 20% HNO₃ in glycerine

4.1% silicon alloy, as cast. Primary crystals of Zr₄Si in a matrix of eutectic Zr-Zr₄Si.

Fig. 114

Fig. 115

Fig. 116

Fig. 117

Fig. 118

Fig. 119

Fig. 120

Neg. No. 5042 X250
 ZS 5-453; Q1200-6
 20% HF, 20% HNO₃ in glycerine

4.9% silicon alloy, water quenched after annealing 6 hours at 1200°C. Predominantly Zr₄Si in a network of β agglomerated from the annealed eutectic.

Fig. 121

Neg. No. 5044 X250
 ZS 5-435 C
 20% HF, 20% HNO₃ in glycerine

4.9% silicon alloy, as cast. Primary Zr₂Si crystals, peritectic rims of Zr₄Si in a matrix of eutectic.

Fig. 122

Neg. No. 5045 X500
 ZS 9-457 C
 20% HF, 20% HNO₃ in glycerine

9.2% silicon alloy, as cast. Primary Zr₃Si₂ crystals and peritectic rims of Zr₂Si. No detectable Zr₄Si rims, but appreciable residual eutectic.

Fig. 123

Neg. No. 5046 X200 P.L.
 ZS 11-550 C
 Unetched

11.3% silicon alloy, as cast. Cracked primary crystals of Zr₃Si₂, peritectic rims of Zr₂Si, and a small amount of residual eutectic.

Fig. 124

Neg. No. 5047 X250
 ZS 15-411 C
 20% HF, 20% HNO₃ in glycerine

11.5% silicon alloy, as cast. First appearance of Zr₄Si₃ primary crystals, cracked peritectic walls of Zr₃Si₂, secondary rims of Zr₂Si, and some eutectic.

Fig. 125

Neg. No. 5048 X250
 ZS 18-854 C
 20% HF, 20% HNO₃ in glycerine

17.6% silicon alloy, as cast. Nearly single phase Zr₄Si₃. Some residual Zr₃Si₂ at boundaries.

Fig. 120

Fig. 121

Fig. 122

Fig. 123

Fig. 124

Fig. 125

Fig. 126

Neg. No. 5049 X250
 ZS 18.5-856 C
 20% HF, 20% HNO₃ in glycerine
 18.7% silicon alloy, as cast. Primary crystals of Zr₆Si₅, rosette peritectic rims of Zr₄Si₃, and matrix of Zr₃Si₂.

Fig. 127

Neg. No. 5050 X250
 ZS 20.5-862 C
 20% HF, 20% HNO₃ in glycerine
 20.1% silicon alloy, as cast. Nearly single phase Zr₆Si₅ and peritectic rims of Zr₄Si₃ and Zr₃Si₂.

Fig. 128

Neg. No. 5051 X250
 ZS 22-547 C
 20% HF, 20% HNO₃ in glycerine
 22.3% silicon alloy, as cast. Primary Zr₆Si₅ surrounded by peritectically formed ZrSi.

Fig. 129

Neg. No. 5052 X150
 ZS 24-545 C
 20% HF, 20% HNO₃ in glycerine
 23.5% silicon alloy, as cast. Small primary rosettes of Zr₆Si₅ in a matrix of the peritectically formed ZrSi.

Fig. 130

Neg. No. 5053 X250
 ZS 24.5-863 C
 20% HF, 20% HNO₃ in glycerine
 24.3% silicon alloy, as cast. Nearly single phase primary crystals of ZrSi in a matrix of peritectically formed ZrSi₂.

Fig. 131

Neg. No. 3699 X250
 ZS 35-466 C
 20% HF, 20% HNO₃ in glycerine
 36.1% silicon alloy, as cast. Grey primary crystals of ZrSi, peritectic walls of ZrSi₂, and divorced eutectic ZrSi₂-Si.

Fig. 126

Neg. No. 5049 X250
 ZS 18.5-856 C

20% HF, 20% HNO₃ in glycerine

18.7% silicon alloy, as cast. Primary crystals of Zr₆Si₅, rosette peritectic rims of Zr₄Si₃, and matrix of Zr₃Si₂.

Fig. 127

Neg. No. 5050 X250
 ZS 20.5-862 C

20% HF, 20% HNO₃ in glycerine

20.1% silicon alloy, as cast. Nearly single phase Zr₆Si₅ and peritectic rims of Zr₄Si₃ and Zr₃Si₂.

Fig. 128

Neg. No. 5051 X250
 ZS 22-547 C

20% HF, 20% HNO₃ in glycerine

22.3% silicon alloy, as cast. Primary Zr₆Si₅ surrounded by peritectically formed ZrSi.

Fig. 129

Neg. No. 5052 X150
 ZS 24-545 C

20% HF, 20% HNO₃ in glycerine

23.5% silicon alloy, as cast. Small primary rosettes of Zr₆Si₅ in a matrix of the peritectically formed ZrSi.

Fig. 130

Neg. No. 5053 X250
 ZS 24.5-863 C

20% HF, 20% HNO₃ in glycerine

24.3% silicon alloy, as cast. Nearly single phase primary crystals of ZrSi in a matrix of peritectically formed ZrSi₂.

Fig. 131

Neg. No. 3699 X250
 ZS 35-466 C

20% HF, 20% HNO₃ in glycerine

36.1% silicon alloy, as cast. Grey primary crystals of ZrSi, peritectic walls of ZrSi₂, and divorced eutectic ZrSi₂-Si.

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Fig. 126

Fig. 127

Fig. 128

Fig. 129

Fig. 130

Fig. 131

Fig. 132

Neg. No. 5054
ZS 45-417 C

X250

20% HF, 20% HNO₃ in glycerine

45.6% silicon alloy, as cast. Small amount of grey primary ZrSi crystals surrounded by peritectic walls of ZrSi₂ in a matrix of eutectic ZrSi₂-Si.

Fig. 133

Neg. No. 3700
ZS 55-418 C

X200

20% HF, 20% HNO₃ in glycerine

54.9% silicon alloy, as cast. Primary crystals of ZrSi₂ in a matrix of ZrSi₂-Si.

Fig. 134

Neg. No. 3701
ZS 75-420 C

X200

20% HF, 20% HNO₃ in glycerine

76.2% silicon alloy, as cast. Structure of the ZrSi₂-Si eutectic.

Fig. 135

Neg. No. 5055
ZS 85-422 C

X250

20% HF, 20% HNO₃ in glycerine

84.5% silicon alloy, as cast. Primary silicon crystals in a matrix of ZrSi₂-Si eutectic.

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Fig. 132

Fig. 133

Fig. 134

Fig. 135

G. The System Zirconium-Aluminum

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1. Techniques

The standard melting techniques described earlier, involving the use of a copper block insert to the melting crucible, were applicable to the preparation of all zirconium-aluminum alloys.

2. The Phase Diagram

The zirconium-aluminum phase diagram is shown in Fig. 136, based on weight per cent, and in Fig. 137, based on atomic per cent. Figure 138 presents the zirconium-rich phase relationships on an expanded scale.

The analyses of the zirconium-aluminum alloys investigated are listed in Table XXX.

A preliminary study to determine optimum isothermal annealing times for zirconium-rich alloys was made. Alloys containing 2, 6, and 12% aluminum were annealed for three different lengths of time at 700°, 800°, and 900°C. The isothermal annealing schedule was then set up on a basis of these results. The tabulation of pretreatment and annealing data is presented in Table XXXI.

Due to the large number of intermediate phases, complicated phase relationships, and sluggish diffusion rates, the examination of a large number of as-cast alloy structures was more instrumental in establishing most diagram features than the study of annealed and quenched specimens. In the regions where intermediate phases are crowded together, the as-cast structures often contained three or four phases, the arrangement of which told the solidification history of the alloys. Long time annealing of such alloys did not result in equilibrium conditions, and modified only slightly the original arrangement of the phases.

Considering them generally in the order of increasing aluminum content, the principal features of the zirconium-aluminum system may be summarized as follows:

- a. Zirconium forms a eutectic with Zr_5Al_3 (15.07% Al) at 11% aluminum and $1350 \pm 10^\circ\text{C}$.
- b. The maximum solubility of aluminum in beta zirconium is 9.5% at the eutectic temperature.
- c. The intermediate phase Zr_2Al (12.88% Al) is formed in the solid state by the peritectoid reaction: $\beta + Zr_5Al_3 \rightleftharpoons Zr_2Al$, at $1250 \pm 50^\circ\text{C}$.
- d. The intermediate phase Zr_3Al (8.80% Al) is formed at $975 \pm 25^\circ\text{C}$ by the peritectoid reaction: $\beta + Zr_2Al \rightleftharpoons Zr_3Al$.
- e. Aluminum additions raise the $\alpha \rightarrow \beta$ transformation temperature to $940 \pm 10^\circ\text{C}$. At this temperature, the peritectoid reaction: $\beta + Zr_3Al \rightarrow \alpha$ occurs, yielding an alpha solid solution containing about 3.5% aluminum.

