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METALLURGY DIVISION
QUARTERLY PROGRESS REPORT
for Period Ending July 31, 1952

J. H. Frye, Jr., Director

EDITED BY

W. H. Bridges

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METALLURGY DIVISION QUARTERLY PROGRESS REPORT

SUMMARY

The mechanical properties of alloys of thorium with carbon, chromium, vanadium, and chromium and carbon continue under investigation. Tensile and impact tests on a series of specimens of virgin and remelted thorium are being run to determine the nature and extent of differences. The first phase of recrystallization experiments on cold-worked thorium has been completed with the general result that increased cold work decreased the temperature necessary for complete recrystallization. Studies of the electrical resistivity and melting point and of the radiation damage of thorium are under way.

The initial loading of MTR-type fuel units for the CP-5 reactor was fabricated according to specifications and forwarded to ANL.

The fuel concentration in the MTR fuel element has been increased 20% to offset the apparent 6% loss in Δk being experienced in operation of the reactor. Five complete loadings have been delivered to the site. Work on the sixth and seventh loading is 90 and 50% complete, respectively.

The cladding of uranium and thorium with zirconium is being attempted with modified picture-frame techniques prior to rolling. Some degree of success has been attained, with savings.

Continued support has been given to the Homogeneous Reactor Project. Considerable effort has been directed toward accumulating information on materials less subject to corrosion than austenitic stainless steels. The fabrication and properties of titanium are being investigated.

Work has continued on the application of ceramic coatings to metals for possible application in a radiator. A coating was successfully applied for the purpose of preventing adherence between zirconium-thorium compacts and the mild steel used in cladding experiments. The development of a fluoride-resistant coating was also under investigation. A program of study of ceramic-metal combinations (cermets) and an investigation of radiation effects on ceramic materials have been started. A study of the properties of hafnium oxide continues and an investigation has begun on the fabrication, synthesis, and properties of hafnium carbide. Compatibility studies of selected oxide ceramics in contact with various refractories, metals, and halides at elevated temperatures are under way. A preliminary investigation of thoria for subsequent solubility tests was commenced.

Additions of various substances to fluorides in static corrosion tests have been made to determine the fitness of these agents as corrosion inhibitors. The corrosion of Inconel at 816°C by sodium hydroxide does not seem greatly increased by the presence of residual stresses, and the corrosion of *A* nickel was not at all increased.

The dynamic corrosion testing of various materials in zirconium-containing fluoride coolants has continued. In general, the zirconium-containing fluorides are less corrosive than previous fluoride mixtures, but they have the disadvantage of higher vapor pressure. Stress-rupture tests on Inconel and type 316 stainless steel in the presence of fluoride mixtures agree reasonably with expected values, but tube-burst tests give much lower than expected values.

A number of tests intended to give a better understanding of fluoride corrosion have been completed. The indications are that the subsurface voids encountered during fluoride corrosion are caused by the outward diffusion of chromium atoms, which leaves the metal enriched

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with vacant lattice sites that "precipitate" to form voids. This has been repeatedly duplicated when chromium is removed from the metal lattice by either high-temperature oxidation or high-temperature vacuum treatment. Conversely, corrosion tests made with fluoride containing small amounts of chromium powder have shown that void formation can be suppressed.

The mixture of sodium with lead has possibilities as a heat transfer medium. Corrosion tests have indicated that the corrosiveness (including mass transfer) of lead is diminished with the addition of increasing amounts of sodium.

The evaluation of high-temperature brazing alloys for the joining of reactor components continues. The corrosion and oxidation resistance and tensile strength of joints made with the alloys have been tested. The behavior of basic welding variables in the cone-arc welding process is being studied to gain a better understanding of the possibilities of the process for the fabrication of tube-to-header joints in heat exchangers.

A tentative phase diagram has been determined for the zirconium-silver system. Preliminary experiments are under way in the zirconium-indium system.

PHYSICAL METALLURGY OF REACTOR MATERIALS

E. J. Boyle

THORIUM ALLOY DEVELOPMENT

J. A. Milko

Thorium-Carbon Alloys. Mechanical properties for a series of thorium-carbon alloys ranging in carbon content from 0.02 to 0.22% were given in the last quarterly report.(1) This series of alloys was studied further to obtain some indication of a suspected tendency toward precipitation hardening in the lower temperature range, that is, attempt to determine the time required for such hardening, and to make a metallographic determination of the solubility of the carbon at the higher temperatures.

Six thorium-carbon alloys were heated in a purified argon atmosphere for a definite interval of time and quenched. The test specimens selected for this investigation were removed from the grip ends of the sheet tensile bars. The sheet tensile bars were annealed for $^1/_2$ hr at 650°C after a cold reduction of about 85%. Hardness measurements were made on these annealed specimens after the aging treatments listed in Table 1.

The data of Table 1 indicate that the heat treatment of 1 hr at 400°C does not increase the hardness of the 0.02, 0.05, 0.07, and 0.13% carbon alloys over that obtained in the annealed state, which suggests very little precipitation hardening. On the other hand, the 0.19 and 0.22% carbon alloys tend to develop a higher hardness after 1 hr at 400°C than in the annealed state, which indicates precipitation hardening. A microscopic examination will be made later in an attempt to correlate this increase in hardness with the suspected precipitation effects.

Further examination of the data of Table 1 indicates that the lowest hardness values are obtained on the alloys after heat treatment for 1 hr at 600 to 800°C followed by quenching. It is entirely possible that these temperatures are required for full recovery and recrystallization. (The treatment at 650°C for $^1/_2$ hr may not have annealed the original sheet tensile specimens fully.) Heat treatment at increasing temperatures from 1000 to 1500°C increases the hardness of each carbon alloy and suggests solid solution hardening.

The tentative conclusions will be evaluated further by a microscopic study of the alloys. Furthermore, the hardness data suggest that

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(1) J. A. Milko, *Metallurgy Division Quarterly Progress Report for Period Ending April 30, 1952*, ORNL-1302, p. 5.

TABLE 1

EFFECT OF QUENCHING TEMPERATURE ON THE HARDNESS OF PURE THORIUM*

Alloys quenched from: 400, 600, 800, 1000°C held 1 hr prior to quenching
1100, 1200, 1300°C held $\frac{1}{2}$ hr prior to quenching
1400 and 1500°C held $\frac{1}{4}$ hr prior to quenching

ALLOY NUMBER	CHEMICAL COMPOSITION (%)			136° DPH HARDNESS (10-kg load, 16-mm objective)									
				Annealed at 650°C for $\frac{1}{2}$ hr	After Quenching from Indicated Temperature								
	C	W	Cu		400°C	600°C	800°C	1000°C	1100°C	1200°C	1300°C	1400°C	1500°C
F-65	0.02	0.001**	0.003**	54	51	53	44	50	50	62	74	85	101
F-66	0.05	0.001	0.003	72	72	73	59	64	66	71	84		105
F-67	0.07	0.001	0.003	93	90	72	75	83	85	92	109	119	120
F-69	0.13	0.001	0.004	113	112	93	93	99	102	103	118	128	132
F-71	0.19	0.001	0.03	130	138	113	114	118	120	132	143	148	156
F-83	0.22	0.001	0.02	144	158	127	126	131	135	152	154	175	170

*Crystal bar iodide thorium.

**Probably introduced during arc melting.

additional thorium-carbon alloys should be prepared and that the precipitation effects should be studied as a function of time at the low temperatures, 200, 300, and 400°C. This study may correlate and tend to explain the creep behavior observed in Ames thorium at 300°C at several stress levels.

Thorium-Chromium Alloys. The thorium-chromium alloys are of immediate interest because of indications that they develop relatively high strength and probably a certain degree of corrosion resistance. (A tensile strength of about 50,000 psi was obtained on three alloys, as reported in the earlier progress reports. It was also observed that when the thorium-chromium alloys were left exposed to a moist laboratory atmosphere, the 2% chromium and higher alloys did not show the whitish deposit of attack that the low chromium alloys and thorium showed.) This combination of properties may become desirable for certain future applications.

Six thorium-chromium alloys were prepared by arc melting and subsequently cold rolled into a sheet with about 85% reduction in area. After a quench from 1350°C sections were removed for microscopic and hardness evaluations to obtain some information about a possible high-temperature phase and to determine the tendency toward hardening. The data obtained from this investigation are presented in Table 2.

The quench from 1350°C seems to produce an increase in hardness for the 2, 3, and 4% chromium alloys over that obtained on the annealed samples. The change in hardness will be studied later by microscopic methods.

Thorium-Chromium-Carbon Alloys. The addition of carbon and chromium to thorium was considered because both tend to strengthen thorium and because chromium appears to impart a certain degree of corrosion resistance to thorium. Such alloys have been investigated for strength, structure, and high-temperature phases.

Six thorium-chromium-carbon alloys were prepared by arc melting. The intended carbon content was maintained at 0.1%, whereas the chromium content was increased from 0.25 to 4.0%. These alloys were quenched from 1350°C and hardness values obtained. The increase of the hardness of the thorium-chromium-carbon alloys (Table 3) over that of the thorium-chromium alloys (Table 2) can probably be attributed to the carbon. A microscopic examination will be made later in an attempt to correlate the structure, hardness, and mechanical properties.

Thorium-Vanadium Alloys. Alloys of 0.25 to 8% vanadium prepared by induction melting with the use of Ames thorium were swaged into 5/8-in.-dia rounds to obtain several 3/8-in. tensile test bars. The mechanical properties of these alloys have not been determined. Alloys with chromium, molybdenum, and columbium in the same range were also prepared by the same method. These are in various stages of testing and machining.

Lattice Parameter Measurements of Thorium-Carbon Alloys. Measurements of the lattice parameters of the thorium-carbon alloys were attempted after quenching from 1600 to 400°C. These measurements have not been satisfactory in all cases because of the suspected large

TABLE 2

EFFECT OF AGING TEMPERATURE ON THE HARDNESS OF THORIUM-CHROMIUM ALLOYS

ALLOY NUMBER	INTENDED CHROMIUM CONTENT (%)	136° DPH HARDNESS (10-kg load, 16-mm objective)	
		After Quenching from 1350°C*	After an Anneal at 650°C for 1/2 hr
1	0	69	54
2	0.25	78	
3	0.50	78	
4	1.00	95	93
5	2.00	111	73
6	3.00	112	71
7	4.00	123	91

*The specimens, 1/16-in.-thick sheet, were held 15 min at 1350°C prior to quenching.

TABLE 3

EFFECT OF QUENCHING TEMPERATURE ON THE HARDNESS OF THORIUM-CHROMIUM-CARBON ALLOYS

ALLOY NUMBER	INTENDED CHEMICAL COMPOSITION (%)		136° DPH HARDNESS (10-kg load, 16-mm objective) AFTER QUENCHING FROM 1350°C
	Cr	C	
1	0.25	0.1	112
2	0.50	0.1	118
3	1.00	0.1	118
4	2.00	0.1	122
5	3.00	0.1	124
6	4.00	0.1	134

grain size present. Further attempts will be made to determine the solubility of carbon in thorium at various temperatures by x-ray methods.

MECHANICAL PROPERTIES OF THORIUM

W. J. *Fretague*

Tensile and impact tests have been completed on a series of specimens of Ames thorium to determine the properties of virgin and remelted thorium. The results of the tensile and impact tests and the chemical analysis of the billets used are presented in Table 4. In identifying the specimens according to the billet and extrusion from which they were machined the following system was used:

1. Virgin billets are identified by the prefix A.

2. Remelted billets are identified by the prefix MX.

3. The next to the last number (in the series of letters and numbers identifying a particular specimen) denotes the type of extrusion from which the specimen was machined. The identifying number for all $\frac{5}{8}$-in. extrusions is 2, and the number 3 was used to identify 1- by 2-in. extrusions that were cold rolled to $\frac{5}{8}$ by 2 inches.

4. The letter A following the specimen number indicates that the specimen was vacuum annealed at 750°C for 30 min and furnace cooled following the *machining operations.*

In general remelted Ames thorium specimens exhibited higher tensile and yield strengths than virgin material of similar carbon content. This seems to be caused by the increased amounts of nitrogen, aluminum, and beryllium present in the remelted thorium.

