MECHANICAL PROPERTIES AND MICROSTRUCTURE OF ANNEALED ZIRCONIUM

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ABSTRACT

The mechanical properties of unalloyed zirconium are shown to vary markedly depending on the state of anneal of the metal. Hardness is used as an index of annealing condition. Precautions to be taken in obtaining reproducible hardness values in zirconium are outlined. In addition, the appendix contains a hardness conversion table for zirconium base alloys. This covers the hardness range from approximately 60 to 250 DPH (20 to 100 R_B).

MECHANICAL PROPERTIES AND MICROSTRUCTURE OF ANNEALED ZIRCONIUMI. INTRODUCTION

The kinetics of annealing of cold rolled zirconium has been the subject of two recent papers.^{1,2} The characteristics of the annealing behavior of zirconium have been shown by these investigators to differ markedly from those of the more common metals. Bostrom and Kulin,¹ using electrical resistivity, a very sensitive measure of internal strain, obtain excellent correlation with the x-ray texture and hardness studies of McGeary and Lustman.² It is shown that during isothermal annealing, the major changes in hardness, annealing texture, and electrical resistivity take place long after recrystallization is apparently complete as evaluated by standard metallographic examination of the structure. McGeary and Lustman² report a hardness of 148 DPH for "metallographically" recrystallized zirconium and 75 DPH for this same material with a stabilized annealing texture following extended heat treatment.

Data are to be presented which will appraise both the creep and tensile property dependency on the state of anneal of unalloyed zirconium. Inasmuch as hardness is used in evaluating the state of anneal, a critical review of the effect of applied load and surface preparation on the observed DPH of annealed unalloyed zirconium will also be given.

The heat treatment to be referred to as "base-anneal" is defined as that heat treatment which achieves a stabilized annealing texture without excessive grain growth; i.e. the grain sizes as evaluated by

metallographic examination were smaller than 0.05 mm diameter (ASTM 6).

The hardness of "base-annealed" unalloyed zirconium of the purity used in this study is 73 ± 2 DPH (20 kilogram load).

II. EXPERIMENTAL PROCEDURE

1. Material

The unalloyed zirconium used for the tensile and creep studies was obtained from two double arc-melted ingots of WAPD iodide crystal bar (ingots No. F129 and F544). The zirconium used in the hardness study was from an STR Mark I production ingot, No. 1871. The analyses of these materials are listed in Table I.

Table I. Chemical Analysis of Unalloyed Zirconium

	<u>F129</u>	<u>F544</u>	<u>1871</u>
<u>Spectrographic</u>			
Al	.003	.004	.004
Cr	.002	.005	*.001
Cu	*.0005	*.0005	*.0005
Fe	.02	.05	.015
Hf	.04	.04	*.03
Mo	.001	*.001	*.001
Ni	.002	.005	.003
Si	.005	.003	.001
Sn	.001	.001	*.001
Ti	.002	.001	.002
<u>Chemical</u>			
C	.02	.01	.02
N ₂	.001	.001	.001
O ₂	--	.023	.025
H ₂	--	34 ppm	37 ppm

* Less than

2. Specimen Preparation

The sheet stock used for tensile and creep specimens were hot forged and rolled at 750°C (1400°F) from a 4 inch ingot and then cold rolled 10% to 0.06 inch. Specimen blanks were milled to 0.040 inch by removal of equal amounts of material from both sides. Sheet specimens, having the nominal dimensions shown in Fig. 1, were machined after the end tabs were spot welded onto the milled specimen blank.

3. Annealing

The creep and tensile properties are reported for three levels of annealing which are evaluated quantitatively by hardness. Indentation hardness, specifically diamond pyramid hardness (DPH), has been shown to be an effective measure of the state of anneal of zirconium.² The heat treatment schedules used are described below.

Heat Treatment No. 1 is the anneal that was given the F129 specimens from which were obtained the tensile and creep data reported in WAPD-38³ and WAPD-39.⁴ These data are abstracted herein for the sake of comparison. In this treatment the final machined specimens were annealed in a vacuum of less than 0.03 microns at 600°C (1110°F) for 1/2 hour followed by a furnace cool to room temperature. The rate of temperature increase was relatively rapid (to temperature in approximately 1-1/2 hours). The hardness and grain size resulting from this heat treatment were 92.5 ± 2.5 DPH (20 kilogram load) and 0.019 mm diameter (ASTM 8-9) respectively.

The anneal producing the intermediate hardness level of 88 ± 4.6 DPH (20 kilogram load) was a nominal 700°C (1290°F) for 1 hour (Heat Treatment No. 2). This anneal is termed "nominal" in that the integrated time-at-

temperature was variable, since the furnace temperature was controlled so that the system pressure never exceeded 0.03 microns. This was an attempt to minimize gaseous contamination of the specimens. Despite the variation in hardness, the grain size of these specimens was a consistent 0.05 mm diameter (ASTM 6).