FIG.136 - THE ZIRCONIUM - ALUMINUM SYSTEM

FIG.137- THE ZIRCONIUM - ALUMINUM SYSTEM

FIG.138- EXPANDED DIAGRAM OF THE ZIRCONIUM-RICH REGION OF THE ZIRCONIUM-ALUMINUM SYSTEM

TABLE XXX

ANALYSES OF ZIRCONIUM-ALUMINUM ALLOYS

Alloy No.	Aluminum, Wt. %	Alloy No.	Aluminum, Wt. %
ZA 0.2-701	0.24	ZA 24-564	23.3
ZA 0.4-684	0.37	ZA 25-483	23.1
ZA 0.6-685	0.50	ZA 26-566	25.2
ZA 0.8-542	0.75	ZA 27-567	27.5
ZA 1-690	1.0	ZA 28-568	28.0
ZA 2-691	2.4	ZA 29-569	27.7
ZA 3-692	3.2	ZA 30-485	28.7
ZA 4-693	4.5	ZA 31-570	29.7
ZA 5-694	4.9	ZA 32-704	32.0
ZA 6-695	6.2	ZA 33-705	32.5
ZA 7-696	7.0	ZA 34-706	34.2
ZA 8-697	7.8	ZA 35-707	34.8
ZA 9-698	9.4	ZA 36-708	35.4
ZA 10-699	9.7	ZA 37-709	37.9
ZA 11-700	11.6	ZA 38-710	37.6
ZA 12-702	12.6	ZA 39-711	39.7
ZA 13-540	13.5	ZA 40-712	40.6
ZA 14-865	14.1	ZA 41-713	40.5
ZA 14-541	14.6	ZA 42-720	42.7
ZA 14.5-866	14.7	ZA 43-714	44.7
ZA 15-867	15.0	ZA 44-715	42.4
ZA 15.5-868	16.2	ZA 45-716	44.9
ZA 16-869	15.6	ZA 46-717	46.0
ZA 16-556	16.0	ZA 47-718	46.9
ZA 16.5-870	16.5	ZA 48-719	47.4
ZA 17-557	17.2	ZA 49-722	46.9
ZA 17-871	17.5	ZA 45-489	50.1
ZA 17.5-872	17.5	ZA 50-491	55.4
ZA 18-565	17.7	ZA 55-492	60.9
ZA 18-873	18.4	ZA 60-493	63.0
ZA 18.5-874	19.0	ZA 65-494	64.8*
ZA 19-559	18.9	ZA 70-495	71.3*
ZA 19-875	19.7	ZA 75-496	74.2*
ZA 19.5-876	19.2	ZA 80-497	78.7*
ZA 21-560	20.7	ZA 85-498	84.5*
ZA 22-562	21.9	ZA 90-499	90.0*
ZA 23-563	22.3	ZA 95-500	95.5*

*Analyzed for zirconium. Aluminum by difference.

TABLE XXXI

PRETREATMENT AND ANNEALING OF ZIRCONIUM-ALUMINUM ALLOYS

Alloy No.	Cold Pressed, %*	Homogenized 1000°C-5 hr*	Cold Rolled, %*	1100°C 1 hr	1300°C 1 hr
ZO-282 (Zr)	48	**	89	x	x
ZA 0.2-701	36	x	77		
ZA 0.4-684	17	x	72		
ZA 0.6-685	17	x	73		
ZA 0.8-542	24	x	79		
ZA 1-690	8	x	79		
ZA 2-691	6	x	75	x	x
ZA 3-692	8	x	57		
ZA 4-693	3	x	34	x	x
ZA 5-694	8	x	57		x
ZA 6-695	1	x	36	x	x
ZA 7-696	1	x	35	x	x
ZA 8-697	0	x	32	x	x
ZA 9-698	1	x	33	x	x
ZA 10-699	0	x	7	x	x
ZA 11-700		x	2		
ZA 12-702		x	1	x	x
ZA 13-540					
ZA 14-541				x	
ZA 15-478					
ZA 16-556				x	
ZA 17-557					
ZA 18-565				x	
ZA 19-559					
ZA 20-482					
ZA 21-560				x	
ZA 22-562					
ZA 23-563					
ZA 24-564				x	
ZA 25-483					
ZA 26-566					
ZA 27-567					
ZA 28-568				x	
ZA 29-569					
ZA 30-485					
ZA 31-570				x	
ZA 32-704				x	

*The pretreatment (i.e., cold pressing, homogenization, cold rolling) corresponding to each alloy composition is the same for all annealing treatments, and is not repeated in subsequent columns.

**Homogenized at 900°C for 7 hours.

TABLE XXXI (Cont.)

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Alloy No.	Cold Pressed, %	Homogenized 1000°C-5 hr	Cold Rolled, %	1400°C 1 hr	1300°C 1 hr
ZA 33-705					
ZA 34-706				x	
ZA 35-707					
ZA 36-708				x	
ZA 37-709					
ZA 38-710					
ZA 39-711					
ZA 40-712				x	
ZA 41-713					
ZA 42-720					
ZA 43-714					
ZA 44-715				x	
ZA 45-716					
ZA 46-717					
ZA 47-718					
ZA 48-719					
ZA 49-722					
ZA 50-491					

TABLE XXXI (Cont.)

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Alloy No.	1200°C 6 hr	1150°C 16 hr	1096°C 20 hr	1047°C 20 hr	1001°C 20 hr	950°C 45 hr	900°C 50 hr	850°C 99 hr
ZO-282 (Zr)	x	x	x	x	x	x	x	x
ZA 0.2-701						x	x	x
ZA 0.4-684						x	x	x
ZA 0.6-685						x	x	x
ZA 0.8-542						x	x	x
ZA 1-690	x	x	x	x	x	x	x	x
ZA 2-691	x	x	x	x	x	x	x	x
ZA 3-692	x	x	x	x	x	x	x	x
ZA 4-693	x	x	x	x	x	x	x	x
ZA 5-694	x	x	x	x	x	x	x	x
ZA 6-695	x	x	x	x	x	x	x	x
ZA 7-696	x	x	x	x	x	x	x	x
ZA 8-697	x	x	x	x	x	x	x	x
ZA 9-698	x	x	x	x	x	x	x	x
ZA 10-699	x	x	x	x	x	x	x	x
ZA 11-700	x			x	x	x	x	x
ZA 12-702		x	x	x	x	x	x	x
ZA 13-540	x			x	x	x	x	x
ZA 14-541			x					
ZA 16-556	x		x		x			
ZA 17-557	x				x			
ZA 18-565			x					
ZA 19-559	x				x			
ZA 21-560			x					
ZA 23-563	x				x			
ZA 26-566	x				x			
ZA 31-570	x				x			
ZA 33-705	x				x			
ZA 36-708	x				x			
ZA 40-712	x				x			
ZA 44-715	x				x			

TABLE XXXI (Cont.)

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Alloy No.	820°C 95 hr	804°C 138 hr	751°C 245 hr	699°C 240 hr	607°C 400 hr
ZO-282 (Zr)	x	x	x	x	x
ZA 0.2-701	x	x	x	x	x
ZA 0.4-684	x	x	x	x	x
ZA 0.6-685	x	x	x	x	x
ZA 0.8-542	x	x	x	x	x
ZA 1-690	x	x	x	x	x
ZA 2-691	x	x	x	x	x
ZA 3-692	x	x	x	x	x
ZA 4-693	x	x	x	x	x
ZA 5-694	x	x	x	x	x
ZA 6-695	x	x	x	x	x
ZA 7-696	x	x	x	x	x
ZA 8-697	x	x	x	x	x
ZA 9-698	x	x	x	x	x
ZA 10-699	x	x	x	x	x
ZA 11-700	x	x	x	x	x
ZA 12-702	x	x	x	x	x
ZA 13-540	x	x	x	x	x
ZA 14-541		x			
ZA 16-556		x			
ZA 18-565		x			
ZA 21-560		x			
ZA 24-564		x			
ZA 28-568		x			
ZA 31-570		x			
ZA 32-704		x			
ZA 34-706		x			
ZA 36-708		x			
ZA 40-712		x			
ZA 44-715		x			

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- f. The solubility of aluminum in alpha zirconium decreases with falling temperature from 3.5% aluminum at 940°C to 1% at 800°C, and 0.5% at 700°C.
 - g. Zr_5Al_3 (15.07% Al) is formed by the peritectic reaction between Zr_3Al_2 (16.46% Al) and a melt containing about 15% aluminum at 1395±10°C. Zr_5Al_3 breaks down at lower temperatures, probably eutectoidally.
 - h. Zr_3Al_2 (16.46% Al) is formed by the peritectic reaction between Zr_4Al_3 (18.15% Al) and a melt containing about 16% aluminum at 1480±20°C.
 - i. Zr_4Al_3 (18.15% Al) melts with an open maximum at 1530±20°C.
 - j. A eutectic occurs at 22% aluminum between Zr_4Al_3 and Zr_2Al_3 (tentative, 30.72% Al) at 1480±20°C.
 - k. $ZrAl$ (22.82% Al) is formed in the solid state by the peritectoid reaction: $Zr_4Al_3 + Zr_2Al_3 \rightleftharpoons ZrAl$, at 1250±50°C.
 - l. Zr_2Al_3 (tentative, 30.72% Al) is formed at 1595±25°C by a peritectic reaction between $ZrAl_2$ (37.16% Al) and the melt containing about 30% aluminum.
 - m. $ZrAl_2$ (37.16% Al) melts with an open maximum at 1645±25°C.
 - n. A eutectic between $ZrAl_2$ and $ZrAl_3$ (47.00% Al) occurs at 45% aluminum and 1490±20°C.
 - o. $ZrAl_3$ (47.00% Al) melts with an open maximum at 1580±25°C.
 - p. At all aluminum contents higher than 47%, only two phases exist: $ZrAl_3$ and aluminum.
 - q. No work was done on the aluminum solid solution range and its peritectic formation at very high aluminum content. The prior work of Fink and Willey (21) covers these points with high accuracy.