A marked increase in tensile and yield strength was obtained by cold rolling. This increase was apparent both in the remelted and the virgin thorium. Annealing of the cold rolled material seemed to destroy any preferred orientation developed by cold rolling. Specific information is being obtained on the textures developed by extruding; extruding and cold rolling; extruding and annealing; and *extruding, cold rolling, and* annealing. These data should be very helpful in interpreting the results obtained from the tensile tests.

The results of Charpy V-notch impact tests are presented in Table 4. For a given analysis of thorium the extruded and annealed material has the best impact properties. The extruded materials, the extruded, cold rolled, and annealed materials, and the extruded and cold rolled materials exhibit progressively poorer impact properties, in the order listed.

There seems to be very little correlation between specific values of impact strength for different analyses of thorium even though the materials were given identical thermal and mechanical treatments prior to testing.

FABRICATION OF THORIUM

W. J. Fretague

Two $\frac{7}{8}$-*in.-dia extrusions* of Ames thorium billet A344B were made. Extrusion A344B1 was produced at a rate of 588 ft/min and extrusion A344B2 was produced at a rate of 2.32 ft/min; both were quenched as they left the extrusion die. Samples prepared from these two extrusions will be used to study the effect of extrusion rate on the creep properties of thorium.

RECRYSTALLIZATION OF THORIUM

F. H. Eckert

Recrystallization experiments have been completed on Ames (A349B) and iodide thorium that were cold worked 20, 40, 60, and 80%. Procedures for this investigation were outlined in the preceding quarterly report.[2]

Figures 1 and 2 show the effect of cold work on the recrystallization of Ames and iodide thorium as *traced* by Vickers hardness measurements.

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[2] F. H. Eckert, *op. cit.*, ORNL-1302, p. 16.

TABLE 4

MECHANICAL PROPERTIES OF AMES THORIUM

SPECIMEN NUMBER	ANALYSIS (ppm)													YIELD POINT (psi)			TENSILE STRENGTH (psi)	ULTIMATE STRENGTH (psi)	ELONGATION (% in 1.4-in. gage length)	REDUCTION IN AREA (%)	PROPORTIONAL LIMIT (psi)	MODULUS OF ELASTICITY ($\times 10^6$)	IMPACT ENERGY (ft-lb)	REMARKS
	Fe	Mn	N	C	Ca	Al	Be	Si	Mg	B	Cd	Zn	Total Impurities	0.2% Offset	Upper	Lower								
MX322A821	165	<4	245	640	<50	150	200	300	<10	0.65	<0.20	<20	1784.85	30,653	31,709	30,955	37,889	76,014	46.4	70.3	18,593	7.8	16.5	As extruded
22A														28,523	28,643	28,442	36,030	69,966	58.6	70.6	23,618	7.6	18.5	Extruded and annealed
23														31,364	32,323	31,667	38,889	72,555	52.5	68.0	18,687	8.3	16.5	As extruded
24A														28,397	28,654	28,520	36,485	72,635	46.8	69.6	21,069	8.4	18.25	Extruded and annealed
MX325A921	125	<4	375	780	<50	300	225	300	<10	1.00	<0.20	<20	2190.20	37,424	38,687	37,374	43,838	84,570	48.9	66.0	25,253	7.2	9.8	As extruded
22A														30,050	30,402	30,302	38,693	72,059	50.0	65.8	23,116	7.9	13.5	Extruded and annealed
23														38,079	39,482	38,110	44,715	78,571	48.2	64.4	24,390	7.8	9.6	As extruded
24A														29,440	29,915	29,598	38,953	69,364	48.6	63.4	19,556	10.4	12.25	Extruded and annealed
31														54,121			59,799	86,207	22.9	53.4	30,151	10.1	3.5	Extruded and cold rolled
32A														30,905	31,156	30,905	39,548	67,402	51.8	59.0	24,121	9.7	15.0	Extruded, cold rolled, and annealed
33														52,980			58,736	83,503	14.3	49.5	30,832	8.2	3.4	Extruded and cold rolled
34A														30,132	30,285	29,827	38,516	67,376	44.6	57.0	23,374	11.7	10.5	Extruded, cold rolled, and annealed
A328A21	180	<3	70	325	<50	60	120	300	<40	0.45	<0.20	<20	1168.65	20,203			28,810	47,830	54.3	76.6	11,179	6.9	40.0	As extruded
22A														19,596	19,828		28,131	41,667	51.8	74.6	14,394	8.2	39.0	Extruded and annealed
23														19,187			28,600	41,340	51.8	74.2	12,703	6.8	39.5	As extruded
24A														19,168	19,404	19,270	27,235	40,179	55.4	77.0	10,534	10.5	37.5	Extruded and annealed
31														40,101			42,680	47,800	17.9	63.0	22,222	8.9	9.25	Extruded and cold rolled
32A*																							26.0	
33														39,683			41,260	43,730	19.6	65.0	25,536	8.5	8.4	Extruded and cold rolled
34A*																							25.5	
A338B21	210	<4	130	665	<50	<60	100	300	<10	0.45	<0.20	<20	1549.65	24,059	24,585	24,448	32,600	66,540	58.9	72.3	17,087	7.2	30.0	As extruded
22A														23,788	23,869	23,566	31,313	60,241	57.1	74.9	17,677	8.8	29.0	Extruded and annealed
23														23,780	24,339	23,933	32,419	63,636	51.8	72.1	15,752	7.4	28.0	As extruded
24A														24,009	24,289	24,167	31,707	59,353	60.7	71.8	18,039	8.0	29.0	Extruded and annealed
31														41,463			43,700	59,000	23.2	63.8	29,472	8.7	7.6	Extruded and cold rolled
32A														25,384	25,384	23,434	31,061	64,935	47.9	68.9	19,697	12.1	28.75	Extruded, cold rolled, and annealed
33														40,347			42,900	62,840	23.2	62.6	22,472	8.2	8.0	Extruded and cold rolled
34A														25,762	25,762	23,628	31,098	65,517	67.9	70.5	21,596	10.2	28.5	Extruded, cold rolled, and annealed
A339B21**	195	<4	80	500	∼50	150	180	300	<10	0.30	<0.20	<20	1489.50	18,232			27,620	40,650	42.9	75.2	10,101	8.1	38.75	As extruded
22A														17,495			25,606	35,242	60.7	77.1	13,384	7.1	34.25	Extruded and annealed
23														16,112	16,147		27,287	34,483	50.0	75.9	10,395	7.6	41.4	As extruded
24A														17,007	17,109		25,281	31,120	50.0	75.4	13,023	7.0	34.0	Extruded and annealed
31***																	40,125	49,363	19.6	67.2			10.75	Extruded and cold rolled
32A														18,384	18,384	17,677	26,111	50,752	52.5	73.1	13,131	8.1	34.5	Extruded, cold rolled, and annealed
33														36,538			38,981	36,827	17.9	65.4	21,830	7.9	12.5	Extruded and cold rolled
34A														18,702	18,755	17,957	26,064	63,927	66.1	76.7	11,702	9.4	25.25	Extruded, cold rolled, and annealed
A343B21	105	<2	95	835	<50	60	180	300	<10	0.20	<0.20	<20	1657.40	22,610	22,867	22,610	30,730	69,200	57.1	77.0	16,444	6.9	33.0	As extruded
22A														22,298	22,472	22,298	29,980	45,662	56.4	77.6	16,088	8.0	30.5	Extruded and annealed
23														22,217	22,829		30,500	53,500	51.8	75.2	14,811	7.0	32.75	As extruded
24														22,104	22,236	22,104	29,726	48,077	47.1	73.6	16,006	9.9	29.5	Extruded and annealed
31														42,576			44,798	48,649	18.6	62.6	28,283	8.1	8.6	Extruded and cold rolled
32A														24,136	24,136	22,815	30,132	60,837	64.3	73.3	20,071	8.9	25.5	Extruded, cold rolled, and annealed
33														41,113			43,922	60,694	19.3	64.7	24,515	7.8	8.75	Extruded and cold rolled
34A														24,075	24,075	22,236	29,472	60,201	60.7	69.6	18,801	10.0	22.5	Extruded, cold rolled, and annealed

*Specimens A328A32A and A328A34A were cracked and as a result no tensile data are available.

**Billet A339B should be rechecked for carbon content. ORNL analysis gives 0.050% and 0.030% C on two arc-melted samples submitted.

***For specimen A339B31, through an oversight, the strain gage was not attached to the specimen and as a result only tensile strength, ultimate strength, per cent elongation, and per cent reduction in area were recorded.

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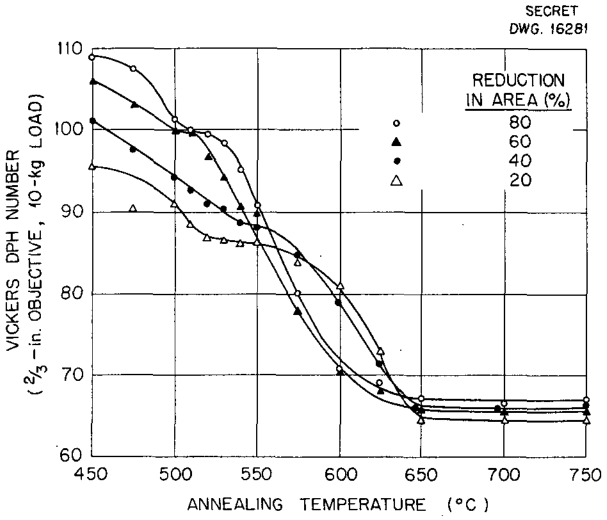

Fig. 1. Effect of Cold Work on the Recrystallization of Ames Thorium.

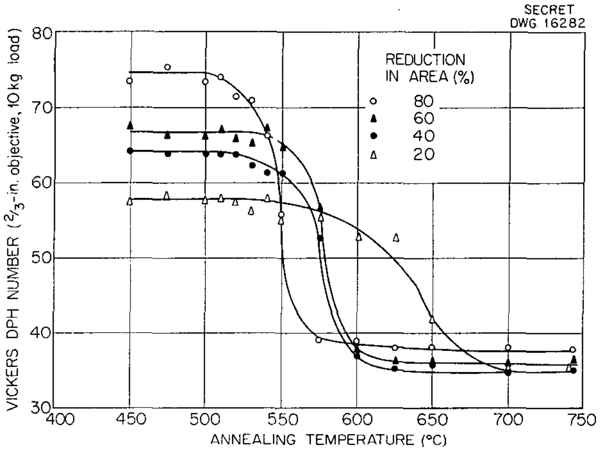

Fig. 2. Effect of Cold Work on the Recrystallization of Iodide Thorium.

Recrystallization is shown as a function of annealing temperature, with time constant at 1 hour. In general, increasing cold work decreased the temperature necessary for complete recrystallization. It has been shown in a previous report that increasing the cold work also reduced the time necessary for recrystallization to take place at any given temperature.

Table 5 shows the annealing temperature at which recrystallization starts and is completed for the various amounts of cold work. These temperatures were estimated from Figs. 1 and 2, and an attempt was made to check them by metallographic examination. However, the start of recrystallization was difficult to ascertain by metallographic means in the 20, 40, and 60% cold-worked samples, so an x-ray technique is being employed to verify the results in Table 5. By observing the line shapes of the powder diffraction pattern with a Norelco x-ray spectrometer, the strain present in the thorium samples may be measured to determine the annealing temperature at which recrystallization starts and is completed.

In all cases, the curves in Fig. 1 showed a rapid drop in hardness at the start of annealing, and microexamination revealed no evidence of recrystallization in this range. It is believed that "recovery" and/or precipitation is possibly responsible for this initial hardness drop. The higher level of impurities in the Ames metal is believed to be responsible for this action since the iodide thorium does not exhibit this "recovery" zone.

TABLE 5

EFFECT OF COLD WORK ON RECRYSTALLIZATION OF THORIUM

REDUCTION IN AREA (%)	ANNEALING TEMPERATURE AT START OF RECRYSTALLIZATION (°C)		ANNEALING TEMPERATURE AT COMPLETION OF RECRYSTALLIZATION (°C)	
	Ames Thorium	Iodide Thorium	Ames Thorium	Iodide Thorium
80	520	500	625	575
60	520	510 to 520	625	600
40	540 to 550	520	650	600
20	550 to 575	550 to 575	650	700

An investigation of the effect of carbon on the recrystallization of iodide thorium is now in progress.

