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METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

TECHNICAL PROGRESS REPORT FOR THE
PERIOD OCTOBER THROUGH DECEMBER
1949

By
A. R. Kaufmann

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By A. R. Kaufmann

ABSTRACT

A review of the casting work on 8"D. beryllium billets indicates clearly that the addition of as little as $\frac{1}{4}\%$ Al greatly increases the probability of obtaining a crack-free casting. Tensile tests on extruded beryllium powders have indicated not only a large ductility in the direction of extrusion (9 to 16%) but also an appreciable ductility in a perpendicular direction ($2\frac{1}{2}\%$). The effect of varying the initial size of the powders is being studied. Recent measurements have confirmed the large anisotropy of hardness in beryllium crystals.

A detailed description of creep apparatus is presented and results on 2S aluminum in the temperature range 300° to 450°C are given.

The recovery and recrystallization of zirconium crystal bar is being studied as a function of amount of cold work, annealing temperature and annealing time. Recrystallization does occur at a temperature as low as 500°C. A brief study of protective gas atmospheres for hot zirconium indicates that high vacuum or highly purified argon are satisfactory. An extensive study of the effect of heat treatment on zirconium indicates that Foote crystal bar shows the largest effect, while graphite-melted sponge zirconium shows little change in properties.

Hydrogen, nitrogen and carbon have been added to zirconium under carefully controlled conditions. Hydrogen appears to have little effect on the corrosion resistance of zirconium to 300°C water, but nitrogen and carbon even in small amounts have a harmful effect.

1. BERYLLIUM METALLURGY

1.1 Beryllium Melting and Casting

1.11 Summary of Recent Developments in the 8" D. Beryllium Billet Casting Program - G. J. Snyder

The writer has recently returned from a temporary 4½-month assignment at the Beryllium Corporation, Reading, Pennsylvania, where a program for the production of 8" D. vacuum cast beryllium billets is being carried out. The purpose of this assignment was to render technical assistance in an effort to accelerate the program both from production and quality standpoints. This report is essentially a summary record of the work done during the aforementioned period. A detailed report presenting an intimate discussion of the various phases of the work is expected to be completed shortly.

The initial difficulties to be overcome at the Beryllium Corporation were concerned with improvements in operational technique and involved among other things: (1) a breakdown and redesign of the vacuum system, (2) charging technique, (3) pouring temperatures, (4) application of heat to molds to eliminate moisture and (5) cleanliness measures.

A greater intensity of productive effort resulted from alterations in the foregoing procedures. From a statistical standpoint, 146 runs were made in these four months; a number approximately 40% of the total number attempted since the plant first went into operation 1½ years ago.

However, the ability to cast billets which are sound internally is still a perplexing problem. It was believed that this problem was, for the most part, solved, when all of a group of consecutive billets were apparently found to be sound internally, as indicated by a very intensive X-ray examination after casting (6 rotations in 180°). However, each one of these billets was found to contain internal defects after extrusion. The major difficulty appears to be the persistence of very fine axial longitudinal defects assuming an appearance of hairline pipe formations rather than cracks. These defects have been reduced to such narrow magnitude that they escape detection upon being exposed to the type of radiographic examination mentioned above.

Among the various steps taken to eliminate these defects have been:

- (1) heating of the molds.
- (2) use of tapered molds.
- (3) experimentations with hot-top materials and design.
- (4) use of small aluminum additions.

It is not intended at this time to go into any descriptive details concerning the results obtained using the above methods. Suffice to say that up to now the use of small aluminum additions has shown the most promise; and, pending results of simulated service corrosion tests now being carried out, these additions may provide the answer. Out of 23 billets cast containing aluminum additions, 18 were indicated to be sound by X-ray and later 14 of the 18 were found to be sound upon inspection after extrusion. The tabulation below shows a breakdown of these billets according to aluminum content.

Table I—Inspection Results of Billets
Containing Aluminum Additions

No. of Billets cast	% Al desired	% Al upon analysis	No. of Billets indicated to be sound by X-ray	No. of Billets found to be sound after extrusion
1	1.00	1.24	1	1
3	0.50	0.39-0.58	3	3
9	0.25	0.07-0.33	7	6
10	0.10	0.08-0.33	7	4

A comparison of these values with those of billets cast without aluminum additions discloses that out of 53 pure beryllium billets X-rayed, 17 were indicated to be sound and out of these 17, 3 were shown to be sound after extrusion.

In the opinion of the writer the casting program has now reached the point where a borderline status exists between the ability to obtain sound billets and defective ones with the following variables demanding further investigation if pure beryllium billets are to be desired.

- (1) More intensive development work should be applied in determining optimum hot-top and mold temperatures along with proper hot-top and mold design.

(2) Another possibility to be considered is the casting of shorter (9" or 10" D.) billets of weights approximating those of present 8" D. billets. The latter step may result in a lesser tendency toward pipe formation due to the reduced length-to-diameter ratio.

(3) It should be attempted to make the present method of X-ray inspection more positive by exploring the possibilities of more powerful machines or the use of radium.

At present, a new furnace, able to accommodate larger diameter molds and wherein facilities to apply auxiliary heat to both hot-tops and molds will be provided, is in the process of construction at M.I.T.

1.2 Beryllium Physical Metallurgy

1.21 Physical Testing of an Extruded Beryllium Flat—C. E. Latham-Brown

Tests have been completed on the extruded beryllium flat Y-5413. This material was received in the form of a billet sintered from Brush Q.M. Premium grade powder. Billet was $6\frac{3}{16}$ " D. $\times$ $16\frac{1}{4}$ " long and weighed 30.13 lb.

The billet was canned at M.I.T. and shipped to the Revere Copper and Brass Company of Detroit, Michigan for extrusion on September 15, 1948. Although this billet extruded completely, the greater part of it was snaked, giving a total sound section of about 15". Flat was $1\frac{1}{8}$ " $\times$ $3\frac{3}{4}$ " giving a reduction ratio of approximately 8 to 1. Extrusion temperature was 1850°F.

Tensile tests were carried out on specimens parallel and perpendicular to the direction of extrusion and the values are tabulated below.

All gages of these bars were etched electrolytically in a solution of 300 cc CH_3OH + 100 cc 10% HNO_3 + 100 cc 2.5% NaF with a current of 2.5 amps for 20 minutes.

Table 2—Tensile Results

Spec. No.	Direction	Ultimate (psi.)	Elongation (%)
632	Transverse	34,470	2.50
633	Transverse	36,486	2.39

Table 2—(Cont'd)

Spec. No.	Direction	Ultimate (psi.)	Elongation (%)
634	Longitudinal	76,702	8.93
635	Longitudinal	73,037	9.34

The stress-strain curves for these tensile tests are given in Figures 1, 2 and 3.

Compression tests were made on pieces in the direction of extrusion. Samples were 0.200" D. x 0.400" long. Results are as follows:

Table 3—Compression Results

Spec. No.	Direction	Ultimate (psi.)	Compression (%)
3	Longitudinal	191,000	9.88
5	Longitudinal	202,900	11.23

Corrosion tests were made on two pieces from different locations in the bars. All testing was done in water at 100°C (See Table 4).

Table 4—Corrosion Results

Spec. No.	Time (hours)	Weight (gms.)	Gain from Original Weight (gms.)
1	0	0.3804	-0.0002
	144	0.3802	
	288	0.3805	+0.0001
6	0	0.3757	
	144	0.3752	-0.0005
	288	0.3756	-0.0001

CURVES FOR Y5413 - TRANSVERSE - SPECIMENS 632 & 633

FIG. 1

8

AECD-4048

CURVE FOR Y5413 - LONGITUDINAL - SPECIMEN 634

FIG. 2

CARRYOVER-FIRST LINE OF TEXT

CURVE FOR Y5413 - LONGITUDINAL - SPECIMEN 635

FIG. 3

END OF TEXT

ACTUAL MS PG.