3. Zirconium-Rich Alloys

The eutectic at 11% aluminum and 1350±10°C is illustrated in Fig. 139, showing the microstructure of an as-cast 11.6% aluminum alloy. The temperature of the eutectic melt was established independently by both thermal analysis and incipient melting. In addition, a series of specimens placed in the furnace for isothermal annealing at 1400°C were almost completely melted, due to the eutectic present in a number of them.

The extent of the beta solid solution is indicated in Figs. 140 and 141, showing 7.8 and 9.4% aluminum alloys, respectively, annealed at 1300°C. The extrapolation of this boundary to the eutectic temperature yields a maximum aluminum solubility of approximately 9.5%. The series of alloys annealed at

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1200°C revealed the existence of an intermediate phase different from that detected in as-cast alloys and specimens annealed at 1300°C. This phase was located close to 13% aluminum, and is therefore believed to be Zr_2Al (12.88% Al). It is formed by the peritectoid reaction: $\beta + Zr_5Al_3 \rightleftharpoons Zr_2Al$, at a temperature between 1200° and 1300°C. Figure 142 is the microstructure of an 11.6% aluminum alloy, annealed at 1200°C, showing a mixture of beta and Zr_2Al phases.

Another peritectoid reaction was found to occur between 1000° and 950°C, involving the phases: $\beta + Zr_2Al \rightleftharpoons Zr_3Al$ (8.80% Al). Figure 143 depicts a 7.8% aluminum alloy, annealed at 1001°C, containing $\beta + Zr_2Al$, while Fig. 144, the same alloy annealed at 950°C, shows the $\beta + Zr_3Al$ field. The phase field $Zr_3Al + Zr_2Al$ is illustrated in Fig. 145, which is the microstructure of an 11.6% aluminum alloy annealed at 950°C.

Since the regular set of isothermal anneals gave evidence of the peritectoid formation of the alpha solid solutions, a special series of heat treatments was made in order to obtain the best evidence of this reaction. Alloys containing nominally 2, 3, 4, and 5% aluminum were pretreated as outlined in Table XXXI, then held at 1050°C for 15 hours and slowly cooled to each of the temperatures 950°, 932°, 900°, 850°, and 808°C, held for about 20 hours, and water quenched. Excellent evidence for the existence and location of the peritectoid reaction: $\beta + Zr_3Al \rightleftharpoons \alpha$ can be seen in Figs. 146 through 149. Figure 146, a 3.2% aluminum alloy with a final hold at 950°C, shows only the transformed beta structure. Figure 147, a 4.5% aluminum alloy similarly treated, depicts transformed beta plus Zr_3Al . Figure 148, a 3.2% aluminum alloy with a final hold at 932°C, represents an $\alpha + \beta$ structure. Figure 149, the 4.5% aluminum alloy similarly treated, gives evidence of the incomplete formation of alpha from a reaction between beta and Zr_3Al .

The decrease in the solid solubility of aluminum in alpha zirconium with falling temperature is indicated by Figs. 150 and 151, representing alloys annealed at 850°C, and Figs. 152 and 153, of alloys annealed at 699°C.

4. Evidence for the Phase Relationships at Higher Aluminum Contents

Due to the large difference between the atomic weights of zirconium and aluminum, small increments in aluminum additions by weight represent relatively large atomic increments of the lighter metal. Accordingly, a very large number of zirconium-rich alloys had to be examined in order to detect all of the intermediate phases and phase changes.

Fortunately, the several intermetallic compounds of this system yielded very distinctive color and extinction reactions under polarized light, and this technique proved to be an invaluable tool in identifying the sequence of phases.

The eutectic reaction at 11% aluminum involves the beta solid solution and an intermediate phase at about 15% aluminum. This phase is therefore assigned the formula Zr_5Al_3 (15.07% Al). Figure 154 represents the as-cast structure of a 14.7% aluminum alloy, showing primary crystals of Zr_5Al_3 in a matrix of eutectic. Figure 155 shows a 15.0% aluminum alloy, as cast. A new type of primary crystal exists in this three phase alloy, surrounded by peritectic walls of Zr_5Al_3 and a matrix of eutectic. Zr_5Al_3 is therefore formed by the peritectic reaction between the second phase formed from the melt (assigned the formula Zr_3Al_2 , 16.46% Al) and the liquid at about 15% aluminum. Numerous anneals in the solid state have shown that Zr_5Al_3 has a minimum temperature of stability. It is likely that this phase decomposes eutectoidally; however, the temperature of decomposition could not be ascertained because anneals over a wide range of temperatures (600°-1100°C) neither completely eliminated the phase nor maintained it entirely without decomposition. This could be interpreted in two ways: (1) the reaction could be a sluggish one at high temperature; or (2) it could be an unsuppressible (by quenching) one at lower temperature. Accordingly, this temperature remains open on the phase diagrams. Figure 156, depicting a 13.5% aluminum alloy annealed at 950°C, presents typical evidence of the decomposition of the Zr_5Al_3 phase.

Figure 157 is the as-cast structure of a 15.6% aluminum alloy, depicting the same phases and phase arrangement as those in Fig. 155. The as-cast structure of a 16.5% aluminum alloy, Fig. 158, however, reveals the presence of another new primary phase, and a new peritectic arrangement. Zr_3Al_2 (16.46% Al) is therefore formed peritectically by the reaction between the new primary phase (assigned the formula Zr_4Al_3 , 18.15% Al) and a melt with approximately 16% aluminum. Zr_3Al_2 is stable to room temperature.

Zr_4Al_3 , 18.15% aluminum, melts with an open maximum and is shown in Fig. 159, which is the structure of an 18.9% aluminum alloy, as cast. Zr_4Al_3 forms a eutectic with an intermediate phase located at about 30% aluminum. Figure 160, representing the cast structure of a 21.9% aluminum alloy, shows this eutectic mixture.

The isothermal anneals of specimens containing between 19 and 30% aluminum give rise to three phase structures, indicating that another intermediate phase must be formed in the solid state. A special set of anneals at various temperature levels proved that $ZrAl$ (22.82% Al) is peritectoidally formed between 1200° and 1300°C. Figure 161 is the microstructure of a 22.3% aluminum alloy annealed at 1300°C. Only the divorced eutectic constituents, Zr_4Al_3 and Zr_2Al_3 (tentative), are present. Figure 162, showing the same alloy annealed at 1200°C, represents a nearly single phase $ZrAl$ structure. $ZrAl$ appears to exist only at a singular composition.

Figure 163, the as-cast structure of a 29.7% aluminum alloy, depicts nearly 100% the next intermediate phase. This phase might be represented by either of the formulae Zr_3Al_4 (28.27% Al) or Zr_2Al_3 (30.72% Al). Most of the present evidence supports the latter, so this designation is tentatively adopted. Figure 164 is the as-cast structure of a 32.0% aluminum alloy. New primary crystals are detected in a matrix of Zr_2Al_3 . Accordingly, Zr_2Al_3 is formed by a peritectic reaction between the new phase (assigned the formula $ZrAl_2$, 37.16% Al) and a melt containing about 30% aluminum.

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$ZrAl_2$ (37.16% Al) has an open maximum melting point. The structure of this phase is given in Fig. 165, an as-cast 37.6% aluminum alloy. A powder sample of this alloy was subjected to X-ray analysis. An orthorhombic structure with the lattice parameters $a = 10.40 \text{ \AA}$, $b = 7.21 \text{ \AA}$, $c = 4.97 \text{ \AA}$ was obtained. The X-ray pattern is tabulated in the Appendix.

$ZrAl_2$ forms a eutectic melt with an intermediate phase containing 47% aluminum at about 45% aluminum. Figure 166 shows the eutectic structure in an as-cast 44.9% aluminum alloy.

The intermediate phase at 47% aluminum melts with an open maximum and is the previously known (13,21,22) $ZrAl_3$ (47.00% Al). The structure of this phase is shown in Fig. 167, which is an as-cast 47.1% aluminum alloy. The X-ray investigation of this phase showed the structure to be tetragonal with the following lattice parameters: $c = 16.90 \text{ \AA}$, $a = 4.306 \text{ \AA}$, $c/a = 3.92$. Brauer (22) has also reported the phase to be tetragonal, with $c = 17.29 \text{ \AA}$ and $a = 4.01 \text{ \AA}$.

5. Aluminum-Rich Alloys

All alloys containing more than 47% aluminum consisted of two-phase mixtures of $ZrAl_3$ and aluminum solid solution. A structure typical of this very broad two-phase field is shown in Fig. 168, representing a 64.8% aluminum alloy.

According to Fink and Willey (21), the peritectic reaction: $ZrAl_3 + L \rightleftharpoons Al_{ss}$ occurs at 660.5°C . The melt entering into this reaction contains 0.11% zirconium, and the maximum solubility of zirconium in aluminum at the peritectic temperature is 0.28% zirconium. No attempt was made to repeat this work under the present contract.