RADIATION DAMAGE OF THORIUM

R. E. Adams

As part of the thorium research program, a study will be made of the physical and mechanical properties of thorium before and after irradiation and of the effects of postirradiation annealing. Duplicate test specimens will be preserved and tested while the irradiated specimens are being tested. For the nondestructive tests, the same specimens will be tested before and after irradiation.

Several thorium test specimens are scheduled to be irradiated in the LITR starting late in July. These will be exposed for six months at a neutron flux of about 0.5 to 1.0 × 10^{13} neutrons/cm^2 · sec. Specimens will be canned in aluminum, and it is estimated that the maximum temperature of the thorium will not exceed 400°F during irradiation.

The following test specimens will be irradiated for the purposes given:

1. three tensile specimens ($^3/_{16}$ in. in diameter, 1-in. gage length) for measurements of tensile strength, yield point, per cent reduction in area, and per cent elongation;
2. two cylindrical specimens ($^1/_4$ in. in diameter, 3 in. long) for study of possible changes in dimensional stability, density, dynamic elastic modulus, electric conductivity, and thermal conductivity;
3. four specimens (0.204 in. in diameter, 4$^3/_4$ in. long), each of which can be broken in four places, for impact tests;
4. eight specimens ($^7/_{16}$ in. in diameter, $^1/_8$ in. thick) for study of changes in hardness, microstructure, and x-ray patterns; specimens clad with zirconium and aluminum will also be included to see whether changes in structure of the bond layer occur.

In addition, it is proposed to irradiate thorium specimens in the MTR to learn the effects of more intense exposure. At present these plans are contingent upon space that may be available for irradiation.

ELECTRICAL RESISTIVITY AND MELTING POINT OF THORIUM

R. E. Adams

An electric resistance furnace is being used to study the melting point and electric resistivity of thorium at high temperatures. The furnace, patterned after one used by Chiotti(3) at Ames Laboratory, contains a thorium rod $^1/_4$ in. in diameter held between two water-cooled copper electrodes 4$^1/_2$ in. apart. The bar is heated by direct current in an atmosphere of purified argon. A small hole ($^1/_{32}$-in. in diameter and 0.15 in. deep) serves as a sight hole for temperature measurements. Temperatures are measured through a quartz window with a disappearing filament optical pyrometer.

Several experiments have indicated that the melting points of pure materials can be determined to within about 10°C by this method. Experiments with thorium, however, have thus far given anomalous results, and the melting point of Ames thorium bars has ranged between about 1710 and 1755°C.

Electric resistivity is found by measuring the current through the specimens and the voltage drop between two thorium wires attached $^1/_2$ in. apart at the center of the specimen. Experiments thus far indicate a sharp increase in resistivity of thorium specimens in the temperature range between 1375 and 1450°C. Work on this phase of the project is continuing.

PHYSICAL PROPERTIES OF PURE METALS

W. J. Fretague

Six melts of pure nickel were prepared by induction melting of electrolytic nickel in a

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(3) P. Chiotti, *Thorium-Carbon System*, ISC-103, June 5, 1950.

zirconia crucible and casting in a graphite mold. The surface of the ingots was machined to a depth of $\frac{1}{16}$ in. to remove any carbon picked up from the graphite mold; and the machined ingots were swaged to $\frac{3}{4}$-in.-dia rod, vacuum-annealed at 750°C for $3\frac{1}{2}$ hr, and furnace-cooled.

Standard 0.505-in.-dia tensile specimens will be prepared and used to test experimentally the theory proposed by Taylor and Frye[4] on the application of absolute reaction-rate theory to plastic deformation.

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[4] W. E. Taylor and J. H. Frye, *Application of Absolute Reaction Rate Theory to Plastic Deformation*, CF 50-10-79, Oct. 16, 1950.

REACTOR COMPONENT FABRICATION

J. E. Cunningham
R. B. Small
R. J. Beaver
J. F. Delaney
T. A. Olsen
C. C. Stone
J. H. Erwin
W. A. McNeish

FUEL AND CONTROL ELEMENT FABRICATION

MTR Fuel and Control Rod Elements. Fabrication work on the assembly of fuel and control rod elements for Arco continues at an increased and efficient pace; two units a day are now being produced.

During the quarter, the remainder of the third and all of the fourth and fifth reactor loadings were completed and shipped to Arco. A loading consists of 23 enriched fuel units and 4 cadmium control rods for the three by nine rectangular loading arrangement.

Work on the sixth loading is 90% complete. An order has been placed to procure the additional 61S aluminum alloy extrusions needed in the construction of the control rods. Delivery is expected by August 15.

It has been proposed to substitute a relatively inexpensive aluminum extrusion for the lower stainless steel section in cadmium shim safety control rods. Such a change would result in substantial saving in the cost of fabricating the control rod.

In an effort to offset the 6% loss in Δk being experienced in operation of the reactor, the fuel concentration in the uranium-aluminum alloy has either been increased 20% or the U^{235} content raised from 140 to 168 g per assembly. Other experimental work in progress in connection with this problem includes (1) tests to qualitatively determine the extent to which LiCl contained in the fuel unit by flux entrapment during brazing is influencing reactivity; (2) preparation of a mock aluminum assembly in which the aluminum side-plate thickness has been reduced 33% to improve the aluminum-to-water ratio; and (3) investigation of the possibility of further improving the aluminum-to-water ratio by lowering the thickness of the aluminum cladding on the active plates.

LITR Fuel and Control Rod Elements. Three replacement cadmium shim safety control rods and one enriched fuel unit were constructed for operation of the LITR.

Bulk Shielding Fuel Unit. The special enriched fuel unit needed to obtain more reliable data for calculating the heat release per fission of U^{235} was completed for the Bulk Shielding Facility.

CP-5 Fuel Units. The initial loading of 16 enriched uranium fuel units for the CP-5 reactor was fabricated according to specifications and shipped to ANL. The unit is similar to an MTR fuel assembly, except for thinner aluminum side plates and a wider water-gap spacing between plates, and there are only ten active plates.

ZIRCONIUM CLADDING OF URANIUM

The picture-frame technique of cladding does not lend itself readily to inexpensive, large-volume production of clad plate. Methods are being developed to roll large sheets of uranium *clad on both sides with a thin layer of zirconium.* The sheets will be sheared into strips of the desired size and sealed around the periphery by automatic welding. A saving would result from the decrease in the number of jacketed, exhausted, sealed, and rolled billets and from the method of jacketing itself.

The billet assembly is shown in Fig. 3. The uranium core for the present experimental work is an 0.8-in. slice cut from a 4-in. square cast ingot with a carborundum saw. The core is electropolished just prior to jacketing. The zirconium cover plates are 4-in. squares sheared from 0.09-in. sheet, which is obtained by rolling arc-melted sponge ingot in a steel jacket at 1400°F. The cover plates are rough ground to remove surface layers. The steel jacket is flame cut from $\frac{1}{2}$-in. steel plate in four pieces; two 6-in. square cover plates, one 6-in. square frame with a flame cut 4-in. square hole, and one 6-in. square

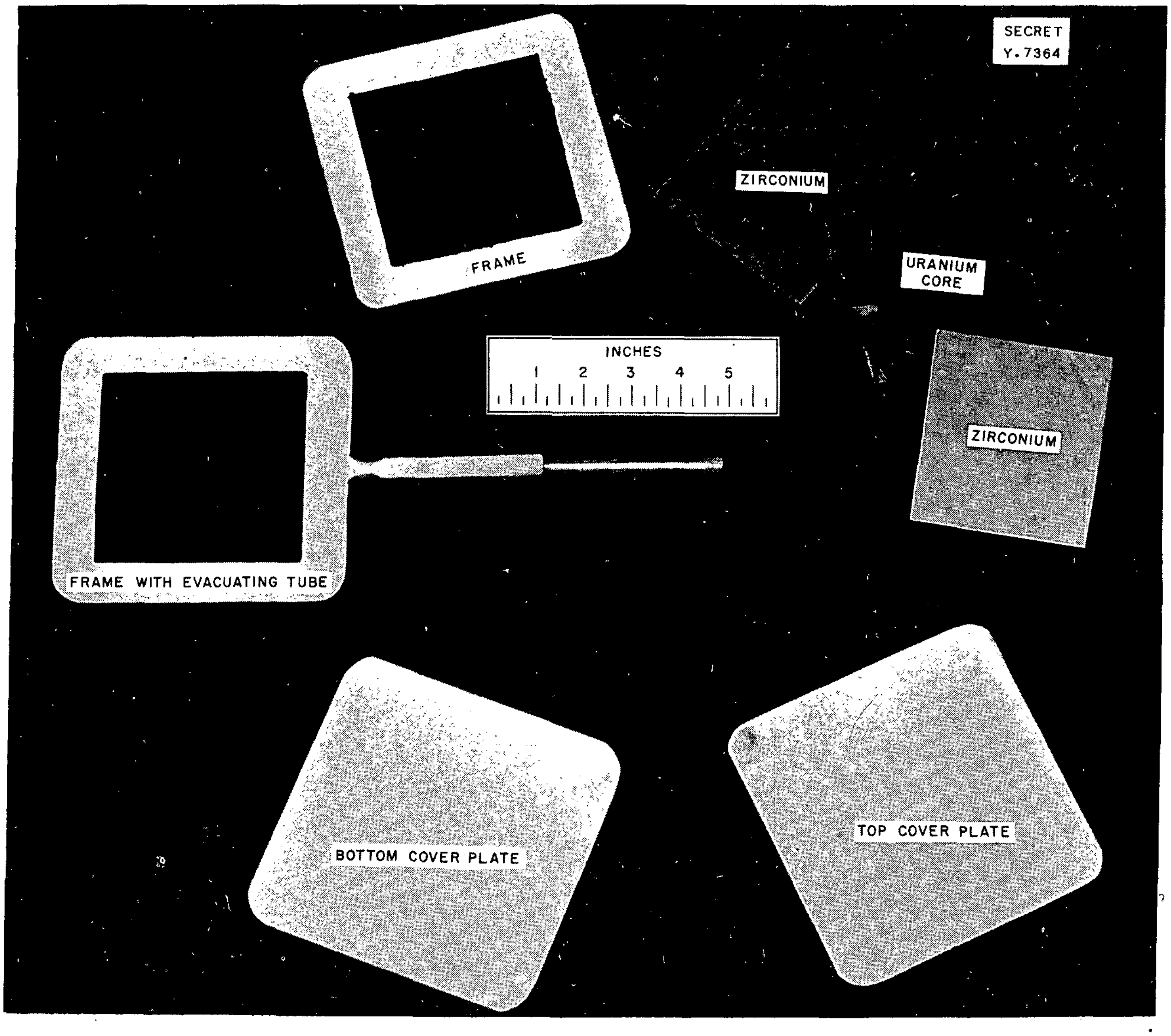

Fig. 3. Uranium Billet Assembly.

frame with a flame cut 4-in. square hole and an integral extension to be used as an exhaust tube. The extension is drilled for a $^1/_4$-in. hole and the end is internally threaded for attachment to a $^1/_8$-in. IPS nipple. All the steel jacket components are sandblasted before assembly.

The assembly is held together with C clamps, and the seams are welded with a gas-shielded torch without filler wire. A slight, positive pressure of grade XX helium is maintained within the billet to prevent oxidation of the components during welding. The welded assembly is leak checked with a Consolidated, Model 24, leak detector. The assembly is then attached to a $^1/_8$-in. nipple on a vacuum header maintained at 10^{-4} mm Hg or less. The billet is gradually heated to about 1200°F with a gas torch, the pressure is maintained at 10^{-4} mm or less, and the exhaust tube is forged shut.

The 2-in.-thick sealed billet is preheated at 1200°F for $1^1/_2$ hr and rolled to 0.130 in. by using 20% reduction per pass and reheating for 5 min between passes. The edges are sheared off and the steel is stripped from the faces to leave a clad plate about 4 in. wide and 48 in. long. The hot-rolled plate is about 0.080 in. thick and is flattened and surface finished by cold rolling to 0.065 in. in thickness.