GALLEY NO.

Examination of the pieces at 144 hours showed no signs of corrosion in any way. At 288 hours pits appeared on both the ends and sides of the sample, along with a raised surface and stringer formation along the sides.

Density measurements give values of 1.842 gm/cc and 1.845 gm/cc on pieces taken from opposite sides of the extruded flat. This is in line with the normal value of 1.84 gm/cc.

Analysis of the original billet before extrusion was as follows: Al, 800 ppm; Ca, 1300 ppm; Cr, < 100 ppm; Fe, 850 ppm; Mg, 480 ppm; Mn, 120 ppm; Si, 750 ppm.

1.22 Physical Properties of Sized and Extruded Beryllium Powders— C. E. Latham-Brown

The material used in the study of physical properties as a function of particle size was premium grade beryllium powder which was prepared by the Brush Beryllium Company. This material as received was reported to be -200 mesh.

Separation of this powder into the various sizes was effected by the use of a Haultain Infra-sizer. The material submitted for sizing was resolved into the following: Cone #1, 80-56 microns; Cone #2, 56-40 microns; Cone #3, 40-28 microns; Cone #4, 28-20 microns; Cone #5, 20-14 microns; Cone #6, 14-10 microns and the bag fines were -10 microns. The material tested was in the range of 56 microns to -10 microns.

The material obtained from the separation was packed into the form of steel-jacketed billets 1.4" D. by 4" long, and extruded into $\frac{1}{4}$ " rods. Extrusion temperature was 1900°F and the reduction ratio was 33:1. All billets extruded giving good rods. The extruded rods were then sampled in such a manner as to give values over the length of the rod.

The samples were subjected to the following tests: tensile, compression, density, corrosion, hardness, micro-examination and spectrographic analysis.

Tensile Tests

Series I tests were made on specimens (0.100" D., 1.00" long) with the gage lengths treated in the following manner. The work hardened surface of the gage length was etched electrolytically in a solution of

10% HNO_3 , 2.5% NaF , the remainder of the solution ethyl alcohol. Current was 2.5 amps at 80 volts D. C. for 15 minutes. This treatment removed about 0.008" from the diameter of the specimen.

The specimens of Series II were of the same size, but the treatment for this group consisted of a 1-hour anneal at 800°C in vacuum. All tests were made at room temperature with a loading rate of 60 lb per minute. Results of the tests are as follows in Tables 5 and 6.

Compression Tests

Specimens were also taken from the extruded rods for compression testing. Samples were 0.150" x 0.300" and all were tested in the as-extruded condition. Tests were made at a loading rate of 500 lb per minute. A Tinius Olsen 20,000 lb hydraulic testing machine was used with a ball socket arrangement devised to insure proper alignment of the specimen with the traveling head of the machine. The results, as reported in Table 7, all fall below the normal compressive strength for cast and extruded beryllium which is in the range of 250,000 psi.

Density Measurements

Measurements were made on samples taken from both the front and rear sections of the rods. The calculations were based on weight and direct measurements, and these values compare very favorably with the established density of 1.84 gms/cc. However, it must be pointed out that with reference to the analysis of the material, the impurities increase with the decrease in particle size. We may, therefore, assume that this increase is partially responsible for the higher density. Results are reported in Table 8.

Corrosion Tests

Corrosion tests were made in boiling water at 100°C. All specimens were without visible defects at the start of the tests. The results are reported in Table 9.

It is felt that if these specimens were continued they would corrode more completely at the ends and then along the direction of extrusion. This observation is made on the basis of samples of powdered beryllium which have been run within the past few months.

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Table 5—Series I Tensile Results

Particle Size (microns)	Ultimate (psi.)	Yield (.1% offset, psi.)	Elongation (%)
56-40	97,400	50,800	13.99
	98,100	48,800	15.24
	98,800	48,700	13.91
40-28	102,000	49,600	16.00
	103,200	53,750	14.54
	87,700*	49,750*	9.77*
28-20	101,900	55,750	13.26
	110,800	64,000	10.96
	Broke in machining		
20-14	98,900	58,700	9.82
	100,000	62,100	7.91
	101,200	68,800	8.64
14-10	104,500	64,400	7.73
	98,900	53,800	9.81
	100,000	51,300	12.94
-10	109,500	71,000	10.87
	110,500	78,400	8.72

* Faulty

Table 6—Series II Tensile Results

Particle Size (microns)	Ultimate (psi.)	Yield (.1% offset, psi.)	Elongation (%)
56-40	97,100	46,500	12.97
	98,100	46,800	14.0
	96,750	46,500	12.98
40-28	103,500	47,400	16.43
	103,800	48,700	14.38
	102,900	47,500	14.17
28-20	105,500	53,600	16.22
	104,950	53,800	15.24
	105,800	53,800	14.47

CARRYOVER-FIRST LINE OF TEXT

Table 6—(Cont'd)

Particle Size (microns)	Ultimate (psi.)	Yield (.1% offset, psi.)	Elongation (%)
20-14	107,800	66,000	13.47
	107,400	66,200	13.50
	107,800	66,000	13.17
14-10	107,500	59,700	10.21
	102,500	48,000	12.66
Broke in machining			
-10	109,000	72,500	7.25
	114,800	72,500	11.44
	116,500	77,600	10.28

Table 7—Compression Results

Particle Size (microns)	Ultimate (psi.)	Yield (.2% offset, psi.)	Elongation (%)
56-40	158,700	69,800	26.63
	190,500	66,700	36.0
	187,000	65,200	29.0
40-28	190,000	41,300	38.19
	215,000	69,700	34.65
	283,500	93,500	28.35
28-20	178,500	66,600	29.5
	164,500	76,400	18.45
	177,500	65,200	25.42
20-14	173,100	68,500	34.0
	188,200	68,000	31.2
	131,500	73,500	30.15
14-10	147,400	66,800	34.82
	165,500	61,200	38.50
	150,000	66,200	35.6
-10	188,000	77,700	30.0
	167,200	72,500	33.3
	158,800	66,400	27.82

Table 8—Density Results

Particle Size (microns)	Sample	Density (gms/cc)
56-40	A	1.840
	B	1.844
40-28	A	1.852
	B	1.849
28-20	A	1.850
	B	1.843
20-14	A	1.838
	B	1.839
14-10	A	1.852
	B	1.852
-10	A	1.867
	B	1.868

Hardness Tests

A series of samples were taken from the bar for the express purpose of investigating any hardness change which could be effected by heat treatment as applied to specimens.

Readings were taken on both the transverse and longitudinal faces of the bars in the following conditions: as-extruded, annealed for 1 hour at 800°C in vacuum, and annealed for 1 hour at 1000°C in vacuum (See Table 10).

The trend of the values for the as-extruded and 800°C anneal samples fall in line with the values obtained for the yield strength of the tensile tests. The yield strength increases both in the as-extruded and 800°C anneal tensile tests from the 56-40 micron range to the 20-14 micron range after which it drops off sharply, and then shows an appreciable increase in the -10 micron material.

Microstructures

A series of photomicrographs have been prepared for each particle size. The as-extruded structure (Figure 4) appears to conform to the stated decrease in particle size.