Subsequent to the work of McGeary and Lustman² specimens of this same material were vacuum heat treated to give a "base-anneal" structure. The prescribed conditions were 750°C for 20 hours in a vacuum of less than 0.03 microns. This heat treatment (No.3) resulted in a hardness of 73 ± 2.2 DPH (20 kilogram load) and a grain size of 0.05 mm diameter (ASTM 6), the same grain size as that obtained in Heat Treatment No. 2.

4. Test Procedure

a. Creep

The series of creep tests to be noted herein were conducted at 260°C (500°F) using the sheet specimen of Fig. 1. The creep testing technique was similar to the one described in WAPD-39.⁴

b. Tensile

The tensile tests were made on sheet specimens of the design shown in Fig. 1 and were conducted in air at room temperature, 150, 260, 315, 400°C (75, 300, 500, 600, 750°F). The tensile testing technique was similar to that described in WAPD-38.³ The tests were made at a constant head motion of 0.05 inch per minute which is equivalent to an extension of 100% per hour. A statistical analysis⁵ of the tensile testing technique indicates that the 0.2% yield strength data have a standard deviation of ± 200 psi at 260°C (500°F)

and the tensile strength data have a standard deviation of ± 400 psi at this temperature.

c. Hardness

Hardness tests, unless otherwise specified, were made on a standard Vickers Hardness Testing Machine using a 20 kilogram load applied for 10 seconds.

III. RESULTS AND DISCUSSION

1. Creep

Listed in Table II are the steady state creep rates at 260°C (500°F) of unalloyed zirconium annealed to the following three levels of hardness: (1) 89 - 93 DPH, (2) 83 - 88 DPH, and (3) 71 - 76 DPH. These data are plotted in Fig. 2.

The upper curve, data from WAPD-39,⁴ are for the highest hardness level and evidence a uniform change in creep rate with changes in stress. This is closely approximated by a straight line on the semi-logarithmic plot with an increase in creep rate of a factor of 10 for an increase in stress of 2000 psi.

The intermediate, dashed curve of Fig. 2 expresses the best curve that can be drawn through the scattered data points obtained from specimens given Heat Treatment No. 2. Unalloyed zirconium heated to this intermediate hardness level has an approximate increase in creep rate of a factor of 10 for a 500 psi increase in stress.

Material from the same double arc-melted ingot F544 was "base-annealed" (Heat Treatment No. 3) to a hardness of 73.2 ± 2.2 DPH. In this condition the data of the lower curve of Fig. 2 were obtained. In

this "base-annealed" condition, lower creep strengths for zirconium were obtained than any heretofore reported for equivalent grain size. This shows an increase in creep rate by a factor of 10 for increase in creep stress of approximately 70 psi, and is considerably higher than the creep rate-stress response resulting from either of the other heat treatments.

Thus, with a more thorough anneal, the hardness decreases continuously for a specific grain size, and the creep strength decreases, yielding creep rates much higher than heretofore reported.

2. Tensile

Table II lists the tensile properties of unalloyed zirconium over the temperature range of R.T. to 400°C (75 to 750°F). These are divided, as were the creep data, into three hardness groups resulting from the heat treatments noted above. Fig. 3 is a plot comparing the tensile strengths of unalloyed zirconium having the hardness values indicated. As would be expected, throughout the temperature range there is the marked trend to lower strengths the softer the material.

Fig. 4 is a plot of the 0.2% yield strength with an expanded stress scale. The data from Heat Treatments 1 and 2 give evidence of wider scatter than those from 3. Tensile tests were made at 400°C (750°F) only on specimens having Heat Treatments 2 and 3. At present it is not known why the yield strength either levels off or rises in the testing temperature range of 315°C to 400°C (600°F to 750°F).

Table II. Minimum Creep Rate of Unalloyed Zirconium
At 260°C (500°F)