The resultant bond shows a slight diffusion layer between the uranium core and the zirconium cladding. The core is 0.049 ± 0.004 in. thick; the cladding is 0.008 in. in average thickness and may be as thin as 0.005 in. and as thick as 0.010 inch. This high percentage of variation in cladding is believed to be caused by the method of obtaining the core, that is, slices from a cast ingot, and is expected to be reduced by using rolled or forged material for cores.

Initially, mild steel containing about 0.25% carbon was used for jacketing material. Occasional cracking during rolling, difficulty in obtaining leak-tight assemblies, and imperfect bonding led to the adoption of the 0.04% carbon titanium-killed steel that was used in the STR production with great improvement of all three difficulties.

EDGE WELDING OF ZIRCONIUM-CLAD URANIUM PLATE

The previous quarterly report outlined the method of sealing the sheared edge of zirconium-clad uranium plate. The method consists of pickling to remove the uranium core material to form a groove in which zirconium filler wire is placed. This joint is then fused with an automatic, gas-shielded welder and produces a clad edge. The defects that have been found are porosity, shrinkage cavities, crater cracks, weld metal dilution by the uranium core, and weld metal contamination by the atmosphere.

Porosity appears as small (<0.004 in.), round voids at the base metal–weld metal interface and is believed to be caused by the entrapment of either shielding gas or gas released by the clad plate during welding. By the use of heat inputs of 35 w-min/in. and slow welding speeds of 15 in./min, the porosity has been almost eliminated. In any case, the porosity is deep seated and should not affect the corrosion resistance of the joint.

Shrinkage cavities result from an insufficient heat input to completely fuse the zirconium filler wire but are eliminated in the course of reducing porosity.

Crater cracks at the end of a weld bead have been eliminated by gradually reducing the welding heat during the last $^1/_8$ in. of travel. Because of the accumulation of heat at the end of the weldment, it was possible to eliminate the crater cracks without adverse affect of the porosity.

Unfortunately, weld metal dilution by the low-melting uranium core material is increased by the method used to reduce porosity. The seriousness of this dilution is not yet known, however, since the weld metal appears unaffected by exposure in boiling water for 500 hours. The dilution is presumably reduced by the use of the lower melting zirconium–3% nickel alloy, but the resultant ductility is less and a greater tendency to surface cracking appears.

Atmospheric contamination has been greatly reduced by auxiliary shielding jets installed near the arc. The weld metal and the heat-affected zone appear bright, and some cold rolling has been done with only a slight tendency toward surface cracking.

ZIRCONIUM CLADDING OF THORIUM

Brazing of Thorium to Zirconium Prior to Rolling. The zirconium-thorium system has a eutectic at approximately 1300°C consisting of 78% thorium and 22% zirconium. Alloys of this composition have been arc melted and rolled to 0.010-in. foil for use as a brazing alloy.

Initial efforts were confined to brazing under inert atmosphere conditions. The technique consisted of sealing the foil between the thorium and zirconium by heliarc welding around the billet circumference in a dry box. The assembled billet was protected by coating with a ceramic frit, NBS A-418, and furnace brazing at 1350°C. Although considerable alloying was accomplished, as shown in Fig. 4, porosity occurred in the brazed joint. The method was discontinued in favor of vacuum brazing.

Vacuum brazing was carried out in a pyrex bell jar by using an induction heater. A thorium billet 2 by 2 by 0.8 in., brazing foil 2 by 2 by 0.010 in., and zirconium cover plates 2 by 2 by 0.1 in. were assembled in air and placed within the glass bell jar that was evacuated to 5×10^{-5} mm Hg. Melting the alloy foil between the zirconium and thorium with the induction heater resulted in a thorium-alloy-zirconium brazed joint. When the brazed billet was sectioned, it appeared to be sound. Three billets were prepared in this manner and rolled to 0.065-in. plate at 1400°F. One plate was sectioned, and metallographic examination showed that no defects were present. The bonded interface after rolling is shown in Fig. 5. Shear tests of the as-rolled bond indicate strengths of approximately 28,000 psi.

Bond Improvement by Diffusion. Previous work has indicated that a diffusion treatment at 1800°F improves bonding between thorium and zirconium. An experiment was conducted in which zirconium cover plates 2 by 2 by 0.1 in. were welded to a thorium billet 2 by 2 by 0.8 in. under the helium atmosphere of a dry box. The assembled billet was coated with ceramics frit, NBS A-418, which protected the zirconium and thorium from eutectic formation with the steel sheath. After the billet was sheathed in steel, it was rolled at 1400°F to a 38% reduction, annealed at 1800°F for 30 min, and rolled again at 1400°F to 0.065-in. finished plate. Fairly good bonding between thorium and zirconium resulted. The metallographic appearance is shown in Fig. 6.

Roll-Cladding at 1500°F. Past experience has shown that roll-cladding zirconium to thorium by the use of conventional canning methods does not result in reliable bonding. Experiments have shown that when the billets are sheathed in steel, evacuated, heated to approximately 1000°F while under vacuum, sealed, and preheated at 1500°F for 1 hr, the core elements are visibly contaminated. The source of contamination is not yet known but is believed to be from gases released from the steel or thorium during the 1-hr preheat at 1500°F. A billet gradually heated under vacuum to 1500°F over a period of 3 hr was rolled without success. Pressure measurements made during the heating showed that little gas is released to the interior of the billet up to 1100°F but that a very large quantity appears between 1100 and 1500°F.

ALUMINUM CLADDING OF THORIUM

Thorium may be clad with aluminum by rolling evacuated sandwiches at 400°C with a 10:1 reduction. Above this temperature, an intermetallic layer is formed at the bond line; below this temperature, the degree of bonding is poor.

Samples of aluminum-clad thorium rolled at this optimum temperature were annealed for $\frac{1}{2}$ hr at 350°C. An intermetallic layer had formed, and the bond strength was completely destroyed. Further annealing tests are to be made to determine the time-temperature characteristics of this intermetallic formation, which has been identified as principally $ThAl_3$.

As a result of the above tests, straight roll-cladding techniques do not appear to be promising.

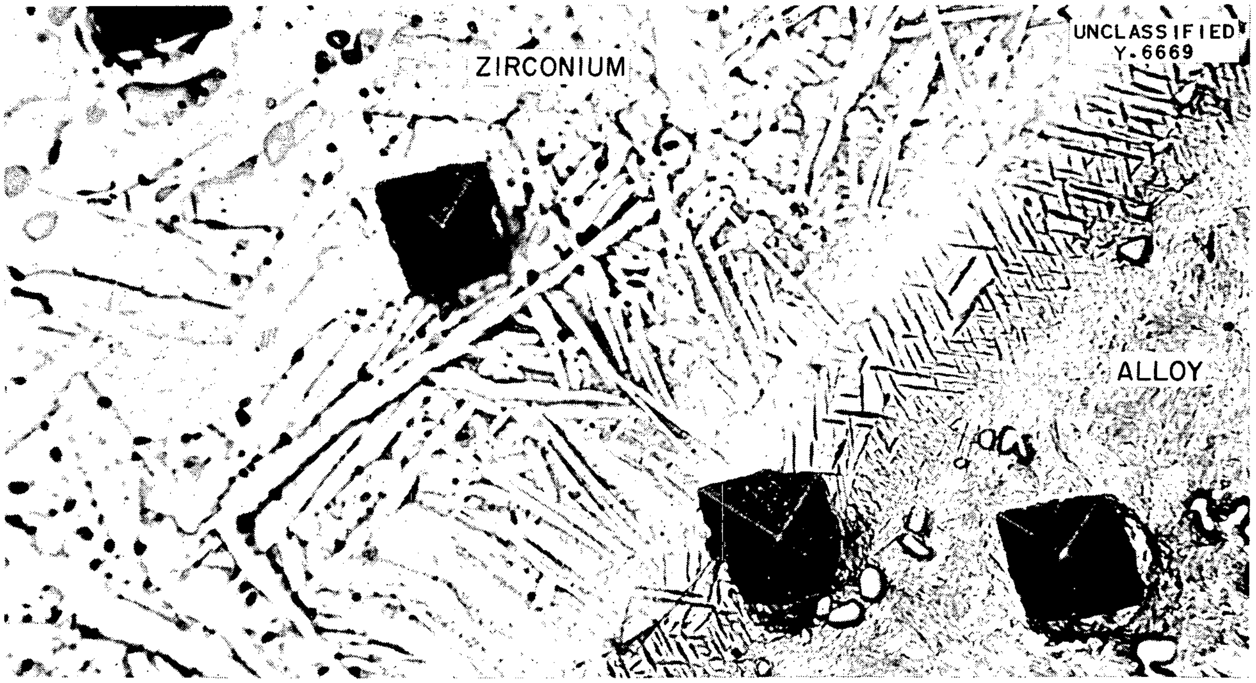

Fig. 4. As-Brazed Interfaces of Thorium Billet Brazed to Zirconium with 73% Thorium–22% Zirconium Alloy. Etched with perchloric and acetic acids. 500X

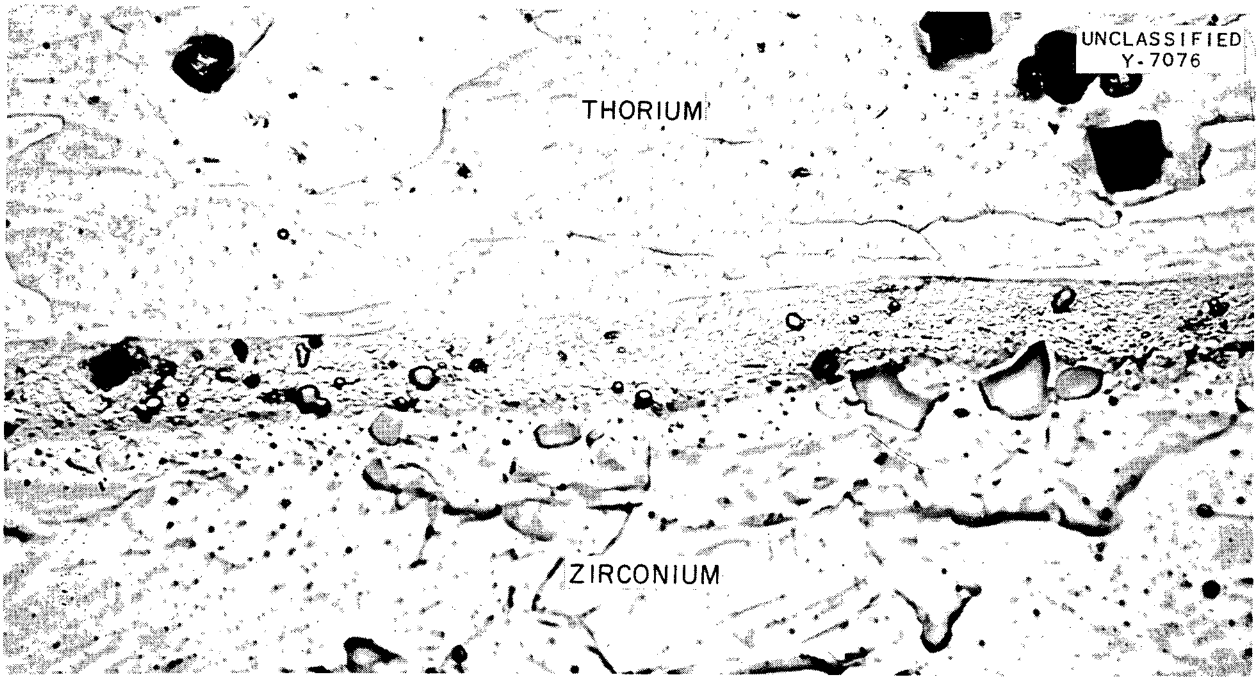

Fig. 5. Bonded Interface Between Thorium and Zirconium of Plate Produced from Brazed Billet. Etched with perchloric and acetic acids. 750X