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Table 9—Corrosion Results

Sample	Particle Range (microns)	Time (hours)	Weight Gain (mg/cm ²)	Remarks
P-30	56-40	50	0	Small pits
		100	.01	appearing on ends
		150	.02	Pits on outside
P-31	40-28	50	0	Pits on outside
		100	.01	edge only
		150	.01	
P-32	28-20	50	0	Spalling in
		100	.03	direction of
		150	.05	extrusion
P-33	20-14	50	.04	Pits and spalling
		100	.08	on ends
		150	1.40	
P-34	14-10	50	.03	Spalling and pits
		100	.05	in direction of
		150	1.00	extrusion
P-35	-10	50	.01	Pits and spalling
		100	.04	on ends. Thin
		150	.08	spalled lines in
				direction of
				extrusion

Table 10—Hardness Results

Particle Size P (microns)	Surface	Hardness (Rockwell 30T)		
		As-Extruded	Annealed 1 Hour at	
			800°C	1000°C
56-40	Transverse	67.78	64.02	60.13
	Longitudinal	72.18	71.36	65.50
40-28	Transverse	62.96	62.20	60.94
	Longitudinal	73.16	73.88	62.24
28-20	Transverse	68.46	67.80	63.08
	Longitudinal	75.34	74.24	72.76

Table 10—(Cont'd)

Particle Size (microns)	Surface	Hardness (Rockwell 30T)		
		As-Extruded	Annealed 1 Hour at	
			800°C	1000°C
20-14	Transverse	70.97	65.76	62.00
	Longitudinal	76.38	75.30	70.80
14-10	Transverse	70.16	69.10	65.86
	Longitudinal	77.76	74.10	64.90
-10	Transverse	74.11	72.80	72.50
	Longitudinal	78.10	76.90	77.34

Note: The reported values are the average of five readings.

A series of samples of different particle sizes were annealed for 1 hour at 800°C in vacuum. Microscopic examination does not reveal any change in structure. Another series were annealed for 1 hour at 1000°C in vacuum. This treatment appears to have effected a small amount of grain growth in the 40-28 micron range as well as in the 20-14 and the 14-10 micron ranges.

Spectrographic Analysis

A representative sample of each extruded particle size was submitted for spectrographic analysis. The results are reported in Table 11.

Table 11—Spectrographic Results

Particle Size (microns)	Analysis (ppm.)								
	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Si
56-40	1150	170	160	520	770	350	100	<100	480
40-28	1500	220	180	310	870	450	100	<100	470
28-20	1900	380	180	380	820	1400	130	<100	1400
20-14	2100	390	230	550	870	>1500	160	<100	1200
14-10	2300	640	340	630	780	>1500	120	<100	1100
-10	2700	760	540	2400	620	>1500	160	<100	1100

Transverse

Longitudinal

(A) 56 - 40 Micron Range

(B) 40 - 28 Micron Range

(C) 28 - 20 Micron Range

Figure 4: Microstructures of As-Extruded Beryllium Powders with Varying Particle Sizes. Polarized Light. Unetched. 250X

Transverse

Longitudinal

(D) 20 - 14 Micron Range

(E) 14 - 10 Micron Range

(F) Minus 10 Microns

Figure 4: Microstructures of As-Extruded Beryllium Powders with Varying Particle Sizes. Polarized Light. Unetched. 250X

1.23 Properties of Single Crystals of Beryllium—R. B. Russell

To advance our knowledge of beryllium a study of directional properties of beryllium single crystals should prove valuable. Resistance to mechanical deformation may be easily indicated by means of hardness values along various crystallographic directions.

Single crystals of beryllium were obtained from large, slow-cooled castings which had been etched to determine the location of suitable crystals. The test specimens, plane parallel plates large enough to accommodate at least fifteen hardness readings, were etched in dilute H_2SO_4 to reveal in the matrix any seed crystals which could be avoided in the hardness tests.

The location of the pole of the cut face of each crystal was found by the Greninger method of back-reflection X-ray analysis. The tautozonal spot positions on the X-ray photogram were transformed to a stereographic projection by a Greninger net, the (0001) reflection located and then rotated into the standard (0001) projection with a Wulff net.

The unique sector of the hexagonal standard (0001) projection, bounded by the three directions $[0001]$, $[10\bar{1}0]$, and $[11\bar{2}0]$, is presented in Figure 5 together with Rockwell 15N hardness values for several directions. It will be observed that the 15N hardness varies between about 63 and 43 from $[0001]$ to $[hkio]$ respectively, with intermediate values for any other direction. It might be expected¹ that resistance to penetration would be greater for $[10\bar{1}0]$ than for $[11\bar{2}0]$, since $[11\bar{2}0]$ is the slip direction in the basal plane. Although a marked difference is shown between $[0001]$ and $[hkio]$, there is little or no hardness variation observed for various $[hkio]$ types, probably because of presently insufficient data.

2. ALUMINUM METALLURGY

2.1 Aluminum Physical Metallurgy

2.11 Creep Testing of 2S Aluminum in the Range 300°–450°C— E. J. Field, Jr.

As there appears to be no information in the literature at present,

¹F. W. Daniels and C. G. Dunn, "The Effect of Orientation on knoop Hardness of Single Crystals of Zinc and Silicon Ferrite." Trans. A.S.M., 41 (1949), 419-442.

it was decided to make a determination of the creep and stress rupture strengths of 2S aluminum at temperatures 300°, 350°, 400°, and 450°C. Such properties are of interest in the use of aluminum finned tubing in atomic reactors. All tests were conducted in air. The data obtained from these tests form the basis of this report.

The aluminum used in this work was commercially pure 2S 0.750" D. rod. Specimens were machined from the material as received. The typical grain size of the as-received material is shown in Figure 6.

Apparatus

Four testing units were built using a welded steel frame construction. Figure 7 shows two views of the apparatus as used in these tests. A loading beam of 10:1 ratio was used with hardened steel knife edges carefully positioned at the correct locations. In an effort to simplify calculations and loading applications, a steel counterweight was welded at the front end of the beam and a smaller bronze counterweight mounted on an adjusting screw over the fulcrum allowed very fine adjustments of the balance to be made. In order to obtain axial alignment of the load on the specimen, crossed knife edges were used above and below the specimen. These can be seen in Figure 7 as well as in Figure 8. The specimen holders used were made from 18-8 stainless steel.

Creep Test Specimens

Creep specimens were machined to the specifications shown in Figure 9 from 2S aluminum bar stock, $\frac{1}{4}$ " in diameter.

Various methods of measuring elongation were considered and tested. Since the creep tests of aluminum were to be conducted at comparatively low temperatures, the problems of oxidation and scaling found in high temperature creep tests of steel were not necessarily as severe. It was, therefore, decided to adapt the following method: Stainless steel (410 cutlery type) clips were fabricated and heat treated to give them spring characteristics so they could be snapped onto the shoulders of the creep specimens. A seamless platinum tubing (0.025" L. D., 0.010" wall thickness) was spot welded to the clip at the lower end of the gage length on the specimen. Before spot welding, the free end of the tubing was sliced off diagonally, leaving a sharp pointed end on the tube to be used in establishing a fixed reference point. A platinum wire (0.020" diameter) was notched with a sharp, narrow angle chisel to

form "V" shaped reference marks spaced $\frac{1}{16}$ " apart along the entire length of the wire. This wire after notching, was slipped into the platinum tube and the free end spot welded to the clip fastened at the upper limit of the gauge. Before specimens were installed in the furnace, the tube and wire were adjusted so that the fixed reference point and the notches would be properly aligned. Figure 10 shows a specimen with the extensometer attached.