6. Melting Range Determinations

Because of the very complex structures resulting from the crowding together of a large number of intermediate phases in this system, the microscopic detection of incipient melting in quenched samples was difficult and, in certain cases, unworkable.

Since all of the temperatures involved were within the useful range of the platinum/platinum-10% rhodium thermocouple, thermal analysis was adopted as the more reliable approach in this case. The thermal data are summarized in Table XXII.

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TABLE XXXII
MELTING RANGE DETERMINATIONS FOR THE ZIRCONIUM-ALUMINUM SYSTEM

Alloy No.	Weight % Al	Thermal Analysis Arrests, °C	Incipient Melting	
			Melting Observed, °C	No Melting, °C
YZA 11-700	11.6		1365	1340
XZA 11-821	11.9	1350		
YZA 15-867	15.0		1412	1378
XZA 15-822	15.7	1395...1345		
XZA 17-812	18.0	1530...1480		
XZA 19-813	22.2	1530...1485		
XZA 22-811	23.8	1480		
XZA 30-814	32.5	1595		
XZA 37-816	39.4	1645		
XZA 45-817	42.4	1490		
XZA 47-818	48.5	1580		
XZA 80-820	81.3	1328...655		

Fig. 139

Neg. No. 3706 X500
ZA 11-700 C
20% HF, 20% HNO₃ in glycerine

An 11.6% aluminum alloy, as-cast.
Structure of the β -Zr₅Al₃ eutectic.

Fig. 140

Neg. No. 4070 X250
ZA 8-697; PO-H1000-5; XR32-Q1300-1
20% HF, 20% HNO₃ in glycerine

A 7.8% aluminum alloy, quenched after annealing 1 hour at 1300°C. Transformation structure obtained on quenching. This alloy was single-phase beta solid solution at 1300°C.

Fig. 141

Neg. No. 4071 X250
ZA 9-698; P1-H1000-5; XR33-Q1300-1
20% HF, 20% HNO₃ in glycerine

A 9.4% aluminum alloy, quenched after annealing 1 hour at 1300°C. Isothermal crystals of Zr₅Al₃ in a matrix transformed β .

Fig. 142

Neg. No. 4072 X250
ZA 11-700; PO-H1000-5; XR2-Q1200-6
20% HF, 20% HNO₃ in glycerine

An 11.6% aluminum alloy, quenched after annealing 6 hours at 1200°C. Zr₂Al crystals in a matrix of transformed β . The peritectoid $\beta + \text{Zr}_5\text{Al}_3 \rightleftharpoons \text{Zr}_2\text{Al}$ must lie between 1200° and 1300°C.

Fig. 143

Neg. No. 4073 X250
ZA 8-697; PO-H1000-5; XR32-Q1001-20
20% HF, 20% HNO₃ in glycerine

A 7.8% aluminum alloy, quenched after annealing 20 hours at 1001°C. Principal phase is Zr₂Al in a matrix of transformed β . Some unreacted third phase particles of Zr₅Al₃ remain within the Zr₂Al, evidence of the peritectoid.

Fig. 144

Neg. No. 4074 X250
ZA 8-697; PO-H1000-5; XR32-Q950-45
20% HF, 20% HNO₃ in glycerine

A 7.8% aluminum alloy, quenched after annealing 45 hours at 950°C. Crystals of Zr₃Al in a matrix of transformed β . The peritectoid $\beta + \text{Zr}_2\text{Al} \rightleftharpoons \text{Zr}_3\text{Al}$ must lie between 950° and 1000°C.

Fig. 139

Fig. 140

Fig. 141

Fig. 142

Fig. 143

Fig. 144

Fig. 145

Neg. No. 4075 X250
ZA 11-700; P0-H1000-5; XR2-Q950-45

20% HF, 20% HNO₃ in glycerine

An 11.6% aluminum alloy, quenched after annealing 45 hours at 950°C. Annealed in the field Zr₃Al (darker phase) + Zr₂Al (white). This places the composition of Zr₃Al between 7.8 and 11.6% aluminum.

Fig. 146

Neg. No. 4060 X150
ZA 3-692; P8-H1000-5; XR57-H1050-15-SC-Q950-20

20% HF, 20% HNO₃ in glycerine

A 3.2% aluminum alloy, held at 1050°C for 15 hours, slowly cooled to 950°C, held 20 hours and quenched. Transformed β structure.

Fig. 147

Neg. No. 4061 X150
ZA 4-693; P3-H1000-5; XR34-H1050-15-SC-Q950-20

20% HF, 20% HNO₃ in glycerine

A 4.5% aluminum alloy, held at 1050°C for 15 hours, slowly cooled to 950°C, held 20 hours and quenched. Crystals of Zr₃Al in a matrix of acicular α . Annealed in the β + Zr₃Al field.

Fig. 148

Neg. No. 4062 X150
ZA 3-692; P8-H1000-5; XR57-H1050-15-SC-Q932-20

20% HF, 20% HNO₃ in glycerine

A 3.2% aluminum alloy, held at 1050°C for 15 hours, slowly cooled to 932°C, held 20 hours and quenched. Isothermal α in a matrix of transformed β . Compare with Fig. 146.

Fig. 149

Neg. No. 4064 X250
ZA 4-693; P3-H1000-5; XR34-H1050-15-SC-Q932-20

20% HF, 20% HNO₃ in glycerine

A 4.5% aluminum alloy, held at 1050°C for 15 hours, slowly cooled to 932°C, held 20 hours and quenched. Three phase structure showing the incomplete peritectoid formation of α (white) from the original Zr₃Al + β structure. Compare with Fig. 147. The peritectoid, β + Zr₃Al $\rightleftharpoons$ α , must lie between 932° and 950°C.

Fig. 150

Neg. No. 4080 X500
ZA 1-690; P8-H1000-5; XR79-Q850-99

20% HF, 20% HNO₃ in glycerine

A 1.0% aluminum alloy, quenched after annealing 99 hours at 850°C. 100% isothermal α solid solution.

Fig. 145

Fig. 146

Fig. 147

Fig. 148

Fig. 149

Fig. 150

Fig. 151

Neg. No. 4081 X500
 ZA 2-691; P6-H1000-5; XR75-Q850-99
 20% HF, 20% HNO₃ in glycerine

A 2.4% aluminum alloy, quenched after annealing 99 hours at 850°C. α + Zr₃Al crystals.

Fig. 152

Neg. No. 5038 X250
 ZA 0.4-684; P17-H1000-5; XR72-Q699-240
 20% HF, 20% HNO₃ in glycerine

A 0.37% aluminum alloy, quenched after annealing 240 hours at 699°C. 100% α solid solution.

Fig. 153

Neg. No. 5037 X250
 ZA 0.6-685; P17-H1000-5; XR73-Q699-240
 20% HF, 20% HNO₃ in glycerine

A 0.50% aluminum alloy, quenched after annealing 240 hours at 699°C. α + fine precipitate of Zr₃Al. Note decrease in grain size on crossing the α/α + Zr₃Al boundary.

Fig. 154

Neg. No. 4065 X150
 ZA 14.5-866 C
 20% HF, 20% HNO₃ in glycerine

A 14.7% aluminum alloy, as-cast. Primary crystals of Zr₅Al₃ in a matrix of β -Zr₅Al₃ eutectic.

Fig. 155

Neg. No. 4066 X150
 ZA 15-867 C
 20% HF, 20% HNO₃ in glycerine

A 15.0% aluminum alloy, as-cast. Primary crystals of Zr₃Al₂, peritectic walls of Zr₅Al₃ in a matrix of eutectic. The composition of the peritectic liquid must lie between 14.7 and 15% aluminum.

Fig. 156

Neg. No. 5036 X250
 ZA 13-540; Q950-45
 20% HF, 20% HNO₃ in glycerine

A 13.5% aluminum alloy, quenched after annealing 45 hours at 950°C. The original primaries of Zr₅Al₃ display a pearlitic breakdown in some cases and none in others. The decomposition stops abruptly in the middle of the large Zr₅Al₃ crystal.

Fig. 151

Fig. 152

Fig. 153

Fig. 154

Fig. 155

Fig. 156

Fig. 157

Neg. No. 4067 X150
ZA 16-869 C

20% HF, 20% HNO₃ in glycerine

A 15.6% aluminum alloy, as-cast.
Primary crystals of Zr₃Al₂ in a complete peritectic matrix of Zr₅Al₃.

Fig. 158

Neg. No. 4068 X250
ZA 16.5-870 C

20% HF, 20% HNO₃ in glycerine

A 16.5% aluminum alloy, as-cast.
Primary crystals of Zr₄Al₃ (white), peritectic walls of Zr₃Al₂ and a matrix of Zr₅Al₃ (cross-cracked).
The peritectic melt must be situated between 15.6 and 16.5% aluminum.

Fig. 159

Neg. No. 3708 X150
ZA 19-559 C

20% HF, 20% HNO₃ in glycerine

An 18.9% aluminum alloy, as-cast.
Nearly 100% of Zr₄Al₃ primary crystals.