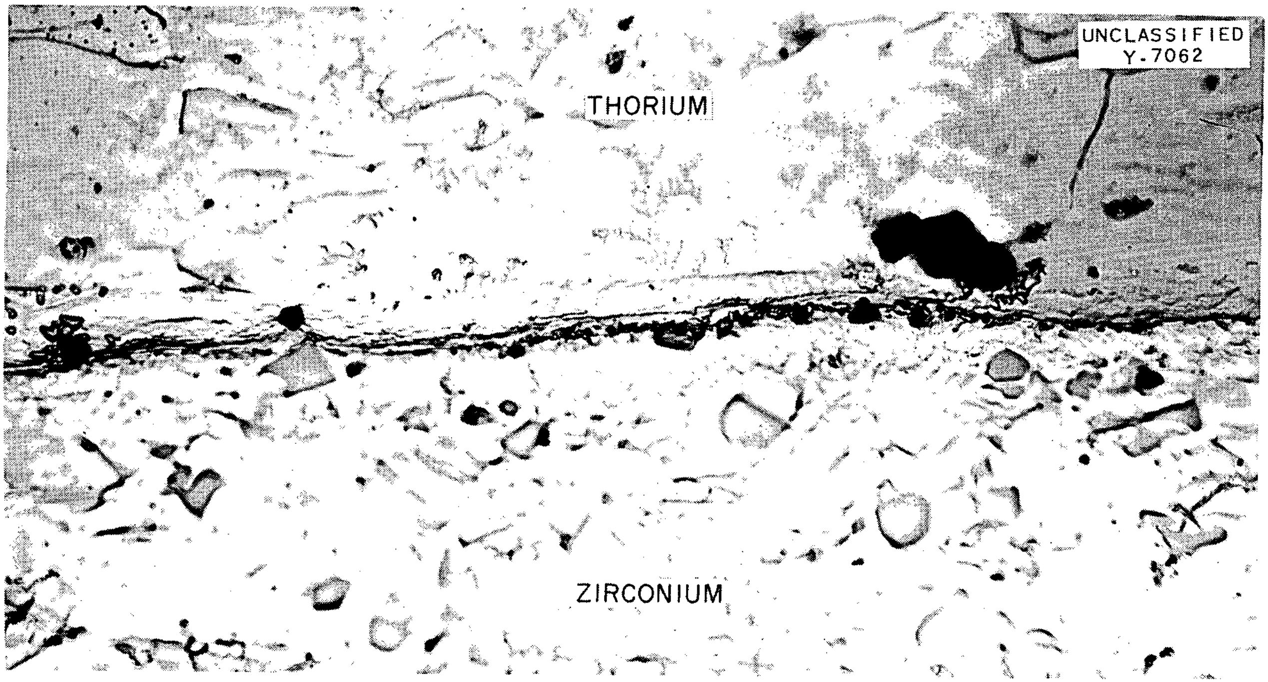

Fig. 6. Bonded Interface Between Thorium and Zirconium of Plate Subjected to Diffusion Treatment at 1800°F During Rolling Sequence. Etched with perchloric and acetic acids. 750X

A survey of possible diffusion barriers is being made.

SERVICE WORK

Casting and machining of 650 normal "J" slugs was completed. Shipment to Hanford will be made as soon as analyses are available.

Six special Chalk River fuel rods were assembled for the Westinghouse Atomic Power Division.

Preliminary work has been started for the rolling of highly enriched and depleted uranium foil.

Approximately 850 lb of $^1/_{16}$-in. uranium plate was cast and rolled for the California Research and Development Corporation.

HOMOGENEOUS REACTOR PROGRAM

E. C. Miller

The corrosion-erosion attack of austenitic stainless steels that has occurred under some conditions in dynamic corrosion loops has accelerated interest in alternate materials that may have better resistance to this type of attack. Considerable effort has been spent in accumulating available information that will permit a realistic evaluation of the engineering feasibility of such alternate materials. Titanium, which is of particular interest on the basis of corrosion-erosion behavior, is receiving much attention at this time. Unfortunately, it is relatively new as an engineering material, and the required data are frequently unavailable or uncertain. A very extensive titanium developmental program is being carried on under the sponsorship of a number of military agencies, and a considerable effort is being made here to keep pace with the current developments. In addition to titanium, similar, but less extensive, consideration is being given to modified, austenitic, chromium-nickel-iron alloys and to some of the rare metals.

WELDING AND FABRICATION SPECIFICATIONS

W. J. Leonard

Equipment used and planned for various engineering tests and the intermediate reactor design call for welding and fabrication of thick sections (up to 3 in.) of carbon steels (0.15 to 0.25% carbon) and of austenitic stainless steels, particularly type 347. Standard specifications will be used where available and acceptable, particularly in the welding of carbon steels. However, the welding of type 347 stainless steel and the welding of dissimilar metals, such as type 347 stainless steel to carbon steel, present a number of problems. Some experimental work will be done to apply available methods to present facilities and problems so that specifications and standard procedures can be established.

TITANIUM FABRICATION

A. R. Olsen P. Patriarca

The specific objective of the experimental work on the welding of titanium has been to approximate the configurations involved in making an impeller for a Westinghouse, Model 100A, pump. Tensile samples approximating the joint configurations were made with RC-70 base material and Ti-75A filler rod. Tensile tests of these welding assemblies gave maximum loads ranging from 3500 to 8300 pounds. Based on the encouraging results of these tests, it was decided to use both welding and riveting, rather than riveting alone, in assembling the actual pump impeller. Unfortunately, the available stock for machining the impeller has a carbon content higher than that generally considered suitable for welding; consequently, the additional precaution of riveting was considered advisable. The actual welding of the impeller is to be performed in the Y-12 welding shops.

The excellent corrosion-erosion resistance of titanium recommends its possible use as a valve trim; however, its tendency to gall indicated the desirability of surface hardening the material. Accordingly, a titanium poppet was hardened by a modification of the procedure that was developed by the Armour Research Foundation for surface-hardening titanium in a nitrogen atmosphere. The results are encouraging and further testing is planned.

TITANIUM RIVETING OF PUMP IMPELLER

E. S. Bomar

Because of the reputed brittleness of welds on titanium containing more than 0.25% carbon, and because of the limited knowledge of the behavior of such welds under dynamic conditions, reliance is being placed on rivets to fasten the two parts of the titanium impeller for the Westinghouse, Model 100A, pump.

In the initial tests, consideration was given to heating the rivets in a furnace, followed by upsetting in a hydraulic press. Considerable difficulty was encountered, however, in controlling the time factor and obtaining a consistently uniform upsetting. Because of this control difficulty, the procedure was modified to permit resistance heating in place by passing an electric current through the rivet and by using spot welding equipment. The results of this method of riveting give considerable promise of being satisfactory and the work is being continued.

PROPERTIES OF TITANIUM

W. J. Fretague A. R. Olsen

Modified, Izod, V-notch impact specimens of Titanium Metals Corporation, commercially pure titanium (Ti-75A) and of iodide titanium have been prepared and will be used to determine transition temperatures for commercial-purity and high-purity titanium and to study the effect of hydrogen on the impact properties and transition temperatures.

The specimens of the commercially pure titanium were prepared from annealed rod that was swaged to $^1/_4$ in. in diameter from 1-in. bar. Specimens of the high-purity titanium were prepared from annealed rods that were swaged to $^1/_4$-in. dia after arc-melting of iodide-titanium crystal bar.

The fiber textures developed in commercial titanium by swaging from 1-, $^1/_2$-, and $^1/_4$-in.-dia rods and by vacuum annealing for 1 hr at 500°C have been determined. Similar determinations were made on iodide titanium that was: arc melted and swaged; arc melted, swaged, and annealed (in the alpha range); and arc melted, swaged, and annealed (in the beta range).

CERAMICS RESEARCH AND DEVELOPMENT

J. M. Warde S. D. Fulkerson
C. E. Curtis J. R. Johnson
L. M. Doney A. J. Taylor
G. D. White

CERAMIC COATINGS FOR METALS

Radiator Coatings. Work continues on the application of ceramic coatings to metals for possible use in a radiator. Attempts were made to coat pyrometallurgical-grade nickel with National Bureau of Standards coating A-418. It was difficult to obtain satisfactory adherence because carbon in the metal formed CO_2 during the firing process. In an effort to overcome this problem, specimens of as-received nickel were annealed for 2 hr at 2000°F in an atmosphere of dry hydrogen. After this treatment, coating A-418 applied at 1700°F adhered well; however, when the specimens so coated were subjected to a 65-hr oxidation test at 1500°F, bubbles were formed under the surface of the coating. It is proposed to investigate the adherence of coating A-418 on vacuum-melted electrolytic nickel and on nickel specimens annealed in an atmosphere of wet hydrogen.

Zirconium and Thorium Enameling. Samples of zirconium and thorium have been coated with NBS coating A-418 in connection with the thorium cladding investigation being carried out at the rolling mill.

Fluoride-Resistant Coatings. Work is proceeding on the development of a ceramic coating that could replace the present nickel metal coating in lining tanks that are used in the early separation states of the gaseous diffusion process. The coating is required to withstand fluoride attack and to be nonsusceptible to spalling. Trial compositions consisting of a phosphate glass applied to mild steel are being tested at K-25.

RADIATION DAMAGE STUDIES

A study of the effect of radiation upon various ceramic materials is in process. Test specimens of about 30 different ceramic materials are being prepared in the form of thin disks 3/4 in. in diameter by 20 mils thick to be sent to Hanford for irradiation periods of three and six months. About 70% of the disks has been fabricated, and they are being given preliminary measurements by the Solid State Division.

Pyrex glass specimens that were exposed in the graphite reactor for periods of seven weeks and four months were examined. All the specimens were medium red-brown in color, similar to glasses exposed to x rays. The color disappeared on heating to 200 to 300°C. A transmission curve was made showing high absorption below 5000 Å. The color of the irradiated specimens was probably due to trapped electrons (face centers). No evidence of devitrification could be found.

CERMET INVESTIGATION

A study of ceramic metal combinations (cermets) has started; the initial phase of the investigation, comprising the design and assembly of equipment and the procurement of raw materials, is nearing completion. An investigation of the fabrication and properties of ZrC-Fe cermets has been started at the Ohio State University Engineering Experiment Station under the auspices of the ceramic laboratory. They have also undertaken the problem of joining cermets.

HAFNIA RESEARCH

Hafnia (HfO_2) received from the Chemistry Division contained the following principal impurities, according to spectroscopic analysis:

Zr	0.35%
Ti	1.00%
Fe	0.10%
Na	0.004%

It was demonstrated that this material can be changed from the monoclinic to the cubic crystal form by adding 8 mole % of CaO and firing for 1 hr at 1600°C in air. This behavior, not previously noted in the literature, is similar to that of zirconium oxide (ZrO_2), which is commercially stabilized in this manner for the purpose of increasing heat-shock resistance.

The thermal expansion behavior of hafnia from room temperature to 1300°C was determined; no inversions were found in this range.

Equimolecular mixtures of HfO_2 and SiO_2 were fired for 1 hr at 1500°C; x-ray examination indicates that hafnium silicate was synthesized by this procedure.

HAFNIUM CARBIDE INVESTIGATION

An investigation was started at the ceramic laboratory on the synthesis, fabrication, and properties of HfC. A survey of the meager available literature on the subject was made and as an initial experiment, a stochiometric mixture of HfO_2 and carbon (lampblack) was cold pressed and sintered to 2200°C by induction heating in a graphite container. At 1190°C, the burning of gases in the sight tube indicated that a reaction had apparently started. At 2200°C, volatilization of some unidentified material caused the sight tube to plug, and the test was stopped. X-ray examination of the sinter indicated the possible presence of HfO_2 and HfN, but no recognizable pattern of HfC was observed. X-ray examination of the volatile material that had clogged the sight tube was made, but the patterns obtained were not similar to any data available. Further work is in progress.

Work on the syntheses of HfC, utilizing induction-welding equipment, has commenced at the U. S. Bureau of Mines Electrotechnical Laboratory at Norris.

COMPATIBILITY STUDY OF CERAMIC OXIDES

A study of the compatibility of selected refractory materials with various oxides, metals, carbides, and halides is in progress. Crucibles have been successfully cast of HfO_2, ThO_2, $ZrSiO_4$, and ZrO_2. It is proposed to fire the crucibles and investigate their behavior in contact with the various materials at elevated temperatures.

THORIA INVESTIGATION

A preliminary investigation of thoria for subsequent solubility tests was begun. Samples of thoria were prepared and fired to 700, 1200, and 1600 to 1630°C. The fired specimens were sent to the x-ray laboratory for determination of parameters and crystal size. Specimens have been sent to the Chemistry Division for a determination of the rate of solution.