A Gaertner Creep test microscope (M-350D, one microscope type) was used. This gave a direct reading to 0.001 mm. (0.0001 mm. by interpolation) a working distance of 84 mm., and a magnification of 40X. Figure 11 shows closeup of microscope in use.

Since the internal lighting system supplied proved unsatisfactory, an outside source of light was used and reflected, by means of an adjustable prism attached to the microscope tube, into the furnace viewing port. This method proved very satisfactory and supplied ample illumination for readings during tests.

Creep Furnace Construction

An 18" alundum tube was used for these furnaces, $1\frac{3}{4}$ " bore $\frac{1}{4}$ " wall thickness.

Viewing ports were made from beryllia slip which were fitted and cemented into the alundum core and fired in a furnace previous to winding coils (Figure 12).

Three coils were used top, center and bottom. These coils were wound from #18 Chromel A wire with a resistance of 0.410 ohms per foot resulting in the following values: Top Coil, 13.0 ohms; Center Coil, 3.0 ohms; Bottom Coil, 16.0 ohms. The center coil was wound on a steel rod $\frac{1}{8}$ " in diameter and used approximately 7.5 feet of wire. Figure 13 shows the wound furnace cores before the coating of #562 alundum cement was applied. All leads to the coils were protected against shorting by covering with single-hole alundum tubing.

Furnace cans were fabricated from 0.0625" stainless steel and were $5\frac{1}{4}$ " $\times$ $5\frac{1}{4}$ " $\times$ 18" long with flanged ends for fastening to transite end plates. Figure 12 shows construction details.

Insulating material for all furnaces consisted of Babcock and Wilcox K-23 fire brick broken into small pieces of various grades. Variations in gradients were corrected in the furnaces by varying the size of the brick particles to obtain greater or less insulation properties in different areas. The final gradient of all furnaces proved to be

$\pm 1^{\circ}\text{C}$ within the limits of the total length of the specimens.

Control equipment consisted of Leeds and Northrup Micromax controllers in conjunction with D.A.T. units. No voltage stabilizers were used. The control thermocouple was installed in close proximity to center coil.

Throughout all tests, a continuous record of furnace temperature was provided by a Leeds and Northrup multiple point potentiometer recorder. This was used as a check on the continuity of each test. This recorder enabled us to observe any errors in temperature and any thermal accidents due to relay or power failure, etc., which might have occurred. Chromel-alumel thermocouples were used and a couple was fastened to the shoulders of each end of the specimen during tests. One thermocouple was connected to the recorder and the other to an outside potentiometer for spot checking during tests. These couples were interchanged at various times during tests to cross check each other and show any errors in either the recorded temperature or the observed temperature.

Test Procedure

The creep test data shown were obtained as follows:

The test specimen was heated to the desired temperature, held there for two hours, long enough to establish a constant and uniform temperature within the specimen, and then the test load was applied. A zero reading was taken previous to applying the load, a few minutes after applying the load, and then at desirable intervals thereafter for the duration of the test. The data recorded were time and elongation in terms of mm. per mm. of gage length. This information when plotted on coordinate paper gave typical creep curves from which second stage creep rates were obtained (Table 12). These rates when plotted against the loads producing them on log-log coordinates (Figure 14) give a straight line relationship. The slope of these lines might be used to describe the resistance to flow, but numerous values or rates can be obtained from these lines depending on the application or use the designers have in mind.

Stress rupture properties of 2S aluminum (Table 13) are shown in Figure 15. These tests were conducted on the same apparatus and under the same conditions as the creep except the tests were carried to failure.

Discussion

It was found that any temperature drop and subsequent return to stabilization resulted in an increase in the creep rate. Therefore, all specimens in which this occurred and any other questionable specimens were discarded.

Figure 16A shows a typical failure with the characteristic "orange peel" effect on its surface. This specimen failed after 500 hours at 1280 psi., 350°C. The failed cross section is shown in Figure 16B, with a typical coarse break characteristic of all fractured specimens. A longitudinal section was cut along the axis of the specimen and etched to show the structure (Figure 16C). Examination showed no trans-crystalline failure but separation at the grain boundaries indicative of intercrystalline failure. Further metallographic study is being carried out at present.

Table 12—Creep Results

Stress (psi)	Temperature (°C)	Minimum creep rate (mm/mm/hr)
2030	300	2.2×10^{-4}
1780	300	1.44×10^{-5}
1530	300	1.01×10^{-5}
1280	300	1.6×10^{-5}
1280	350	5.25×10^{-5}
1130	350	3.17×10^{-5}
1030	350	2.06×10^{-5}
774	350	3.4×10^{-6}
430	400	1.02×10^{-5}
380	400	4.6×10^{-6}
280	400	5.0×10^{-7}
530	450	2.5×10^{-4}
430	450	5.26×10^{-5}
330	450	1.93×10^{-5}
305	450	1.2×10^{-5}
180	450	8.8×10^{-7}

DIRECTION OF ROCKWELL 15N BRALE PENETRATION INDICATED BY CROSSES (x) AND IMPORTANT CRYSTALLOGRAPHIC DIRECTIONS BY OPEN CIRCLES (o).

HARDNESS OF BERYLLIUM SINGLE CRYSTAL FOR DIFFERENT DIRECTIONS. STANDARD (0001) STEREOGRAPHIC PROJECTION.

FIG 5

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Figure 6: Microstructure of As-Received 23 Aluminum Rod.
Polarized Light.. 50X

(A) Front View

(B) Rear View

Figure 7: General View of Creep Testing Apparatus.

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Figure 8: Specimen in Holders in Position
Showing Upper Knife-Edge Supports.

Dimensions and Tolerances of Creep Test Specimens

FIG. 9

Figure 10: Creep Specimen with
Extensometer Attached.

Figure 11: Creep Test Microscope in Use.

CREEP FURNACE ASSEMBLY**Figure 12**

Front

Side

Figure 13: Furnace Cores before Alundum Coating.

Table 13—Stress Rupture Results

Stress (psi)	Temperature (°C)	Time to Failure (hours)
1280	350	499.5
1130	350	651
1005	400	124
768	400	335
530	400	779
430	400	1761
530	450	112.5
430	450	169
330	450	624

3. ZIRCONIUM METALLURGY

3.1 Zirconium Reduction and Purification

3.12 Drip Melting—A Technique for Melting Zirconium or Other Reactive Metals without Contamination—T. T. Magel and R. F. Knowlton

Melting zirconium without impairing its ductility is regularly carried out in graphite molds and crucibles by the Bureau of Mines. Oxide refractories introduce sufficient impurities to embrittle the metal. Likewise, the special refractories, CeS , ThS and refractory metals tungsten, tantalum and columbium react rapidly with molten zirconium causing serious impairment of physical properties. Unfortunately, all zirconium which has been melted and/or cast in graphite while still ductile has extremely poor resistance to corrosion in 300°C water.

Arc melting in a water-cooled, copper crucible using tungsten or graphite electrodes has been carried out by Bureau of Mines and Battelle Memorial Institute. While contamination from the tungsten or graphite has been relatively small, no arc-melted zirconium specimens received at M.I.T. have ever exhibited satisfactory corrosion resistance.

In attempting to find a satisfactory method for melting zirconium, a new technique was devised whereby the metal is induction melted without being in contact with any other material—the so-called “drip-melting” technique. A description of this technique is given in MIT-1034 (Section 3.12). Melts of about 110 grams have been made in a simple quartz tube apparatus within one to two minutes. Good corrosion resistant crystal bar zirconium has been drip-melted into a copper mold and found to have a corrosion resistance equal to or perhaps somewhat better than the unmelted crystal bar (refer to Table 14).