Fig. 160

Neg. No. 3709 X500
ZA 22-562 C

20% HF, 20% HNO₃ in glycerine

A 21.9% aluminum alloy, as-cast.
Structure of the eutectic Zr₄Al₃-Zr₂Al₃.

Fig. 161

Neg. No. 4076 X250
ZA 23-563-Q1300-1

20% HF, 20% HNO₃ in glycerine

A 22.3% aluminum alloy, quenched after annealing 1 hour at 1300°C. Separation and agglomeration of the eutectic phases Zr₄Al₃ and Zr₂Al₃ on annealing.

Fig. 162

Neg. No. 4077 X250
ZA 23-563-Q1200-6

20% HF, 20% HNO₃ in glycerine

A 22.3% aluminum alloy, quenched after annealing 6 hours at 1200°C. Nearly single phase ZrAl. The peritectoid Zr₄Al₃ + Zr₂Al₃ $\rightleftharpoons$ ZrAl must lie between 1200° and 1300°C.

Fig. 157

Fig. 158

Fig. 159

Fig. 160

Fig. 161

Fig. 162

Fig. 163

Neg. No. 3710 X100
ZA 31-570 C

20% HF, 20% HNO₃ in glycerine

A 29.7% aluminum alloy, as-cast.

Nearly single phase Zr₂Al₃.

Fig. 164

Neg. No. 4069 X150
ZA 32-704 C

20% HF, 20% HNO₃ in glycerine

A 32.0% aluminum alloy, as-cast.

Primary crystals of ZrAl₂ surrounded by a complete peritectic matrix of Zr₂Al₃. The peritectic melt must lie between 29.7 and 32% aluminum.

Fig. 165

Neg. No. 3711 X100
ZA 38-710 C

Unetched, polarized light

A 37.6% aluminum alloy, as-cast.

Nearly 100% ZrAl₂.

Fig. 166

Neg. No. 3712 X150
ZA 45-489 C

20% HF, 20% HNO₃ in glycerine

A 44.9% aluminum alloy, as-cast.

Structure of the eutectic ZrAl₂-ZrAl₃.

Fig. 167

Neg. No. 3713 X100
ZA 48-591 C

20% HF, 20% HNO₃ in glycerine

A 47.1% aluminum alloy, as-cast.

Nearly single phase ZrAl₃.

Fig. 168

Neg. No. 3714 X150
ZA 65-494 C

Unetched

A 64.8% aluminum alloy, as-cast.

Primary crystals of ZrAl₃ in a matrix of aluminum-rich solid solution.

Fig. 163

Fig. 164

Fig. 165

Fig. 166

Fig. 167

Fig. 168

H. The System Zirconium-Magnesium

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Zirconium melts at 1850°C , while magnesium boils at 1110°C , so it must be expected that the binary system of these two components might be greatly affected by the vapor state, and that preparation of alloys might be impossible. No phase diagram could be determined in the present work, because attempts to prepare alloys met with little success.

1. Previous Literature

Magnesium-rich alloys containing less than 1% zirconium have achieved some commercial importance, and have been the subject of considerable research (23, 24, 25, 26, 27, 28, 29, 30, 31). Mellor (24) states that most investigators have not been able to introduce more than about 0.7% zirconium into magnesium, and that this is considered to be the upper limit. When more zirconium is introduced into a magnesium bath, it is generally agreed that zirconium is held in a mechanical mixture with magnesium.

Nowotny, Normnes and Mohrheim (32) claim to have made alloys over the entire composition range, and have discussed the phase relationships. The zirconium used was of very low purity. Attempts at this laboratory to make alloys by the methods described by Nowotny, et al. were completely without success. These authors propose that there is a broad solid solution of magnesium in zirconium, that slightly less than 1% zirconium is soluble in magnesium, and that a mixture of these solid solutions separates the single phase fields. On a basis of lattice parameter data only, they suggest that there is slight, though uncertain, evidence for the existence of ZrMg_2 . No other investigators have found any evidence supporting the occurrence of such a phase.

Dr. W. J. Kroll has written (33) that many attempts by the Bureau of Mines to produce zirconium-magnesium alloys resulted in failure. Interruption of the zirconium reduction reaction yielded only mechanical mixtures. Long-time heating of finely divided mixtures produced no alloying. Mellor (24) also stated that powder metallurgy methods were not successful, and that no evidence of diffusion was found.

Similar experiences have been noted with other systems in which the melting point of the second component is higher than the boiling point of magnesium. Notably, Payne and Houghton (34) have reported that all attempts to produce alloys of beryllium with magnesium proved abortive.

2. Experimental Procedures and Results

For the present work, the region of interest was that of zirconium-rich alloys. Over fifty experiments were conducted with the aim of producing these binary alloys. Six different types of approach were followed in these experiments:

- a. Induction melting of mixed charges, claimed successful by Nowotny, et al.
- b. Introduction of increasing zirconium charge increments to a magnesium bath.
- c. Solid zirconium-liquid magnesium diffusion couples.
- d. Heating of magnesium inside zirconium "bombs".
- e. Powder metallurgy:
 - (1) Sheath-rolling of mixed powders.
 - (2) Alternate annealing and cold working of compacts.
- f. Special arc-melting techniques.

The results of these experiments may be briefly summarized as follows:

- a. Platelets of zirconium and crystals of magnesium were induction melted in an iron crucible under a positive pressure of helium gas. The melting point of zirconium (1852°C) could not be approached because of the low boiling point (1110°C) of magnesium. Holding such charges at temperatures which precluded excessive vaporization of magnesium for as long as fifteen hours produced no evidence of true alloy formation.
- b. It was hoped that the liquidus curve, which rises steeply from the magnesium-rich peritectic point, could be followed to much higher zirconium contents than heretofore achieved by a painstaking program of small zirconium additions with simultaneous upward adjustment of temperature. This could be accomplished if increasing zirconium content appreciably lowers the vapor pressure of magnesium.

Magnesium baths were induction melted in iron crucibles under a positive pressure of helium. Platelets of zirconium were attached to a spiral of wolfram wire and lowered into the bath. The temperature was constantly increased until vaporization became excessive, then the temperature was dropped, and gradually increased again. The zirconium platelets were attacked and disappeared into the bath, and were replaced by more. This process was repeated until an amount of zirconium equivalent to the weight of the magnesium bath had been "dissolved". Examination of several ingots prepared in this way revealed that there was a large sludge deposit of zirconium at the bottom of each. Induction stirring caused the dispersion of some zirconium particles through the bath, which were entrapped during solidification. Such areas were easily identified in the microscopic examination. The microstructures of the relatively homogeneous areas were typical of those described by Sauerwald and Mellor (Fig. 169), and invariably analyzed only 0.5 to 1% zirconium. With higher zirconium additions, the structures included colonies of unreacted zirconium particles, as in Fig. 170.

c. Diffusion couples were made by suspending zirconium rods in molten magnesium baths. A series of couples, employing various times and temperatures, was investigated. Here, as in the case of the zirconium platelets, molten magnesium seemed to attack zirconium rapidly, but this appears to be a case of intergranular attack, subdividing the massive piece into small particles, but not alloying with them. Cross-sectional micrographs of several couples revealed an interface zone different from either metal (Fig. 171). This zone was usually cracked, and contained some very small, sharp, angular particles of high microhardness. This at first was believed to represent an intermetallic compound, although a solid zone of the phase would normally be expected. In other couples there was no evidence of such a zone. It is now considered likely that such zones may represent contamination layers (oxides, nitrides, etc.) rather than binary zirconium-magnesium phases. The experiments were conducted under ambient helium atmospheres, but there may have been sufficient agitation in the induction heated bath to permit interfacial contamination. These couples gave no clear information on the constitution of the system. A solid-solid couple, held at 600°C, showed no evidence of diffusion at the interface.

d. "Bombs" were made from short lengths of zirconium crystal bar. These were drilled out and magnesium charges were inserted. Zirconium caps were then welded on in the arc melting furnace under a reduced pressure of helium. Such bombs were sealed in quartz capsules and heated at temperatures between 700° and 1300°C for 2 to 20 hours. There was, again, no reproducible evidence of alloy formation in these tests. The conditions here should have been the optimum for alloying, since magnesium vapor could not escape. As before, magnesium attacked the zirconium intergranularly, dislodging particles which were discernible as a discrete phase in the solidified magnesium (Fig. 172). The zirconium container had the microstructure of unalloyed zirconium, even at the bimetal interface.

e. Attempts were made to prepare alloys containing 0 to 20% magnesium by the following powder techniques:

(1) Mixed powder charges were placed in a mild steel tube closed at one end. The open end was closed in a vise and sealed with a heli-arc weldment, the tube being partially immersed in water to avoid melting of the magnesium. The sheathed powders were then hot rolled at temperatures just below the melting point of magnesium. The sheath was reduced to plate by many small-reduction passes with an anneal between passes. No evidence of alloying by interdiffusion was obtained.

(2) Compacts of various composition mixtures in the above range were cold pressed, using several different powder sizes down to -325 mesh. Such compacts were given a sintering anneal at 625°C, then alternately cold pressed and annealed twice at the same temperature. Confirming the observations of Mellor and Kroll, no alloy formation was observed.

f. Although it was theoretically unsound because of the intense local heat produced, arc melting techniques were investigated for alloy production. Initial trials, involving the insertion of magnesium into the drilled cavity of a pre-melted zirconium ingot, plugging the cavity with a zirconium cylinder, and arc melting at low power, were completely unsuccessful. Magnesium vapor was rapidly ejected from the melt and no alloying was obtained.