FLUORIDE FUEL EXAMINATIONS

Petrographic Examinations. Over 300 petrographic examinations were made of fluoride mixtures during the past quarter. Several samples of fuels taken from capsules and loops were also examined. The optical properties of the following fluoride compounds have been determined; their values are not in the literature:

Li_3CrF_6
Biaxial negative
2V = about 40 deg
Alpha = 1.444
Gamma = 1.464

K_3CrF_6, cubic
$n = 1.422$

Na_3CrF_6, cubic
$n = 1.411$

KU_2F_9, orthorhombic
Biaxial negative
2V = 10 deg
Alpha = 1.544
Gamma = 1.588

UF_4, monoclinic
Biaxial negative
2V = 75 deg
Alpha = 1.500
Beta = 1.585
Gamma = 1.598
Anomalous interference colors
z = dark green
x = light green

The following systems and indices were determined by previous investigators:

Na_2BeF_4, orthorhombic
$Y \parallel C$, low birefringence
Average indices = 1.303

$NaUF_5$, hexagonal
Uniaxial negative
$O = 1.512$

UF_3, hexagonal
Low birefringence
$n = 1.73$
Anamolous interference colors

BeF_2, crystallized
Anisotropic
Low birefringence
$n = 1.328$

All index of refraction determinations are probably accurate to about ±0.003.

In the examination of capsules containing fuel No. 21, it was found that the oxygen present will react with ZrF_4 to form well-crystallized ZrO_2.

Differential Thermal Analysis. Differential thermal analyses were made of six selected fuel mixtures. These data supplemented existing information on melting points and phases present in the fuels.

FUNDAMENTAL PHYSICO-METALLURGICAL RESEARCH

L. K. Jetter

FUNDAMENTAL PRINCIPLES OF ALLOYING

Silver-Zirconium System (J. O. Betterton, T. M. Kegley, Jr.). The silver-zirconium system is of interest in that it shows the effect of alloying silver, with a filled *d* band and one *s* electron in the free atom, with zirconium with a free atom containing two *d* electrons and two *s* electrons. The two elements are on the same row of the periodic table, and the atoms are of approximately the same size, the silver atom being only 7.7% smaller on the basis of the closest distances of approach in the element crystal structures. The system is of further interest because of a martensitic type of transformation of the beta phase that, upon cooling, results in hardness effects in silver-zirconium. These effects are similar to those encountered in many other zirconium and titanium systems involving a eutectoid on the solvent-rich end of the phase diagram. Vickers hardness values of alloys cast on the water-cooled copper plate are shown as a function of composition in Fig. 7. The hardness maximum occurs within the beta solid-solution region.

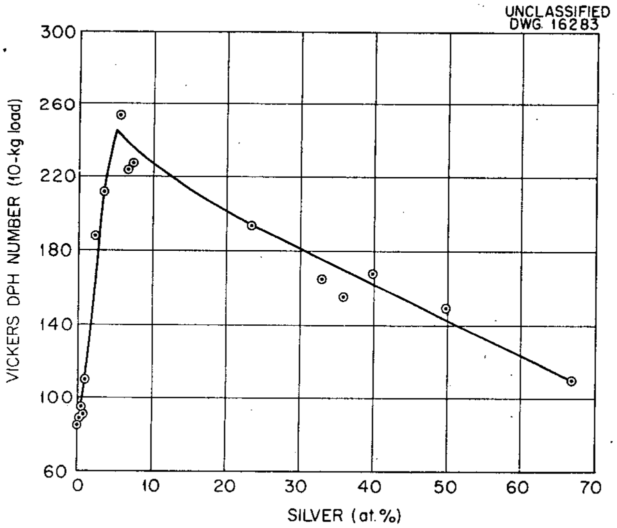

Fig. 7. Vickers Hardness of Silver-Zirconium Alloy After Arc-Casting.

The results of quenching experiments on small specimens of arc-melted, iodide zirconium alloys are shown in the tentative silver-zirconium phase diagram of Fig. 8. These alloys had been annealed for periods of time varying from 1 day at 1150°C to 29 days at 523°C. The alloys were carefully weighed, and the compositions shown are based on the changes in weight during the casting and annealing. The critical specimens will be analyzed chemically, although these results have not yet been obtained. Since pure zirconium specimens did not appreciably change in weight during similar casting and annealing, for the drawing of Fig. 8 it was felt justified to assume that the whole weight loss in the alloys was entirely silver.

The eutectoid decomposition temperature of the beta phase has been investigated by observing the temperature at which the transformation structure is replaced by a structure of isothermal alpha grains. On this basis, the eutectoid temperature has been shown in Fig. 8 as being somewhat less than 703°C. For example, after the alloy 2.1(1) was annealed for 22 days at 702.9°C, it contained transformed beta phase after quenching. On the other hand, after the alloy 5.4 was annealed for 29 days at 523°C, it still showed a transformed beta structure; it may be that the grain boundaries resulting from the transition $\alpha \leftrightarrows \beta$ are changed to isothermal alpha boundaries only very slowly at this temperature. In the first place, it is not thought probable that the eutectoid temperature could be so low as 523°C on the basis of the slope of the β/β + compound boundary. If grain boundaries of the transformed beta phase are so persistent at 523°C, there is question concerning the interpretation of the transformed structures observed in the 703°C anneal. A new method of heat treatment would seem to be advantageous.

Experiments are now being done in which alloys of 3 to 5 at. % silver are heat treated at 1000°C and then slowly cooled to avoid the formation of

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(1) The alloy number is the atomic per cent of the solute.

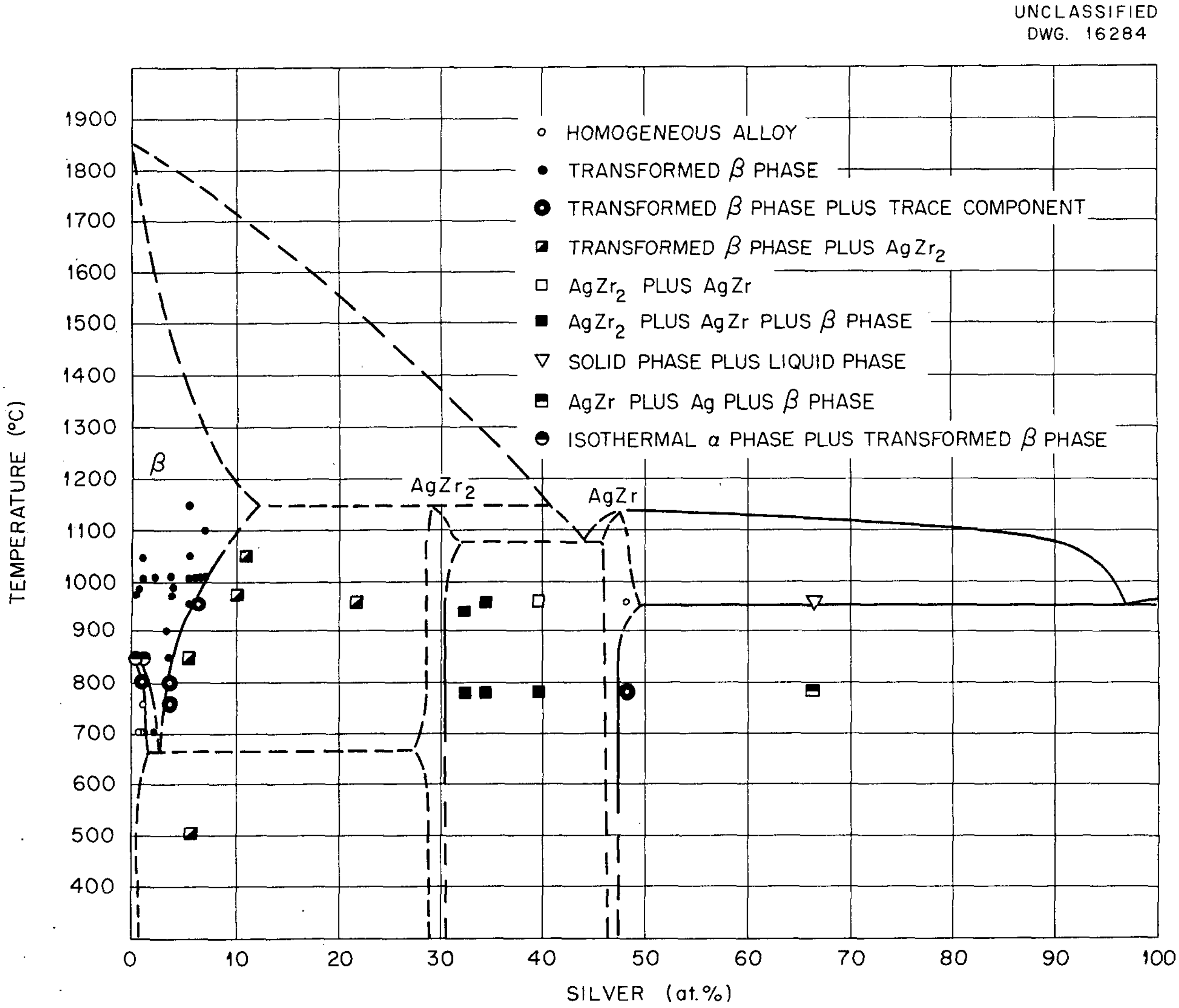

Fig. 8. Tentative Phase Diagram of the Silver-Zirconium System.

the transposed beta structure. It may be that equilibrium can then be more easily attained by annealing at 500 to 700°C the alloys that contain the eutectoid rather than the transposed beta phase. Some evidence in support of the sluggishness of the change of transformed beta grain boundaries to the isothermal alpha grain boundaries is the slowness found by McPherson and Hansen(2) in the change from transposed beta structure to isothermal alpha structure in pure zirconium annealed near the transition temperature. For example, an anneal of 24 hr at 852°C still contained some transformed beta structure, although this temperature is 10 to 11°C under the transformation temperature of pure zirconium given in the literature. This effect could also be explained by slight impurities in the iodide zirconium, as McPherson and Hansen pointed out; but if the present explanation is accepted instead, the results agree with that observed at 523°C.

Investigation of the phase boundaries between the alpha and beta regions has shown that when the beta phase is quenched in a two-phase ($\alpha + \beta$) alloy, the phase appears to undergo the eutectoid reaction during quenching. Figure 9 shows the

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(2) D. J. McPherson and M. Hansen, *The Phase Diagrams of Binary Zirconium Base Alloys*, COO-89, Armour Research Foundation, March 31, 1952.