The rate of melting is controlled by the rate of raising the induction coil. If coupling is good, the rate can be relatively rapid and the droplets of zirconium will completely fuse together in the mold. When the rate is slower, however, it is possible to observe in the solidified metal the boundaries between successive drops and these boundaries become even more pronounced after corrosion in 300°C. Preliminary experiments have indicated that by heating a slowly drip-cast ingot to 1500°C for about 1 hour the sharp boundaries become quite diffused and the corrosion resistance improves considerably.

During melting, while a considerable portion of the end of the rod is hot and the very end is molten, impurities (magnesium, iron, calcium, aluminum and chlorine) distil out and condense on the quartz vessel. With crystal bar the condensate is mainly iron; with Bureau of Mines, it is magnesium. Generally with Bureau of Mines compacted sponge—evenly previously vacuum heated to 1400°C to remove the bulk of residual magnesium—some violent splattering takes place projecting tiny particles of metal throughout the apparatus. This is thought to be caused by residual magnesium chloride entrapped in sealed voids in the compacted zirconium. It might also be noted that Foote crystal bar always degasses during drip melting to such an extent that the diffusion pump is choked off; never has this amount of gas been obtained from Bureau of Mines metal. (It has been found at M.I.T. that crystal bar contains between 1 and 2 cc (STP) of H_2 per gram of metal and perhaps this is the cause for the effect just mentioned.)

A modified, larger apparatus is being designed in which the induction coil will be stationary and the zirconium will be moved into the field. Thereby the dropping distance of the liquid zirconium can be better controlled.

To date it has been possible to drip melt crystal bar zirconium and not impair its resistance to corrosion whatsoever. Drip-melted Bureau

of Mines sponge has corrosion resistance of about one half to one third that of crystal bar for the first 100-200 hours. After that time, however, the corrosion takes place more rapidly than is considered satisfactory but still at a rate very much slower than graphite-melted metal.

The role of carbon in lowering zirconium's corrosion resistance is under intensive study but is not yet clearly understood. All evidence points to small amounts of carbon as causing serious lowering of corrosion resistance. Likewise, nitrogen in an amount greater than about 200 ppm, causes extensive corrosion. If the metal being melted already is contaminated with carbon or nitrogen, there will be no appreciable removal by the drip melting process. Only those metallic impurities with relatively high vapor pressures will be eliminated during melting.

Some chemical analyses have been obtained on zirconium before and after drip melting and some information has also been obtained on corrosion resistance of drip cast metal. In general, it can be said that in drip melting magnesium, calcium, iron, aluminum and chlorides distill out. Accurate quantitative data are not yet available.

It should be noted that the drip-melting method provides opportunity for preparing alloys without contamination by refractories. Some work has already been done along this line by slotting a bar of zirconium and inserting therein a wire or rod of the alloying material. After closing the slot by pressing, the rod is then drip melted in the usual manner. Alloys of zirconium with aluminum, nickel and molybdenum have been prepared by a single drip melting. It is thought that best uniformity of alloy will be obtained by re-drip melting the alloy casting and work along this line is in progress. Multiple re-drip melting has been done on Bureau of Mines sponge with little apparent improvement, but further work is in progress.

3.3 Physical Metallurgy of Zirconium

3.31 Recrystallization of Zirconium—R. M. Treco

Introduction

An extensive investigation of the effect of cold work and annealing on the properties of pure zirconium has been started in order to obtain optimum conditions for fabricating, control final condition in the metal

for use, and to further our basic knowledge of working and annealing of metals.

Work has been started on crystal bar zirconium since the minimum annealed hardness and the lowest recrystallization temperature were obtained on this material in a preliminary survey. Extension of the work to Bureau of Mines zirconium and uranium alloys up to 10% by weight are planned.

Preparation of Material

Crystal bars of the usual purity from Foote Mineral Company were selected for maximum diameter, brightness (1 surface and absence of core wire. The bars thus selected were swaged down to a uniformly round bar of 0.310" D. and annealed for 2 hours at 1000°C in a vacuum resistor furnace maintaining a maximum pressure of 5×10^{-4} mm Hg. The annealed hardness varied between 60 and 62 Rockwell F which is comparable to crystal bar as received. This treatment produced a fairly regular though coarse grain size.

Cold working was accomplished by swaging in steps of $\frac{1}{32}$ " in diameter. No intermediate anneals were necessary to obtain a total reduction of 96% and an even greater reduction could be obtained if necessary.

Annealing Procedure

Since zirconium is hardened by exposure to various gases at relatively low temperatures, the procedure used was designed to minimize this effect. The swaged bars were sectioned longitudinally through the center, packed in crystal bar chips and sealed into a Pyrex or Vycor tube with a vacuum better than 5×10^{-4} mm Hg. This procedure was quite successful, the surfaces of the specimens neither darkening nor brightening for any of the heat treatments, although some reaction was observed between the chips and container in a few cases.

In order to study recovery, recrystallization and grain growth, the following schedule for annealing was used:

Temperatures, °C: 475° to 650° by 25° steps with other temperatures where required.

Annealing Time (each temperature), Hours: 0.1, 1, 4, 40, 120 and 400.

Table 14— Comparison of Corrosion Resistance of Some Drip-Melted Zirconium*

Sample No.	Description	Approximate Hours in 300°C Water							
		20	45	125	500	650	800	1200	1600
1	Foots Crystal Bar As Received	0.06	0.07	0.09	0.17		0.17	0.20	0.22
159	Drip Cast Crystal Bar	0.08	0.08	0.07	0.12	0.13	0.11	0.09	0.09
105	Bureau of Mines	0.37	0.66	†	1.00				
262	Drip Melted Bureau of Mines	0.13	0.09	0.12	0.35	0.85	1.38		
286	Drip Melted Bureau of Mines		0.06	0.25	1.00	1.03†	1.58		
285	Same as #286 but Homogenized 1 Hour at 1500°C		0.00	0.20	0.35	0.54	0.59		
324	0.3 Wt. % Al. Alloy † Made by Drip Melting Sponge								

* Since samples in general are observed at different times, values given in table are only approximate but do give clear indication of relative corrosion rate.

† Sample flaking off too much to obtain weight.

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The evacuated tubes were placed in furnaces already at temperature, and time allowed for heating up. (This was previously determined to be 2.5-3 minutes depending on the temperature.) For the shortest time (0.1 hour) a lead bath was used. After annealing, the tubes were removed from the furnace and cooled in air.

Preparation of Specimens for Examination

Specimens were mounted in bakelite and polished by hand through 000 paper, then broken out of the mount for electrolytic polishing in a perchloric-acetic acid reagent.

The polished specimens were examined microscopically and then remounted in bakelite in such a way as to preserve the polished surface. Back-reflection X-ray patterns were then made on selected specimens using copper K-alpha radiation in order to follow the course of recovery and recrystallization.

After X-raying, specimens were tested for hardness using the Rockwell 30-T scale, which allowed the maximum number of impressions on the smallest specimens without destroying the polished surface completely. Since zirconium samples stay bright over a long period, these were retained for reference.

Results

The work hardening of zirconium occurs very rapidly and most of the hardening occurs in the first 30-35% of reduction in area as shown in Figure 21.