	<u>Stress</u> <u>1000 psi</u>	<u>Creep Rate</u> <u>Per Hour</u>	<u>Grain Size</u> <u>mm</u>	<u>Hardness</u> <u>DPH (20 Kg)</u>
<u>Heat Treatment No. 1</u>				
F129-34L	11.0	5.8×10^{-7}	.018	89
-16L	13.0	6.4×10^{-6}	.019	93
	16.0	4.3×10^{-4}		
-22L	14.0	1.5×10^{-5}	.017	90
	16.0	1.8×10^{-4}		
-41L	17.0	4.7×10^{-4}	.017	90
<u>Heat Treatment No. 2</u>				
F544-24	10.0	2.5×10^{-7}	.06	84
-12	12.8	2.8×10^{-3}	.05	83
-15	13.9	2.24×10^{-1}	.06	83
-18	14.0	3.5×10^{-6}	.05	87
-5	14.0	3.7×10^{-5}	.045	86
-1	15.6	9.8×10^{-2}	.045	88
-3 (b)	17.1	1	(a)	92
<u>Heat Treatment No. 3</u>				
F544-44	10.75	1.0×10^{-6}	(a)	72
-33	11.0	8.23×10^{-7}	.05	76
-60	11.0	4.17×10^{-7}	.06	74
-27	11.25	4.0×10^{-3}	(a)	72
-36	11.5	5.8×10^{-4}	(a)	71
-29	12.0	2.16×10^{-2}	(a)	72
-31	13.1	2.1×10^{-1}	(a)	73
-26 (b)	14.0	1	(a)	76

(a) Not determined

(b) Tensile test

570-10

WAPD-T-46

- 11 -

81-07

- 11 -

81-07

- 11 -

81-07

(b) Not determined

81-07

(d) Values listed are averages.

A comparison of the effect of state of anneal on the mechanical properties of unalloyed zirconium is presented in Fig. 5.

3. Hardness

The data presented above indicate that metallographic structure is not an index of the state of anneal of worked zirconium and that hardness or other mechanical properties are much more reliable criteria. As in other materials, surface preparation is an important factor in obtaining representative diamond pyramid hardnesses on zirconium. In addition, the load used in making the indentation is also important. Fig. 6 shows the influence of specific surface preparations and indentation load upon the hardness.

Each of the hardness values of Curves I and II is the average of 5 separate indentations; those of Curve III are each the average of 20. The material on which this hardness study was made is a block of unalloyed zirconium 1" x 1-1/2" x 4" from STR production ingot No. 1871. Chronologically the curves of this plot were obtained in the following sequence: The hardnesses of Curve I are those obtained on this block of zirconium carefully machined flat with parallel surfaces following an alpha heat treatment at 800°C (1470°F) in vacuum for 3/4 hour. The machining was accomplished by removal of metal with 0.001 inch cuts and a final cut of 0.0005 inch. There is a marked decrease in DPH with increasing applied load. The hardnesses plotted on this curve have standard deviations ranging from ± 0.6 to ± 1.9 .

From the work of Thomas and Goldman⁶ it is known that even with care in machining there is distortion of the lattice to a depth of 0.002 inch. The depth of the indentation at these hardness levels is within the range where the cold work from machining could affect the hardness determination; i.e. at the 80 DPH level with a 5 kilogram load the indent is 0.0013 inch deep, and only 0.003 inch at a 70 DPH level with a 30 kilogram load. Thus it was reasoned that both the level of hardness and decrease in hardness with increase in applied load might well be functions of the cold worked surface layer. The block was etched with removal of 0.005 inch of metal whereupon the data of Curve No. II were obtained. There was decrease in overall hardness level but still the observed hardnesses appeared to be a function of the applied load. As indicated, the standard deviations of these points range from ± 0.4 to ± 3 at indenter loads of 2.5 kilograms and above. The standard deviation for the 1 kilogram load was considerably higher, ± 18 , and will be discussed in connection with Curve III.

The possibility of a residual cold worked surface layer could still explain this decrease; therefore the block was annealed in a vacuum of less than 0.03 microns at 800°C (1470°F) for 3/4 hour. DPH was determined as a function of load, and there was a decrease in hardness with increase in applied load. These values are averaged on Curve III with those hardnesses obtained following the two subsequent treatments. The decrease in hardness with increase in applied load despite the care exercised in annealing might, in this case, be due to a contaminated surface layer containing small quantities of gaseous impurities. The block was etched,

with removal of 0.007 inch, and hardnesses obtained which showed a decrease in hardness with increase in applied load and are also averaged in Curve III. The decrease now, if a function of a surface layer, might result from a hydride layer, which could be a consequence of the etching. The block was wrapped in a double envelope of sheet zirconium and annealed at 350°C (660°F) for 20 hours. This is a temperature high enough to dissolve hydrogen present as the hydride into zirconium,^{7,8} and a time long enough to permit for uniform distribution in the block. The hardnesses were again sufficiently close to those of the last two treatments to enable the values from all three to be averaged together in Curve III. The standard deviations of these points ranged from 1.3 to 4.8 for loads from 2.5 and above. The standard deviation calculated from the hardnesses obtained on the Vickers Machine at an indenter load of 1 kilogram was again considerably higher than those obtained at higher loads, ± 21 . This increase in standard deviation with decreased load is a function of the hardness testing machine used.⁹ All of these aforementioned hardnesses were obtained on a Vickers Hardness Tester. Hardness indentations at 1 kilogram load made on the same block of material using a Wilson Tukon Hardness Tester gave a standard deviation of only 3.5. Also, the indicated decrease in DPH with increase in load obtained from the Vickers machine data was substantiated by hardnesses obtained on the Wilson Tukon Tester.