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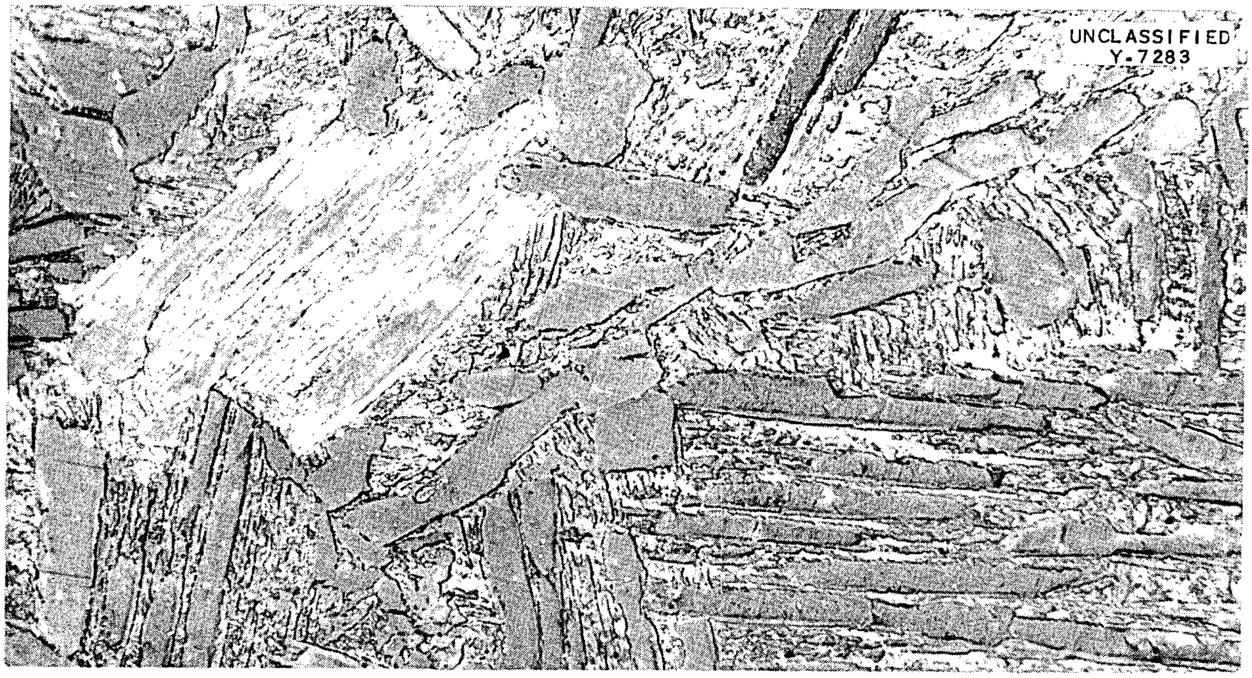

Fig. 9. Alloy 0.51 Quenched from 857.4°C Showing the Two-Phase Microstructure with Large Grains of Alpha Phase in a Matrix of Decomposed Beta Phase. Etched with 0.5% HF–50% alcohol–49.5% glycerine mixture; polarized light. 250X

microstructure of the alloy 0.51 quenched from 857.4°C in this region. A similar effect was found in alloy 0.78 annealed at 802°C, but in the alloys annealed at 703°C no structures of this type were observed; the alloys 0.52, 0.71, and 0.78 were isothermal alpha plus a small amount of a second phase, although in alloy 0.71 some residual, coarse, transformed beta (apparently from the homogenization quenching) remained evident. The alloys 1.08 and 2.09 were of transposed beta structure with very small particles of second phase. If the transformed beta structure is regarded, as suggested earlier, as being unaffected by 22 days at 703°C, then the presence of very small particles of second phase in these alloys would be consistent with placing them in the alpha plus compound region; and the eutectoid reaction would, in this case, be between 762 and 703°C. This may be better understood after new experiments involving slow cooling have been performed, and the diagram of Fig. 8 has been left with the eutectoid temperature less than 703°C.

The microstructure of the alloy 21.4 in the as-cast condition is shown in Fig. 10. This photograph shows the white phase, tentatively called $AgZr_2$, surrounding large primary beta grains, which have since decomposed eutectoidally. The reaction between the liquid and the beta phase did not go to completion, and a small residue of chilled eutectic may be seen inside the $AgZr_2$ phase. After alloy 21.4 was annealed for 9 days at 963°C, the microstructure shown in Fig. 11 was observed. If the white grains in the photograph of Fig. 11 are observed carefully, graduations in color, which indicate the presence in $AgZr_2$ of alloy gradients from the peritectic reaction, may be seen. These gradients indicate that the $AgZr_2$ phase exists over a definite range of composition, as has been indicated very roughly by the dashed lines around this phase in Fig. 8.

Other alloys in the (β + $AgZr_2$) region were heated as high as 1050°C, and in the beta region as high as 1150°C, but without incipient melting; therefore future quenching experiments will be

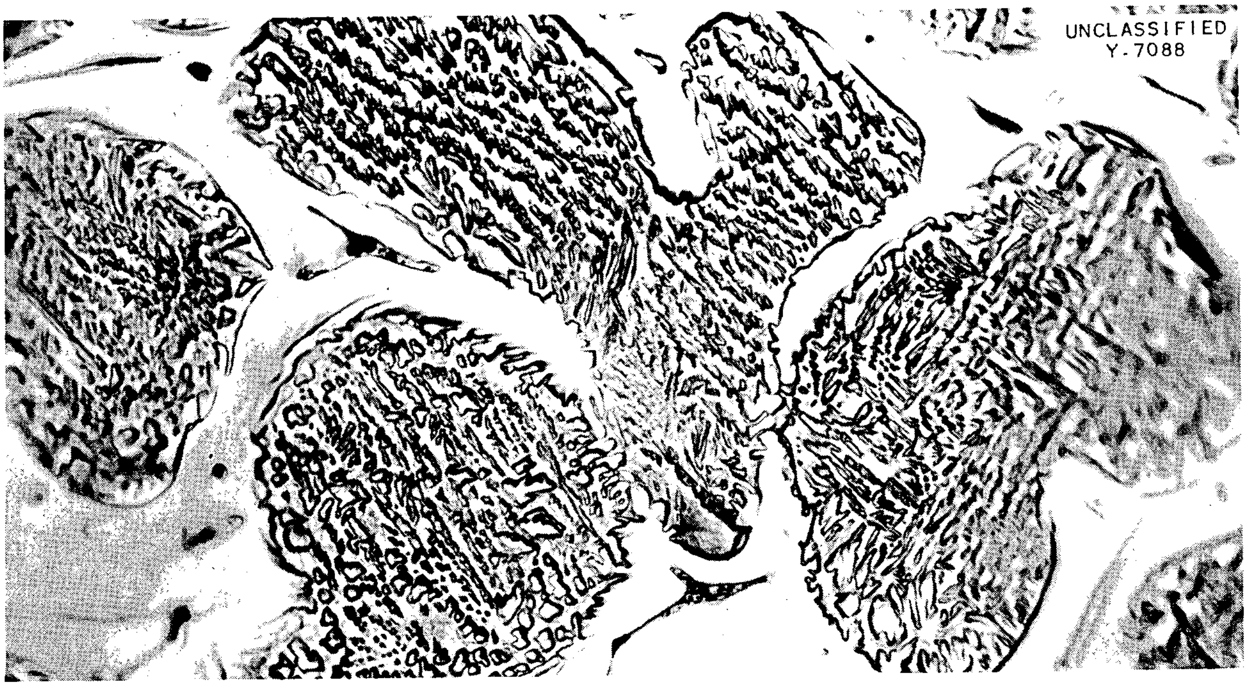

Fig. 10. Microstructure of Alloy 21.4 in the As-Cast Condition Illustrating the Peritectic Formation of $AgZr_2$. The eutectoid areas were formerly beta-phase primary grains that reacted with liquid in the grain boundaries to form the white phase. The third phase in the middle of the white areas is a eutectic. Etched electrolytically with perchloric and acetic acids very briefly and then swabbed with acetic acid. 1000X

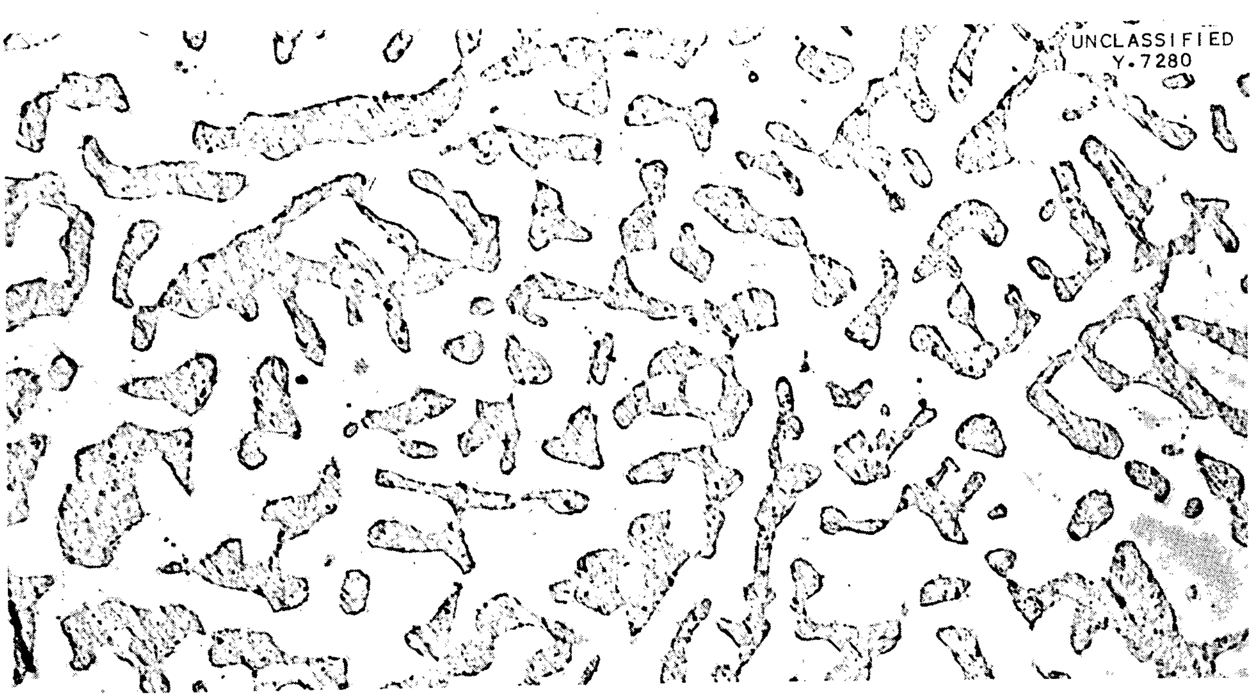

Fig. 11. Alloy 21.4 Annealed Nine Days at 963°C Showing Transformed Beta Phase in Matrix of $AgZr_2$ Phase. Hand polished without etching. 250X

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required to determine the temperature of the peritectic horizontal. The alloy 32.4 annealed for five days at 951.5°C consists of mostly $AgZr_2$ phase with a small amount of the AgZr phase as shown in Fig. 12. The actual composition of this phase is therefore slightly lower in silver than that given by the formula $AgZr_2$.

Alloys 34.2 and 39.7 were found to be in the two-phase region ($AgZr_2$ + AgZr) after annealing for seven days at 963°C, whereas alloy 48.3 was found to be within the homogeneous region of the phase, which is tentatively called AgZr, after annealing for eight days at 963°C. The microstructure of this alloy is shown in Fig. 13. This phase appears gray-white in bright-field illumination and in various shades of blue during rotation in polarized light. The polished surfaces of the microscopic specimens have frequently shown in this phase a needle-like deformation twin that appears as bright blue in polarized light and as a yellow-gray in bright-field illumination. At lower temperatures, the alloy 48.3 is not homogeneous but contains a trace amount of the silver solid solution. This is illustrated by the photograph of alloy 48.3 annealed for ten days at 779°C, shown in Fig. 14. Tentatively then, it would appear that the AgZr region is somewhat displaced toward the zirconium side from the composition represented by AgZr.