The course of working is revealed readily in the microstructure, as the original annealed grains are first twinned, then marked with deformation bands, elongated and finally a complete fibering of the structure occurs. A pronounced preferred orientation is produced which is visible under polarized light in the most heavily worked metal. This appears in the transverse section as four light areas symmetrically disposed about the longitudinal axis. A section parallel to the bar axis shows light and dark bands parallel to the length of the bar. This does not conform to the preferred orientation for swaged and drawn wire found by Burgers, Fast and Jacobs in which the basal plane (0001) and the (1010) direction were parallel to the wire axis. Further work is planned for this phase of the program.

Recrystallization appears to be normal in zirconium, the recrystallized grain size being very fine. The results of metallographic examination, X-ray diffraction, and hardness tests obtained to date have been summarized in Tables 15-17. Further results will require grain size measurements on all recrystallized specimens.

Grain growth following recrystallization has been found to proceed with an abnormally large degree of internal twinning.

**Table 15—Recrystallization of Zirconium Annealed
1 Hour at Temperature**

Temperature (°C)	Reduction in Area (%)						
	19	36	51	64	75	91	96
400							
425						0	0
450					0	0	0
475					0	0	0
510		0	0	0	0	X	X
534		0	0	0	X	X	X
560	0	0	0	X	X	X	X
583	0	0	X	X	X	X	X
600	0	X	X	X	X	X	X
625	X	X	X	X	X	X	X
650	X	X	X	X	X	X	X

0: Recovery complete

X: Recrystallization complete

Table 16—Recrystallization of Zirconium Annealed
4 Hours at Temperature

Temperature (°C)	Reduction in Area (%)						
	19	36	51	64	75	91	96
450					0	0	0
475		0	0	0	0	0	0
510		0	0	0	X	X	X
534	0	0	X	X	X	X	X
560	0	X	X	X	X	X	X
583	X	X	X	X	X	X	X
600	X	X	X	X	X	X	X
625	X	X	X	X	X	X	X
650	X	X	X	X	X	X	X

0: Recovery complete

X: Recrystallization complete

Table 17—Recrystallization of Zirconium Annealed
40 Hours at Temperature

Temperature (°C)	Reduction in Area (%)								
	6.7	13	19	36	51	64	75	91	96
510				X	X	X	+	X	X
534				X	X	X	+	X	X
560	X	X	X	X	X	X	+	X	X
583	X	X	X	X	X	X	+	X	X
600	X	X	X	X	X	X	+	X	X
625	X	X	X	X	X	X	+	X	X
650	X	X	X	X	X	X	X	X	X

X: Recrystallization complete

+: Incomplete

CREEP RATE OF 2S ALUMINUM

FIG 14

STRESS RUPTURE RESULTS ON 2S ALUMINUM

FIG. 15

(A) Typical Failure of Creep Specimen.

(B) Cross Section at Failure.

(C) Longitudinal Section of Failure.

Figure 16: Views of Typical Creep Failures.

**HARDNESS VERSUS REDUCTION IN AREA FOR
COLD-SWAGED ZIRCONIUM CRYSTAL BAR**

FIG. 21

3.32 Heat Treating Atmospheres for Zirconium—L. R. Allen

It is a well-known fact that zirconium metal is an excellent getter for many gases and that the gettering efficiency increases with temperature. Both the fabrication and the heat treatment of zirconium usually involve heating to an elevated temperature. It thus becomes important to know which if any atmosphere may be used for treatment without excessive gas pickup, which alters both physical and corrosion properties of zirconium metal. To this end a study was made to determine usable atmospheres for large-scale work as well as laboratory research.

Pieces of zirconium metal from the Bureau of Mines were weighed accurately and placed in a platinum boat inside an electrically heated muffle through which a selected gas stream was passed. A slight pressure over atmospheric was maintained. The pieces were reweighed after one hour at temperature and a per cent weight gain calculated.

Two forms of gas were used; gas as it comes from the tank and purified gas. Purification involves complete dehydration and, when applicable, deoxygenation by hot copper and uranium chips. Table 18 best summarizes the work.

Vacuum gives the least weight pickup, but it must be remembered that these pressures are not readily maintained commercially at low cost. Nor is quenching easily done from vacuum chambers.

Both cracked carbon dioxide and ammonia used commercially are undesirable due to the presence of oxygen and hydrogen respectively.

The most practical atmosphere for commercial work seems to be pure dry argon, with helium presumably acting in a similar fashion. The weight pickup while appreciable is not prohibitive.

3.33 Response to Heat Treatment of Zirconium from Various Sources—L. R. Allen

It is generally known that small amounts of impurities substantially affect the physical properties and heat treatability of pure metals, notably the recrystallization temperature. The previous work on zirconium heat treatment was carried out with Foote Mineral Company crystal bar and the considerable variation in impurity content has been evident in the varying response to heat treatment.

In an effort to more clearly understand the effects of impurities, zirconium from other sources was obtained and heat treated. The lack of ideal chemical analysis precludes quantitative discussion of the

Table 18—Percent Weight Pickup of Zirconium Slugs in Various Atmospheres at Different Temperatures for One Hour (Ground Surface)

Temperature (°C)	Atmosphere									
	Pure N ₂	Pure O ₂	Pure H ₂	Dry Air	Pure NH ₃	Pure CO ₂	Pure Argon	Vacuum 10 ⁻⁴ mm	Tank NH ₃	Tank CO ₂
400	.10	.02	.02	.03	.02	.02	.00	.00	.02	.04
500	.04	.03	.04	.05	.04	.03	.00	.00	.03	.03
600	.09	.04	1.00	.10	.07	.08	.03	.00	.07	.08
700	.18	.10	1.45	.45	.17*	.21†	.02	.00	.17*	.21†
800	.22	.24	‡	1.42	.21*	.39†	.02	.01	.24*	.19†
900	.38	.39	‡	‡	.41*	.77†	.08	.02	.98*	1.01(?)†,‡

* hydrogen flame observed

† CO detected in exit gas

‡ sample spalled- weighings inaccurate

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results. However, it is felt that the reported analyses may be considered accurate insofar as the relative impurity content is concerned.

Sources of the zirconium samples used were: Foote Mineral (1) production bar (2) low-hafnium bar: Bureau of Mines production material; and Philips Company (Eindhoven, Holland) crystal bar.

The annealing series were run to check the maximum softness obtainable (as a measure of the ease in fabrication), and to observe the effect of impurities which remain in solid solution on heating to and cooling from elevated temperatures.

The quenching series were run to see whether impurities would remain or go into solution at elevated temperature and be retained with a rapid cool. An effort was also made to observe the percentage rise in yield strength as compared with the rise in ultimate strength as a function of composition and treatment.

The tempered series were run to determine whether a precipitation of impurities would occur, further raising the elastic properties. The tempering is also a measure of the strength that may be expected at elevated temperatures. The quenching temperature chosen for the tempering series (950°C) gave the maximum hardness rise in regular Foote Mineral crystal bar used in previous work.

The data are summarized in Table 19.

3.4 Zirconium Alloys

3.41 Zirconium-Uranium Alloys—W. H. Titorchok

Samples of the alloys heretofore discussed^{3,4} have been subjected to 100-hour treatments at various temperatures after rolling and are in process for metallographic and X-ray examination.

Four small melts of nominal analysis 33, 49, 60 and 69 wt. % U have been prepared, rolled and treated (quenched from 100-hour soaks at temperature) and studied. The as-cast structures of the four compositions are similar in that they show a duplex granular structure within large "phantom" grains. The results of surveying Phragmen X-ray photograms of part of this series are summarized in Table 20.