A modification in the arc furnace was made, which permitted the insertion of magnesium wire into a molten zirconium bath. A number of runs were made in which 2 to 50 feet of 0.1 in. diameter magnesium wire were rapidly fed into the bath. This was, of course, accompanied by a considerable vaporization and condensation of magnesium within the furnace. The resultant ingots were segregated to variable extents, but good evidence that zirconium will take at least some magnesium into solid solution was found. A few ingots displayed, either wholly or in part, structures of retained beta phase, which in itself is evidence for alloy formation, i.e. the beta phase cannot be retained in unalloyed zirconium, but only in certain beta solid solutions. Most of the ingots, however, yielded the typical beta transformation structure of unalloyed zirconium, and the results could not be correlated with the amount of magnesium wire fed into the bath, nor were they reproducible in any controlled fashion.

One of the "retained beta" alloys (Fig. 173) yielded an analysis of 4.7% magnesium. This alloy was cold worked, then sectioned, and pieces were annealed at 1000°, 950°, 900°, 850°, 800°, and 750°C. It was hoped that these anneals would yield some information on the effect of magnesium on the $\alpha \rightleftharpoons \beta$ transformation. These structures were not informative, perhaps because of lack of homogeneity in the original specimen. The structures displayed the original large beta grain boundaries but contained in some cases a deep etching grain boundary constituent whose presence could not be correlated with the temperature of annealing. For example, it was present in the specimens annealed at 850° (Fig. 174) and 1000°C, but apparently absent from a 950°C sample.

Analysis of an annealed sample showed that only 2.8% magnesium was present. This might be due to segregation in the original ingot or, conceivably, to the separation of a magnesium-rich liquid and its vaporization during annealing.

Considerable coring was noted in some areas of the samples--another evidence of segregation. The matrix of all samples contained a very fine unresolvable precipitate.

A back reflection X-ray photograph of the arc-cast sample yielded a beta zirconium pattern. Debye-Scherrer powder photographs of the same material, both annealed and unannealed, gave an alpha zirconium pattern. The preparation of the sample by filing was apparently sufficient to transform the alloy from beta to acicular alpha (transformed beta). The Debye-Scherrer patterns of the annealed series indicated alpha structures.

3. Conclusions

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Some of the above experiments were directed toward actual production of zirconium-magnesium alloys, others were intended only to yield some information on the nature of the system. Obviously, the evidence is insufficient, and in some cases too conflicting, to permit even a tentative phase diagram to be drawn. Certain other specialized techniques could have been tried, such as simultaneous electrolytic deposition, vapor deposition, etc. It appears, however, that the work done is sufficient to prove that there is, and probably will be, no practical method of preparing homogeneous zirconium-rich zirconium-magnesium alloys in reasonable quantity for study or exploitation.

This investigation has confirmed the approximate extent of alloying at the magnesium end of the system set forth in previous papers. An indication that zirconium takes some magnesium into solid solution was also obtained, but little control could be exercised over the production of such alloys; they were apparently segregated; and attempts to discover the phase relationships in connection with the transformation failed.

Fig. 169

Neg. No. 5076
XZG-6MT

X150

Glycol-Acetic etch

Magnesium alloy containing about 0.8% zirconium. The characteristic coring in the magnesium matrix probably marks the original sites of zirconium particles which were taken into solution with difficulty. This structure is typical of as-cast structures shown by Mellor (24) and Sauerwald (26).

Fig. 170

Neg. No. 5075
XZG-7T

X150

Glycol-Acetic etch

Magnesium to which excess zirconium was added. Analysis: 1.01 to 4.19 (various samples). Colonies of unreacted zirconium particles in the magnesium solid solution matrix.

Fig. 171

Neg. No. 3831
Zr-Mg Diff. 900-1

X250

20% HF, 20% HNO₃ in glycerine

Section of a liquid-solid diffusion couple held at approximately 900°C for 1 hour in the induction furnace. The zirconium rod (at left) is separated from the solidified magnesium bath by a brittle zone containing small, very hard, angular crystals. This could be a zirconium-magnesium intermediate phase, but it is considered more likely to have resulted from interfacial contamination because it was not found in many other tests.

Fig. 172

Neg. No. 5077
XZG-19

X150

5% Nital

Magnesium heated inside a zirconium "bomb" at 1000°C for 7 hours. Magnesium has attacked the zirconium wall, dislodging grains which are apparently unreactive with the bath.

Fig. 173

Neg. No. 5078
XZG-26C

X150

20% HF, 20% HNO₃ in glycerine

A 4.7% magnesium alloy, as-cast, made by feeding magnesium wire into a bath of zirconium in the arc furnace. The retained β structure is an indication of solid solubility of magnesium in zirconium. Unalloyed zirconium would transform to an acicular α structure on cooling.

Fig. 174

Neg. No. 5018
XZG-26-Q848-70

X250

20% HF, 20% HNO₃ in glycerine

The alloy depicted in Fig. 173, water quenched after annealing 70 hours at 848°C. This specimen analyzed only 2.8% magnesium. An unusual precipitate appears at grain boundaries and within the grains after heat treating. This structure could possibly be explained by the separation of a magnesium-rich liquid from the β solid solution on annealing, as the result of a monotectic equilibrium at higher temperatures.

Fig. 169

Fig. 170

Fig. 171

Fig. 172

Fig. 173

Fig. 174

VI. SUMMARY

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Except for zirconium-magnesium compositions, alloys of all the binary systems were prepared by arc melting for determination of the contracted phase diagrams. Additional alloys were made so that the entire diagrams could be determined with reasonable accuracy.

Microscopic evaluation of annealed and quenched, as-cast, and variously heat treated specimens was the principal tool of the investigation.

The features of each system may be summarized as follows:

Zirconium-Tin

1. Three intermediate phases exist; these are Zr_4Sn (24.55% Sn), which is formed by the peritectoid reaction: $\beta + Zr_5Sn_3 \rightleftharpoons Zr_4Sn$ at $1325 \pm 20^\circ C$; Zr_5Sn_3 (tentative; 43.84% Sn), which melts with an open maximum at $1985 \pm 25^\circ C$; and $ZrSn$ (tentative; 56.55% Sn), formed by a peritectic reaction between Zr_5Sn_3 and a melt containing about 83% tin at $1140 \pm 15^\circ C$.
2. Zirconium and Zr_5Sn_3 give rise to a eutectic at 23.5% tin and $1590 \pm 15^\circ C$.
3. The solubility of tin in beta zirconium is approximately 21% at the eutectic temperature, 15% at $1325^\circ C$, and 6.5% at $980^\circ C$.
4. Tin raises the $\alpha \rightleftharpoons \beta$ transformation temperature of zirconium, which results in the peritectoid: $\beta + Zr_4Sn \rightarrow \alpha$ at $980 \pm 20^\circ C$.
5. The solubility of tin in alpha zirconium decreases from 9% at $980^\circ C$ to about 1.5% at $600^\circ C$.
6. Tin displays no detectable solid solubility for zirconium. The eutectic or peritectic (undetermined) between tin and $ZrSn$ lies at higher tin content than 99.5%, and not more than $1^\circ C$ above or below the melting point of tin.

Zirconium-Molybdenum

1. Only one intermediate phase exists in this system. It is peritectically formed at $1880 \pm 20^\circ C$ by the reaction: Melt + molybdenum solid solution $\rightarrow ZrMo_2$. $ZrMo_2$ exists, ideally, at 67.78% molybdenum.
2. A eutectic between beta solid solution and $ZrMo_2$ occurs at 31% molybdenum and $1520 \pm 15^\circ C$.
3. The limit of solubility of molybdenum in beta zirconium is about 22% at the eutectic temperature.
4. A sluggish eutectoid decomposition of beta into $\alpha + ZrMo_2$ occurs at 7.5 $\pm$ 1% molybdenum and $780 \pm 5^\circ C$.

5. The limit of solubility of molybdenum in alpha zirconium is less than 0.18% at all temperatures.
6. The limit of solubility of zirconium in molybdenum is probably less than 10%.

Zirconium-Copper

1. The maximum solubility of copper in beta zirconium is 3.8% at the eutectic temperature. The solubility of copper in alpha zirconium is less than 0.18% at all temperatures. A eutectoid reaction occurs at 1.6% copper and $822 \pm 10^\circ\text{C}$.
2. A eutectic exists at 21% copper and $995 \pm 10^\circ\text{C}$, between zirconium and Zr_2Cu (25.83% Cu).
3. An intermediate phase is formed at about 27% copper and $1000 \pm 10^\circ\text{C}$, which probably corresponds to the formula Zr_2Cu (25.83% Cu).
4. A eutectic occurs at 37% copper and $928 \pm 10^\circ\text{C}$ between Zr_2Cu and ZrCu (41.06% Cu).
5. An intermetallic compound forms at 41% copper and $935 \pm 10^\circ\text{C}$, corresponding to the formula ZrCu (41.06% Cu).
6. A eutectic between ZrCu and Zr_2Cu_3 (51.09% Cu) exists at 47% copper and $890 \pm 10^\circ\text{C}$.
7. An intermetallic compound forms at 50% copper and $895 \pm 10^\circ\text{C}$, corresponding to the formula Zr_2Cu_3 (51.09% Cu).
8. A eutectic between Zr_2Cu_3 and Zr_2Cu_5 (tentative; 63.52% Cu) occurs at 53% copper and $885 \pm 10^\circ\text{C}$.
9. The intermediate phase designated Zr_2Cu_5 is formed peritectically by a reaction between the melt containing 61% copper and ZrCu_3 (tentative; 67.63% Cu) at $1070 \pm 10^\circ\text{C}$.
10. An intermediate phase exists at about 71.5% copper and melts at $1100 \pm 10^\circ\text{C}$. The formula ZrCu_3 (67.63% Cu) has been tentatively accepted for this phase on a basis of previous literature.
11. A eutectic between ZrCu_3 and copper exists at 91% copper and $965 \pm 10^\circ\text{C}$.
12. The solubility of zirconium in copper is very limited. Previous investigators, although in disagreement on exact values, agree that the solubility is less than 1% zirconium.