A minor third phase was observed, in addition to the $AgZr_2$ and AgZr phases, in the alloys 33.1, 35.8, and 39.7 in the as-cast condition and in the specimens that were annealed for ten days at 779°C. This constituent appears to be dendrites of a primary beta phase that crystallized during casting and remained in the alloys as a consequence of an incomplete peritectic reaction, $\beta + \text{liquid} \rightleftarrows AgZr_2$. The tentative phase diagram has been sketched with this in mind, and the formation of primary beta grains is shown up to about 40 at. % silver. An alternate interpretation, not shown on the diagram, would be that the beta phase formed a eutectic with the AgZr phase, and a peritectoid formation of $AgZr_2$ therefore would occur at a slightly lower temperature. This interpretation is favored by the tendency for the minor third phase to occur in conjunction with the AgZr phase rather than with the $AgZr_2$ phase

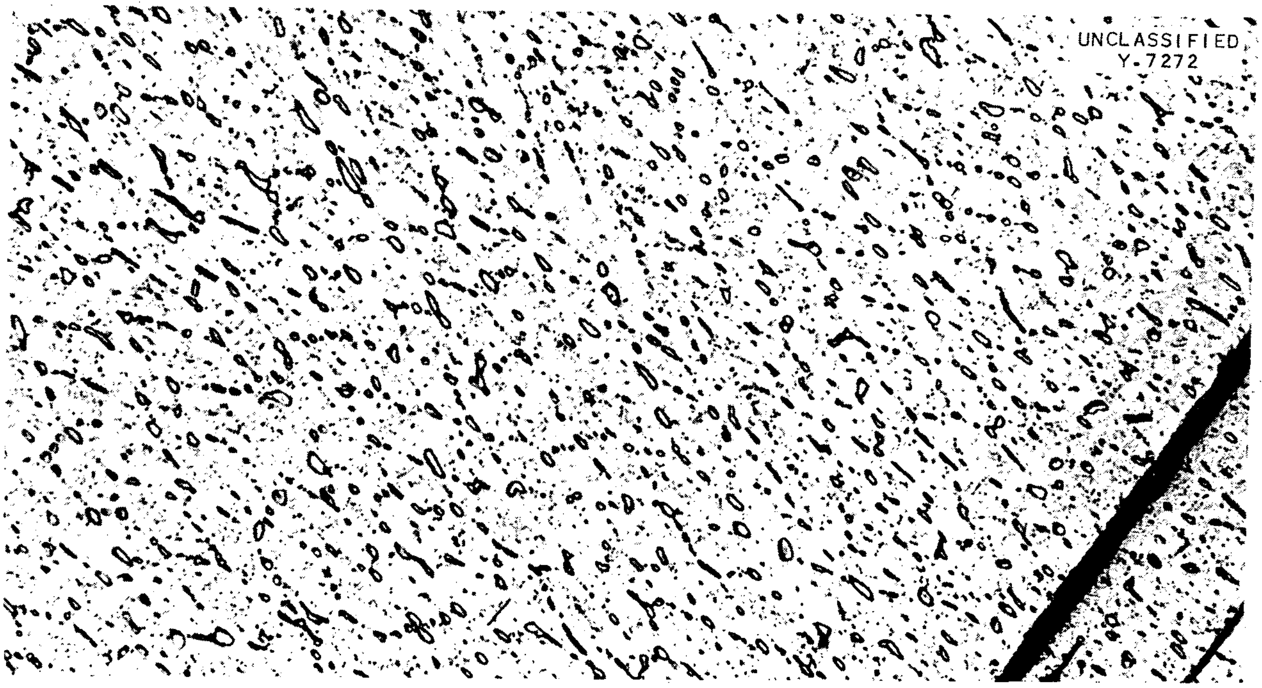

Fig. 12. Alloy 32.4 Annealed Five Days at 951.5°C Showing the Phase Tentatively Called $AgZr_2$ Plus a Small Amount of AgZr Phase. Etched 30 sec with 2% HF–48% HNO_3–50% glycerin mixture; bright field. 250X

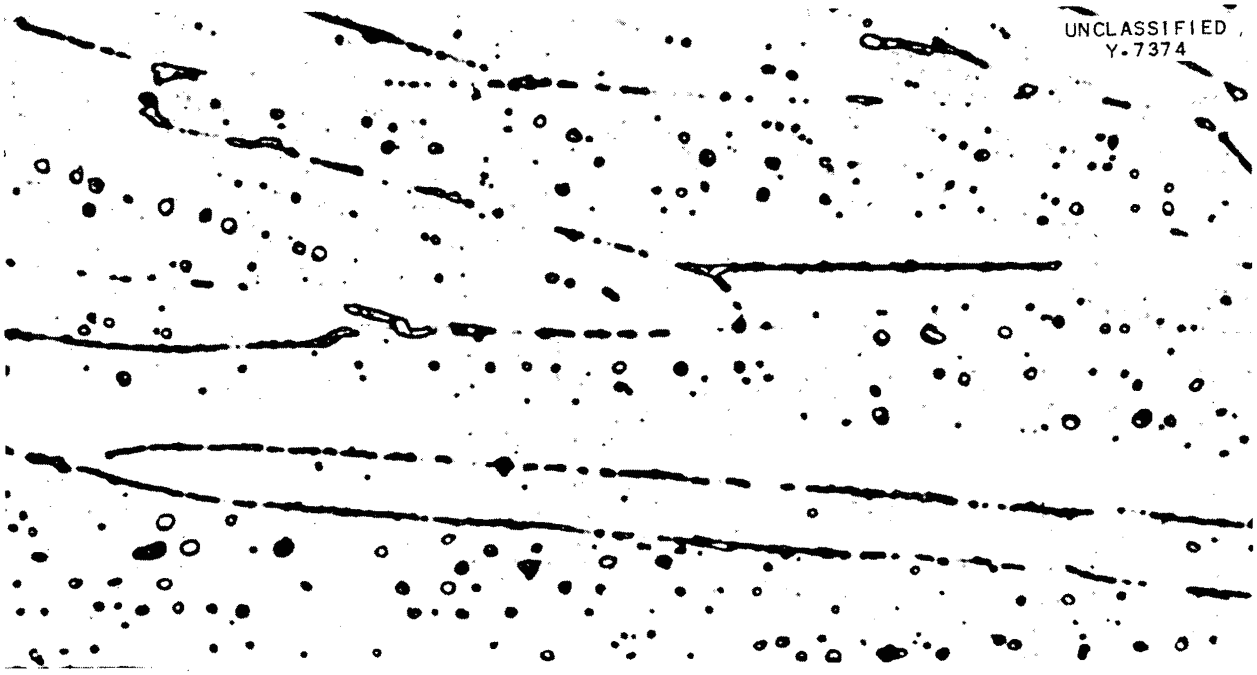

Fig. 13. Alloy 48.3 Annealed Eight Days at 963°C Showing Homogeneous AgZr Phase. Hand polished; polarized light. 250X

Fig. 14. Alloy 48.3 Annealed Ten Days at 779°C Showing the AgZr Phase with a Small Amount of Silver Solid Solution. Etched briefly in 1% HF–49% acetic acid–50% glycerine; bright field. 250X

in the alloys 35.8 and 39.7 annealed at 779°C. Additional experiments at 779°C are planned in order to make certain that the minor phase disappears when equilibrium conditions are obtained.

Etching of the silver-zirconium alloys by electrolytic means has been highly satisfactory in the regions of the zirconium-rich solid solutions, but this method pits and stains the surface badly as the silver content is increased. The best method found for preparing alloys that contain the $AgZr_2$ or AgZr phases is to polish by hand and to chemically etch the surface with one of the following reagents:

1% HF + 49% glycerine + 50% HNO_3,

1% HF + 49% glycerine + 50% alcohol,

1% HF + 49% glycerine + 50% acetic acid.

The use of an acetic acid swabbing during and after etching reduces the amount of general staining.

Because of the uncertainty about the beta eutectoid temperature, preparations are now being made to run a series of heating and cooling curves in this region. The thermal analysis ingots will be arc melted a number of times and then heated for long periods of time to make them uniform in composition. This uniformity will be tested by chemical analysis of the center and surface of the ingots. The thermal analysis will then be conducted with a sensitive potentiometer by the method of Hume-Rothery and Raynor.(3)

A quenching arrangement using silicone diffusion pump oil as the quenching medium has been made for the continuously pumped, mullite, tube furnace. Provisions have also been made to supply the furnace with purified argon. Unfortunately, a defective mullite tube that leaked slightly has prevented the use of the furnace for the determination of the solidus curves. A preliminary trial of the silicone oil quenching bath was quite satisfactory, and the mullite tube is now being replaced with a leak-tight tube.

Indium-Zirconium System (G. W. Boyd, J. O. Betterton). The indium-zirconium system occurs between the silver-zirconium and tin-zirconium systems when these binary systems are arranged in the order of their solutes on the second long period of the periodic table. In the silver-zirconium system the beta phase decomposes eutectoidally, that is, the addition of silver to zirconium depresses the close-packed hexagonal phase at the expense of the body-centered cubic phase. In the tin-zirconium system the opposite is true, and the alpha phase forms by a peritectoid reaction, that is, the addition of tin to zirconium expands the close-packed hexagonal phase region at the expense of the body-centered cubic phase. Since the indium-zirconium system is intermediate in the solute position on the periodic table, it might reasonably be expected to be either a peritectoid type similar to tin-zirconium or at least a system where the α/β boundaries were not depressed so rapidly as in the silver-zirconium system. The atomic size factor of the indium-zirconium system is −5.9%; consequently, there is no reason to expect restricted solid solution.

The preliminary annealing experiments were done with the alloy 9.6(4) that was annealed at the temperatures 1007, 972, 847, and 523°C. The times of annealing varied between 6 and 23 days, and the alloy was cold worked before the anneals. Two results for this alloy, pictured in Figs. 15 and 16, show that at 847°C the alloy consists of isothermal alpha phase, whereas after quenching from 972°C the alloy contains isothermal alpha phase plus transformed beta phase. There is a strong suggestion here that the alpha phase forms peritectoidally from the beta phase and an intermediate phase. This result is of particular interest since it not only fits the general trend of the silver-zirconium and tin-zirconium systems but also agrees with the occurrence of peritectoid alpha phases in the titanium-aluminum and the zirconium-aluminum systems, suggesting that Group III elements may, in general, show this tendency when alloyed with Group IVa elements.

The indium-zirconium alloys containing 2.5, 5, 7.5, 9.6, 12.5, 15, 19.3, 21, 23, 26, 28, and

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(3) W. Hume-Rothery and G. V. Raynor, *J. Inst. Metals* 61, 208 (1937).

(4) As in the silver-zirconium system, the indium-zirconium alloys are numbered according to their atomic per cent of solute.

33 at. % indium have been made successfully by arc melting. Certain arc-melting experiments were tried with higher indium contents but were unsuccessful because the indium metal boiled before the temperature that was needed to melt the zirconium was reached. For the present, attention will be given mainly to the higher zirconium alloys, and only occasional experiments with diffusion cans or with master alloys will be attempted to find a satisfactory method of making alloys with more than 35 at. % indium. The as-cast microstructures of these alloys showed beta to be the primary phase up to 19.3 at. %, with areas of what might be a eutectic between the grains of beta phase increasing with indium content. Between 19.3 and 23 at. % indium, the cast structures show a new primary phase that, from the proportion present, is probably near the composition $InZr_4$. Although only preliminary observations have been made on annealed specimens of alloys other than 9.6 at. % indium, there appears to be a homogeneous phase in this system of the tenative composition $InZr_3$, which at 1007°C includes alloys 26 and 28 within its homogeneity region. There appears to be another intermediate phase of composition near $InZr_4$ and another of still higher indium content than 33 at. %.

In the investigation of these alloys it has been found more satisfactory to use hand polishing followed by brief etching in 20% HF–20% HNO_3–60% glycerine than to use electrolytic etching, which appears to pit the specimens badly. All the alloys will be annealed at various temperatures between 850 to 1200°C in order to determine whether the complete constitution of the α/β boundaries confirm a peritectoid formation of the hexagonal, alpha phase.

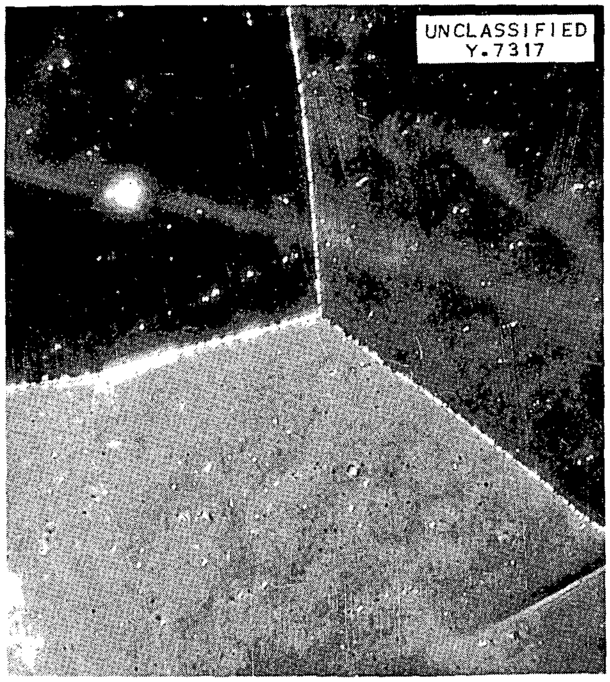

Fig. 15. Indium-Zirconium Alloy 9.6 Annealed for 96 hr at 972°C Followed by Annealing for Nine Days at 847°C Showing Isothermal Alpha Phase. Etched with 20% HF–20% HNO_3–60% glycerine; polarized light. 250X

Fig. 16. Indium-Zirconium Alloy 9.6 Annealed for 96 hr at 972°C Showing Isothermal Alpha Grains Surrounded by Transformed Beta Matrix. Etched with 20% HF–20% HNO_3–60% glycerine; polarized light. 250X