³MIT-1029 (Pt. 1): "Technical Progress Report for the Period January through June, 1949," pp. 107-119.

⁴MIT-1034: "Technical Progress Report for the Period July through September, 1949," pp. 51A-56.

Table 19— Variation in Tensile Properties of Zirconium as a Function of Analysis and Treatment

Treatment	Yield Strength (psi, 10 ³)		Ultimate Strength (psi, 10 ³)	Elongation (%)	Rockwell A Hardness		
	.1% Offset	.2% Offset					
Foote Mineral Crystal Bar Cold Swaged and Heat Treated							
Argon Cool						Average Analysis	
from 700°C	11.15	11.25	39.10	22.11	24	C	0.02
800°C	12.83	16.02	39.21	10.20	20	O ₂	0.03
900°C	20.00	22.79	34.85	23.61	17	Si	0.04
950°C	17.93	19.88	32.08	12.77	15	Al	0.35
1000°C	18.29	20.80	39.39	28.08	12	Mg	0.11
Brine Quench						Ca	0.16
from 700°C	16.03	19.35	40.25	19.87	26	Fe	0.04
800°C	17.62	19.73	34.38	10.20	27	Cr	0.05
900°C	19.22	22.21	45.90	26.72	35	Ni	0.04
950°C	28.85	32.40	45.20	11.84	43		
1000°C	31.05	33.61	42.60	4.84	46		
Brine Quench							
from 950°C							
Temper at							
1 Hr. 400°C	35.00	38.80	52.80	9.13			
450°C	27.25	30.20	44.40	10.42	47		
500°C	26.00	28.81	43.90	19.60			
4 Hr. 725°C	16.38	17.98	35.18	25.91	26		

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Table 19— (Cont'd)

Treatment	Yield Strength (psi, 10 ³)		Ultimate Strength (psi, 10 ³)	Elongation (%)	Rockwell A Hardness	Average Analysis	
	.1% Offset	.2% Offset					
Foote Mineral Low Hafnium Crystal Bar Cold Swaged and Heat Treated							
Argon Cool							
from 700°C	19.45	22.90	52.70	14.04	37	C	
800°C			51.60	25.54	33	O ₂	
900°C					34	Si	0.02
950°C	25.80	28.28	39.21	5.16	35	Al	0.16
1000°C	21.91	27.20	38.92	23.42	27	Mg	0.003
Brine Quench						Ca	0.02
from 700°C			52.30		43	Fe	0.04
800°C	28.25	31.81	58.40	8.12	36	Cr	0.01
900°C					42	Ni	0.01
950°C	33.60	37.10	58.40	10.14	47	Hf	0.27 (?)
1000°C	34.21	37.10	58.40	14.52	46		
Brine Quench							
from 950°C							
Temper at							
1 Hr. 400°C	31.10	33.60	51.20	19.82	44		
450°C	26.85	26.85	42.75	13.74	42		
500°C	31.10	33.95	43.20	3.52	45		
4 Hr. 725°C	27.80	28.30	37.10	21.42	33		

Table 19—(Cont'd)

Treatment	Yield Strength (psi, 10 ³)		Ultimate Strength (psi, 10 ³)	Elongation (%)	Rockwell A Hardness	Average Analysis	
	.1% Offset	.2% Offset					
Philips Crystal Bar Cold Swaged and Heat Treated							
Argon Cool from 700°C	20.80	24.70	53.80	12.84	40	C	
800°C	20.50	23.00	50.20	15.16	37	O ₂	
900°C	20.85	24.05	45.50	19.98	40	Si	0.02
950°C	19.45	22.60	48.00	20.92	32	Al	0.02
1000°C	26.10	28.25	31.80	7.06	39	Mg	0.002
Brine Quench from 700°C	20.20	21.90	51.30	15.52	43	Ca	0.004
800°C	21.20	24.78	57.20	17.80	43	Fe	0.05
900°C					49	Cr	0.01
950°C	29.38	32.50	52.00	12.30	49	Mn	0.002
1000°C	37.80	41.00	60.10	12.44	51		
Brine Quench from 950°C							
Temper at							
1 Hr. 400°C	38.90	40.80	55.20	12.72	51		
450°C	36.40	39.60	58.60	15.22	48		
500°C	38.90	42.40	55.50	9.98	47		
4 Hr. 725°C	14.11	17.00	34.70	14.94	36		

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Table 19— (Cont'd)

Treatment	Yield Strength (psi, 10 ³)		Ultimate Strength (psi, 10 ³)	Elongation (%)	Rockwell A Hardness	Average Analysis	
	.1% Offset	.2% Offset					
Bureau of Mines Sponge Melted in Graphite Cold Rolled and Heat Treated							
Argon Cool							
from 700°C	25.40	29.00	50.55	11.86	53	C	0.10
800°C	28.25	31.10	51.25	6.60	56	O ₂	0.04
900°C	28.61	32.55	56.60	11.34	51	Si	0.04
950°C	33.60	36.80	58.30	11.82	52	Al	0.12
1000°C	37.07	40.30	52.60	11.10	52	Mg	0.07
Brine Quench						Ca	0.10
from 700°C	32.20	35.38	50.20	10.92	54	Fe	0.03
800°C	34.30	37.10	51.90	7.82	56	Cr	0.02
900°C	38.82	42.40	60.00	10.94	54	Mn	0.003
950°C	37.10	41.00	56.50	13.34	56		
1000°C	41.00	43.10	60.20	9.58	55		
Brine Quench							
from 950°C							
Temper at							
1 Hr. 400°C	43.50	46.60	60.50	8.96	56		
450°C	35.75	42.10	61.10	9.96	53		
500°C	35.40	37.10	62.25	11.52	57		
4 Hr. 725°C	35.40	37.10	56.90	10.58	55		

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Table 20—Lattice Types as Indicated by X-Ray Photograms

Nominal Weight Percent Uranium	As Cast	Rolled and Quenched after 100 Hours at			
		450°C	600°C	700°C	1000°C
33		Not Completed			
49	BCT	BCT	BCT	BCC	BCC
60	BCT	BCT	BCT	BCC	BCC
69		Not Completed		BCC	BCC

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Note: BCT: Body-Centered Tetragonal
BCC: Body-Centered Cubic

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Of interest are the following lattice parameter values, measured at room temperature, for the BCC phase retained by quenching from 700°C.

TEXT

OPT. CENTER
SMALL FIG.

Table 21—Lattice Parameter Values of BCC Phases Retained by Quenching from 700°C

OPT. CENTER
SMALL FIG.

Nominal Weight Percent Uranium	a_0 (in Angstroms)
$^1\beta$ Zr	3.61
33	Not Completed
49	3.56 ³
60	3.56 ³
69	3.55 ³
$^2\gamma$ U	3.47 ⁴

FT. NY.
R. TO E.

$^1\beta$ Zirconium at approximately 867°C from W. C. Burger, Z. Anorg. Chem., (1932) 205, 81
 $^2\gamma$ U from KAPL-219

Further work is progressing on these and other alloys with particular attention to the range 0–20 wt. % U.

END OF TEXT

ACTUAL

CARRYOVER-FIRST LINE OF TEXT

4. CORROSION

4.1 Effect of Hydrogen on the Corrosion Resistance of Zirconium in 300°C Water—D. S. Kneppel, P. A. Kulin and T. T. Magel

Crystal bar zirconium which shows good corrosion resistance has been found to contain approximately 0.8–1.6 at. % H₂. The temperature at which zirconium will be used is in the range where hydrogen absorption is possible. Although the pickup of hydrogen in water at 315°C has been reported to be very small, it was deemed advisable to see if hydrogen had any effect on the corrosion resistance of zirconium.