Zirconium-Wolfram

1. One intermediate phase exists in the system. It is peritectically formed at $2175 \pm 25^\circ\text{C}$, by the reaction: Melt + wolfram solid solution $\rightarrow \text{ZrW}_2$. ZrW_2 should exist, ideally, at 80.13% wolfram.
2. A eutectic between beta solid solution and ZrW_2 occurs at $1650 \pm 15^\circ\text{C}$ and 18% wolfram.
3. The limit of solubility of wolfram in beta zirconium is about 8% at the eutectic level.
4. A eutectoid decomposition of beta into $\alpha + \text{ZrW}_2$ occurs at about 0.5% wolfram and $850 \pm 15^\circ\text{C}$.
5. The solubility of wolfram in alpha zirconium is less than 0.5% at all temperature levels.
6. A limited investigation of the wolfram-rich region showed that less than 10 weight per cent zirconium is soluble in wolfram.

Zirconium-Chromium

1. The limit of solubility of chromium in beta zirconium is 4.5%.
2. A eutectic occurs between β and ZrCr_2 at 18% chromium and $1280 \pm 10^\circ\text{C}$.
3. A single intermediate phase exists in the system, at 53% chromium, corresponding to the formula ZrCr_2 . This phase melts at $1700 \pm 25^\circ\text{C}$.
4. A eutectoid decomposition of beta into $\alpha + \text{ZrCr}_2$ occurs at $835 \pm 10^\circ\text{C}$ and $1 \pm 0.25\%$ chromium.
5. The solubility of chromium in alpha zirconium is less than 0.28% at all temperature levels.
6. A eutectic occurs between ZrCr_2 and chromium-rich solid solution, at 70% chromium and $1635 \pm 15^\circ\text{C}$.
7. The maximum solubility of zirconium in chromium is less than 10%.

Zirconium-Silicon

1. The maximum solubility of silicon in beta zirconium is less than 0.2% at 1610°C . The maximum solubility of silicon in alpha zirconium is less than 0.1% at 860°C .
2. Zirconium forms a eutectic with Zr_7Si at 2.9% silicon and $1610 \pm 15^\circ\text{C}$.

3. The intermediate phase Zr_4Si (7.14% Si) is formed by the peritectic reaction between Zr_2Si (tentative; 13.33% Si) and the melt containing 4.5% silicon at $1630 \pm 15^\circ C$.
4. The phase Zr_2Si (tentative) is formed by the peritectic reaction between Zr_3Si_2 (17.02% Si) and the melt containing 2% silicon at $2110 \pm 25^\circ C$.
5. The phase Zr_3Si_2 is formed by the peritectic reaction between Zr_4Si_3 (18.74% Si) and the melt containing 14.4% silicon at $2210 \pm 25^\circ C$.
6. The intermediate phase Zr_4Si_3 is formed by the peritectic reaction between Zr_6Si_5 (20.40% Si) and the melt containing 18% silicon at $2225 \pm 25^\circ C$.
7. The intermediate phase Zr_6Si_5 is formed at 20.1% silicon and melts with an open maximum at $2250 \pm 25^\circ C$.
8. The phase $ZrSi$ (23.53% Si) is formed by a peritectic reaction between Zr_6Si_5 and the melt containing 24.2% silicon at $2095 \pm 25^\circ C$.
9. The phase $ZrSi_2$ (38.09% Si) is formed by a peritectic reaction between $ZrSi$ and the melt containing 46% silicon at $1520 \pm 15^\circ C$.
10. A eutectic exists between $ZrSi_2$ and silicon at 75% silicon and $1355 \pm 15^\circ C$.
11. The solubility of zirconium in silicon is considerably less than 5%, but no attempt was made to precisely determine the value.

Zirconium-Aluminum

1. Zirconium forms a eutectic with Zr_5Al_3 (15.07% Al) at 11% aluminum and $1350 \pm 10^\circ C$.
2. The maximum solubility of aluminum in beta zirconium is 9.5% at the eutectic temperature.
3. The intermediate phase Zr_2Al (12.88% Al) is formed in the solid state by the peritectoid reaction: $\beta + Zr_5Al_3 \rightleftharpoons Zr_2Al$, at $1250 \pm 50^\circ C$.
4. The intermediate phase Zr_3Al (8.80% Al) is formed at $975 \pm 25^\circ C$ by the peritectoid reaction: $\beta + Zr_2Al \rightleftharpoons Zr_3Al$.
5. Aluminum additions raise the $\alpha \rightarrow \beta$ transformation temperature to $940 \pm 10^\circ C$. At this temperature, the peritectoid reaction: $\beta + Zr_3Al \rightarrow \alpha$ occurs, yielding an alpha solid solution containing about 3.5% aluminum.
6. The solubility of aluminum in alpha zirconium decreases with falling temperature from 3.5% aluminum at $940^\circ C$ to 1% at $800^\circ C$, and 0.5% at $700^\circ C$.

7. Zr_5Al_3 (15.07% Al) is formed by the peritectic reaction between Zr_3Al_2 (16.46% Al) and a melt containing about 15% aluminum at $1395 \pm 10^\circ\text{C}$. Zr_5Al_3 breaks down at lower temperatures, probably eutectoidally.
8. Zr_3Al_2 (16.46% Al) is formed by the peritectic reaction between Zr_4Al_3 (18.15% Al) and a melt containing about 16% aluminum at $1480 \pm 20^\circ\text{C}$.
9. Zr_4Al_3 (18.15% Al) melts with an open maximum at $1530 \pm 20^\circ\text{C}$.
10. A eutectic occurs at 22% aluminum between Zr_4Al_3 and Zr_2Al_3 (tentative; 30.74% Al) at $1480 \pm 20^\circ\text{C}$.
11. ZrAl (22.82% Al) is formed in the solid state by the peritectoid reaction: $\text{Zr}_4\text{Al}_3 + \text{Zr}_2\text{Al}_3 \rightleftharpoons \text{ZrAl}$, at $1250 \pm 50^\circ\text{C}$.
12. Zr_2Al_3 (tentative; 30.72% Al) is formed at $1595 \pm 25^\circ\text{C}$ by a peritectic reaction between ZrAl_2 (37.16% Al) and the melt containing about 30% aluminum.
13. ZrAl_2 (37.16% Al) melts with an open maximum at $1645 \pm 25^\circ\text{C}$.
14. A eutectic between ZrAl_2 and ZrAl_3 (47.00% Al) occurs at 45% aluminum and $1490 \pm 20^\circ\text{C}$.
15. ZrAl_3 (47.00% Al) melts with an open maximum at $1580 \pm 25^\circ\text{C}$.
16. At all aluminum contents higher than 47%, only two phases exist: ZrAl_3 and aluminum.
17. No work was done on the aluminum solid solution range and its peritectic formation at very high aluminum content. The prior work of Fink and Willey (21) covers these points with high accuracy.

Zirconium-Magnesium

Numerous special techniques, designed to produce the most favorable circumstances for alloying of these two metals, were employed. Limited alloying appears to take place, if the circumstances are just right, at both ends of the system, but control is lacking and it seems certain that homogeneous zirconium-rich alloys for a systematic study of the system cannot be prepared.

VII. CONTRIBUTING PERSONNEL

The following personnel were the major contributors to the work reported herein:

W. Alexis	Technician, melting
R. F. Domagala	Zr-Mo, Zr-Cr, Zr-W, Supervision of heat treatment
W. A. Dupraw	Analytical techniques
M. Hansen	Supervision
C. A. Johnson	Metallographer
J. W. Lenke	Technician, heat treatment
C. E. Lundin	Zr-Cu, Zr-Si, Zr-Mg, Supervision of melting
D. J. McPherson	Project leader, Zr-Sn, Zr-W, Zr-Al, Zr-Mg
(Mrs.) B. Nielsen	Technician, metallography
H. L. Nurnberg	Technician
R. E. Riley	X-ray
W. Rostoker	X-ray
V. Swanson	Technician

Data relating to the work are recorded in the following logbooks: C-1272, 1276, 1277, 1278, 1556, 1595, 1606, 1612, 1613, 1758, 1759, 1781, 1871, 1878, 2002, 2012, 2013, and 2054.

Respectfully submitted,

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APPENDIX

SUMMARY OF STUDIES ON THE CRYSTAL STRUCTURE
OF INTERMEDIATE PHASES IN ZIRCONIUM BINARY SYSTEMS

Intensity Symbols:

vs	= very strong	vw	= very weak
s	= strong	ft	= faint
m	= medium	vft	= very faint
wm	= weak medium	vvft	= very very faint
w	= weak		

200

Intermediate Phase: Zr_4Sn
Alloy Composition: 24% Tin
Structure: Tetragonal
 $c = 11.10 \text{ \AA}$, $a = 6.90 \text{ \AA}$, $c/a = 1.63$

<u>I_{obs}</u>	<u>hkl</u>	<u>d_{obs}</u>	<u>d_{calc}</u>
ft	101	6.06	5.92
vw	002	5.51	5.55
vw	110	5.01	4.95
ft	103	3.31	3.25
vft	211	3.07	2.93
w	004	2.79	2.77
vft	104	2.55	2.57
wm	203	2.49	2.51
vft	220	2.43	2.41
wm	301	2.28	2.22
ft	330	1.61	1.60
vft	331	1.59	1.59
w	403	1.55	1.55
wm	333	1.49	1.47
vft	404	1.45	1.45
w	316	1.40	1.40
w	521	1.25	1.25
w	504	1.22	1.22
w	440	1.20	1.20

201

Intermediate Phase: ZrSn

Alloy Composition: 53% Tin

Structure: Orthorhombic

 $a = 7.433 \text{ \AA}$, $b = 5.822 \text{ \AA}$, $c = 5.157 \text{ \AA}$

<u>I_{obs}</u>	<u>hkl</u>	<u>d_{obs}</u>	<u>d_{calc}</u>
vft	110	4.645	4.584
vft	111	3.417	3.426
vft	210	3.137	3.133
vw	020	2.890	2.911
s	120	2.663	2.711
vw	002	2.580	2.579
w	300	2.470	2.478
s	102	2.439	2.436
vft	012	2.350	2.359
vw	301	2.225	2.233
ms	221	2.117	2.094
ft	311	2.052	2.041
wm	212	2.007	1.991
vw	222	1.730	1.713
m	322	1.515	1.505
m	123	1.450	1.452
m	303	1.422	1.398
vw	313	1.372	1.372
ft	004	1.303	1.289
w	323	1.258	1.261
vw	600	1.237	1.239
wm	333	1.222	1.134

202

Intermediate Phase: ZrMo_2
 Alloy Composition: 60% Molybdenum
 Structure: Cubic (ZrW_2 type)
 $a = 7.59 \text{ \AA}$
 cf Duwez (12) - $a = 7.58 \text{ \AA}$

<u>I_{obs}</u>	<u>hkl</u>	<u>d_{obs}</u>	<u>d_{calc}</u>
w	220	2.671	2.684
ft		2.478	
ms	311	2.280	2.288
m	222	2.183	2.191
vvft		1.942	
ft	400	1.892	1.898
vft	331	1.737	1.741
vft	332	1.609	1.618
w	422	1.546	1.549
ms	510	1.478	1.489
ms	440	1.339	1.342
vft	531	1.280	1.282
vw	620	1.199	1.200
wm	533	1.156	1.158
wm	622	1.143	1.144
ft	444	1.095	1.096
vft	551, 711	1.063	1.063
w	642	1.013	1.014
m	553, 731	0.9872	0.9881
vw	800	0.9480	0.9488
vvft	821, 742	0.9126	0.9137
vw	660, 822	0.8941	0.8945
wm	555, 751	0.8758	0.8764

Intermediate Phase: Zr_2Cu
 Alloy Composition: 27% Copper
 Structure: Face Centered Tetragonal
 $c = 3.716 \text{ \AA}$, $a = 4.536 \text{ \AA}$, $c/a = 0.819$

<u>I_{obs}</u>	<u>hkl</u>	<u>d_{obs}</u>	<u>d_{calc}</u>
ft		2.775	
ms	111	2.416	2.428
wm	200	2.261	2.268
wm	002	1.852	1.858
vw		1.757	
w	220	1.601	1.616
m	202	1.436	1.437
vft		1.386	
m	131	1.336	1.338
w	222	1.215	1.214
w	113	1.155	1.156
vvft	400	1.134	1.134
vft	331	1.028	1.027
vft	240	1.014	1.014
vft		1.001	
vw	402	0.9665	0.9680
w	133	0.9378	0.9375
vft	004	0.9136	0.9240
w	242	0.8910	0.8903
vw	151, 204	0.8649	0.8651

Intermediate Phase: $ZrCr_2$
 Alloy Composition: 53% Chromium
 Structure: Hexagonal ($MgZn_2$ type)
 $c = 8.262 \text{ \AA}$, $a = 5.079 \text{ \AA}$, $c/a = 1.627$
 cf Wallbaum (17) - $c = 8.372 \text{ \AA}$, $a = 5.127 \text{ \AA}$

<u>I_{obs}</u>	<u>hkl</u>	<u>d_{obs}</u>	<u>d_{calc}</u>
vft	002	4.136	4.131
vft	003	2.786	2.754
wm	110	2.538	2.540
wm	103	2.325	2.343
vft	200	2.197	2.206
m	112	2.162	2.164
wm	201	2.125	2.132
w	004	2.062	2.065
vft	202	1.934	1.946
ft	104	1.863	1.874
vft	120	1.678	1.665
vw	122	1.542	1.545
vvft	204	1.510	1.508
w	300	1.466	1.466
wm	123	1.424	1.425
wm	302	1.383	1.382
wm	205	1.320	1.323
vft	124	1.296	1.296
wm	220	1.271	1.269
vft	116	1.212	1.211

Intermediate Phase: ZrSi
 Alloy Composition: 24% Silicon
 Structure: Hexagonal
 $c = 12.77 \text{ \AA}$, $a = 7.01 \text{ \AA}$, $c/a = 1.823$

<u>I_{obs}</u>	<u>hkl</u>	<u>d_{obs}</u>	<u>d_{calc}</u>
vft	100	6.175	6.144
wm	101	5.558	5.537
w	102	4.488	4.428
vw	003	4.233	4.257
vw	110	3.506	3.502
ft		3.277	
ft	112	3.079	3.071
vw	201	2.965	2.960
vft		2.892	
vw	104	2.799	2.833
vft	202	2.726	2.747
vft		2.604	
m	005	2.551	2.554
wm	203	2.460	2.476
w	120	2.294	2.297
vw	204	2.215	2.203
vft	122	2.164	2.161
vw	006	2.119	2.129
wm	115	2.060	2.064
vft		1.976	
vw		1.882	
w	124	1.866	1.865
m*	305	1.582	1.585
m	314	1.489	1.489
wm	410, 323	1.322	1.324
m	415	1.174	1.175

*Only the stronger lines indexed from here on.

Intermediate Phase: ZrAl_2
 Alloy Composition: 37.2% Aluminum
 Structure: Orthorhombic

$a = 10.40 \text{ \AA}$, $b = 7.21 \text{ \AA}$, $c = 4.97 \text{ \AA}$

<u>I_{obs}</u>	<u>hkl</u>	<u>d_{obs}</u>	<u>d_{calc}</u>
vw	110	5.799	5.927
w	200	5.391	5.200
wm	001	4.906	4.970
vw	101	4.533	4.482
ft	210	4.336	4.219
vw	011	4.014	4.090
vft	111	3.727	3.807
vft	300	3.530	3.473
vft	120	3.293	3.407
vw	310	3.146	3.125
vft	220	2.906	2.963
vft	301	2.802	2.843
vft	400	2.698	2.600
ms	311	2.625	2.645
vft	320	2.569	2.499
s	002	2.446	2.485
vft	030	2.394	2.403
vft	012	2.337	2.348
vw	202	2.274	2.241
s	321	2.251	2.233
vft	500	2.170	2.080
vft	022	2.074	2.045
ft	330	1.965	1.976
vvft	222	1.864	1.903
w	402	1.791	1.796
vft	600	1.757	1.733

Intermediate Phase: $ZrAl_3$
 Alloy Composition: 47% Aluminum
 Structure: Tetragonal

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$c = 16.90 \text{ \AA}$, $a = 4.306 \text{ \AA}$, $c/a = 3.92$
 cf Brauer (22) $c = 17.29 \text{ \AA}$, $a = 4.01 \text{ \AA}$

<u>I_{obs}</u>	<u>hkl</u>	<u>d_{obs}</u>	<u>d_{calc}</u>
wm	100	4.306	4.306
wm	102	3.886	3.838
w	113	3.274	3.247
w	112	2.814	2.864
w	105	2.607	2.659
vft		2.447	
vs	106	2.363	2.357
vft		2.246	
vft		2.196	
wm	200	2.149	2.153
vft	202	2.092	2.086
m	203	1.996	2.006
w	205	1.813	1.816
w	214	1.776	1.753
w	206	1.724	1.711
w	210	1.708	1.709
w	216	1.586	1.590
m	223	1.464	1.469
vft		1.445	
vft	300	1.433	1.435
wm*	302	1.412	1.415
wm	306	1.279	1.279
m	316	1.212	1.225
wm	322	1.181	1.183
wm	423	0.9491	0.9491

*Only stronger lines indexed from here on.

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