A set of samples containing varying amounts of hydrogen was prepared. The starting material was crystal bar zirconium rolled into sheet 0.010" thick. The apparatus for hydrogen is the same as that used for addition of other gases.⁵ The samples were first heated to 1500°C in vacuum to remove the hydrogen originally present in the crystal bar zirconium. The values given for hydrogen added were calculated. The results of the corrosion testing are shown in the following table.

⁵ MIT-1034: "Technical Progress Report for the Period July through September, 1949," pp. 67-73.

Table 22—Effect of Hydrogen on Corrosion Resistance of Zirconium in 300°C Water

Sample No.	At. % of H ₂	Corrosion Data					
314	0	Time (Hrs.)	21	81	171	337	502
		Wt. Gain (mg/cm ²)	0.02	0.06	0.06	0.08	0.06
311	0.4	Time (Hrs.)	22	88	184	348	510
		Wt. Gain (mg/cm ²)	0.01	0.02	0.03	0.06	0.04
308	7.64	Time (Hrs.)	22	88	182	348	510
		Wt. Gain (mg/cm ²)	0.03	0.05	0.09	0.22	0.38
309	22.2	Time (Hrs.)	22	88	182	348	510
		Wt. Gain (mg/cm ²)	0.05	0.08	0.10	0.15	0.16
310	39.5	Time (Hrs.)	22	88	182	348	
		Wt. Gain (mg/cm ²)	0.08	0.33	0.90	2.02	
*306	66.7						

* Sample has been run 670 hours and shows no signs of being attacked. Quantitative data not available.

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Table 23—Effect of Nitrogen on Corrosion of Zirconium in 300°C Water

Sample No.	Amount nitrogen added	Theoretical Nitrogen content corrected for 40-60 ppm in original crystal bar	Results of chemical analysis for N ₂	Corrosion Data*			
317	None, as Cold- Rolled	(40-60)		T	20	41	110 275
				W	0.02	0.04	0.06 0.10
314	None, outgassed in vacuum at 1500°C	(40-60)	60	T	21	42	81 171
				W	0.02	0.03	0.06 0.06
320	62 ppm.	102-122	80	T	21	42	81 171
				W	0.02	0.04	0.05 0.07
315	199 ppm.	239-259	250	T	21	42	81 171
				W	0.02	0.02	0.07 0.40
316	1000 ppm.	1040-1060	1120	T	21	42	81
				W	0.61	1.19	2.32†

* T: Time in hours

W: Weight gain (mg/cm²)

† Oxide flaked off

These results are only preliminary. Further corrosion studies on the effect of hydrogen will be made.

4.2 Effect of Nitrogen on the Corrosion Resistance of Zirconium in 300°C Water—P. A. Kulin and D. S. Kneppel

Our earlier qualitative experiment indicated that the addition of nitrogen to zirconium destroyed the metal's corrosion resistance. In order to determine what amounts of nitrogen could be tolerated without seriously affecting the corrosion resistance of zirconium, a series of alloys have been prepared. The results obtained to date on three of these alloys are tabulated in Table 23.

The alloys were prepared by first cold rolling crystal bar into 0.010" sheet. The bar was tested for corrosion resistance and the nitrogen content determined. The sheet, in form of cylinders $\frac{3}{4}$ " high and $\frac{1}{4}$ " D., was outgassed in a vacuum and measured amounts of high purity nitrogen were added; the metal was heated to 1500°C until all nitrogen had been absorbed by the zirconium and uniform diffusion of the gas through the sample had been achieved.

The calculated nitrogen additions are in good agreement with the results obtained by chemical analysis. Sample #316 (1120 ppm of nitrogen) developed a heavy oxide coat in the first 21 hours. Sample #315 (250 ppm of nitrogen) began to show signs of attack between 81-171 hours; all the other samples seem to have resisted attack so far.

From these data it would seem that nitrogen in concentrations of about 250 ppm. will cause zirconium to corrode.

4.3 Effect of Carbon on the Corrosion Resistance of Zirconium in 300°C Water—P. A. Kulin, D. S. Kneppel, L. R. Allen, C. S. Pearsall, and T. T. Magel

It has already been demonstrated that carbon in sufficient amounts will induce corrosion in zirconium. To ascertain the quantity of carbon allowable, a series of carbon alloys were prepared. In order to avoid contamination, the alloys were prepared in a manner similar to that used in producing gas alloys. The procedure consisted of adding carbon through the thermal decomposition of propane on a zirconium surface

heated to 1500°C. The pyrolysis of the propane is assumed to take place as follows:

The carbon is absorbed by the hot zirconium surface. Since the hydrogen released in the reaction will not combine with zirconium at this temperature, it may be pumped out of the system while the metal is still hot. The composition of the zirconium-carbon alloy given in the table of corrosion results are calculated on the basis of the volume changes in the above reaction. If polymerization takes place and the reaction does not go to completion, as indicated, the values given for carbon in the corrosion data table would be too large. There is also the possibility that the carbon was not distributed uniformly, but might tend to be concentrated on the surface. Initial micro studies did not detect any concentration of carbon on the surface. In addition the corrosion testing of the cross section of these samples did not show any non-uniformity. More work is being done to establish the degree of uniformity of these samples.

The corrosion data, as seen from the following table, definitely show that the addition of carbon to zirconium will induce corrosion.

To confirm the role of carbon evidenced through increased weight gain with increasing carbon, a microspecimen was prepared from a Bureau of Mines cast zirconium billet (0.15% C). The polished surface was indexed with an L-shaped nick and the area photographed (Figure 22A). The greyish inclusions are identified as zirconium carbide. The same microsample was then exposed to water at 110°-120°C for increasing time intervals. The progress of corrosion was observed visually on a metallograph. A photomicrograph of the specimen after 31 hours exposure is given (Figure 22B). A comparison with Figure 22A immediately establishes that the carbides are heavily and preferentially attacked. This trend continues until no free carbide is left and the specimen is then subject to general corrosion.

Table 24—Effect of Carbon in Zirconium on the Corrosion in 300°C Water

Sample No.	Calculated Amount of carbon added* (weight %)	Corrosion Data			
		Time (Hours)	21	42	81
314	0	Weight Gain (mg/cm ²)	0.02	0.03	0.06
334	0.027	Time (Hours)	23	45	115
		Weight Gain (mg/cm ²)	0.13	0.20	0.42
333	0.068	Time (Hours)	23	45	115
		Weight Gain (mg/cm ²)	0.36	0.53	0.60†

* Total carbon analysis not available at the present time.

† Heavy oxide—flaking off.

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(A) Before Corrosion Showing Carbide Inclusions.

(B) After 31 Hours in Water at 110° - 120°C

Figure 22: Microstructures of Bureau of Mines Zirconium with 0.15% C.
Bright Light 250X

Table 25—Solubility of Zirconium and Hafnium Oxychlorides in Hydrochloric Acid Solutions of Varying Concentrations

Agitation period (hours)	Temperature (°C)	Normality of HCl solution	Solubility of ZrOCl_2 (gram mols per liter)	Solubility of HfOCl_2 (gram mols per liter)
24	25	9N	0.069	0.054
24	25	10N	0.105	0.077
24	25	11N	0.166	0.106
24	25	12N	0.292	0.211
48	20	9.5N	0.067	0.052
48	20	10.2N	0.105	0.062
48	20	11.8N	0.311	0.067
48	20	12.2N	0.310	0.090

END