This dependence of DPH number on applied load is not a function of testing machine, indenter or operator. A series of load vs hardness

measurements were taken on a block of annealed steel using the same combination of machine, indenter, and operator. This series showed no statistical difference between the hardnesses over the load range 1 - 50 kilograms. Therefore it is concluded that only those DPH numbers obtained on zirconium at indentation loads greater than approximately 5 kilograms are likely to be representative of true hardness of the material.

IV. CONCLUSIONS

1. The creep strength of "annealed" unalloyed zirconium is a function of the state of anneal, measured by reduction in hardness level, which takes place on heat treating beyond the point where the material is "completely recrystallized" as evaluated by metallographic examination.

2. The increase in creep rate with stress for zirconium vacuum annealed to a hardness level of: (1) 92.5 ± 2.5 DPH is a factor of 10 for a 2000 psi increase, (2) 88 ± 4.6 DPH is approximately a factor of 10 for a 500 psi increase, and (3) 73 ± 2.2 DPH is approximately a factor of 10 for a 70 psi increase, in the most sensitive range.

3. The tensile strength of unalloyed zirconium decreases 10,000 psi at room temperature and 5,000 psi at 316°C (600°F) for a decrease in hardness from 92.5 ± 2.5 to 73 ± 2.2 DPH.

4. Yield strength is less sensitive to minor variations in hardness but decreases in the hardness range investigated approximately 2000 psi.

5. The indentation hardness (DPH) of unalloyed zirconium is a function of the load applied in making the hardness reading below 5 kilograms.

6. DPH numbers taken at loads above 5 kilograms are considered to be reproducible approximations to the hardness of unalloyed zirconium if the surface is stress free.

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REFERENCES

1. W. A. Bostrom and S. A. Kulin, "Recovery of Cold Worked Zirconium," WAPD-T-23, Nov. 15, 1953.
2. R. K. McGeary and B. Lustman, "Kinetics of Thermal Reorientation in Cold Rolled Zirconium," J. Metals, Feb., 1953.
3. C. R. Simcoe and W. L. Mudge, Jr., "Tensile Properties of Zirconium and Zirconium Alloys," WAPD-38, Nov. 20, 1951.
4. M. J. Manjoine and N. D. Pollack, "Creep Rupture Tests of WAPD Grade I Iodide Crystal Bar Arc-Melted Zirconium at 260°C," WAPD-39, Nov. 24, 1951.
5. W. L. Mudge, Jr., "Summary of Materials Specifications Mechanical Property Testing of Mark I Zirconium Strip," WAPD-MM-138, Aug. 29, 1952.
6. K. M. Goldman and D. E. Thomas, "General Corrosion of WAPD Crystal Bar Zirconium, Part II," WAPD-RM-113, March 14, 1952.
7. W. L. Mudge, Jr., "Effect of Hydrogen on the Embrittlement of Zirconium and Zirconium-Tin Alloys". WAPD-55, Aug. 9, 1952.
8. R. W. Dayton, et al, "Hydrogen Embrittlement of Zirconium" BMI-767 Aug. 22, 1952.
9. B. W. Mott and S. D. Ford, "Microhardness Testing of Metals, Parts I and II," A.E.R.E. M/R 1017, Sept. 23, 1952.

APPENDIX IHARDNESS CONVERSION CHART FOR ZIRCONIUM BASE ALLOYS

The ease and rapidity with which indentation hardnesses can be made is reason enough for use of this test as a semi-quantitative mechanical property measure. Inasmuch as a number of different hardness tests are in usage throughout industry, a conversion from one to any other is often a pre-requisite for comparison of materials. The conversion of the hardness number from one scale to another is based on experimental determinations for any group of allied metals or alloys.

Hardnesses were obtained on 30 different zirconium base alloys, the most highly alloyed containing only 5 weight percent of the additive element. All specimens were machined flat and parallel to a fine finish and were then annealed at 800°C (1420°F) for 3/4 hour in a vacuum of less than 0.03 microns. The specified indentors, loads, and times listed in the equipment manufacturers literature and in the ASM Metals Handbook were used.

This conversion chart was obtained by plotting DPH numbers against each of the other hardness numbers, drawing the best curve through the data and reading off values at chosen DPH levels.

HARDNESS CONVERSION CHART
FOR ANNEALED ZR AND ZR ALLOYS

DPH 50 Kg	ROCKWELL			ROCKWELL SUPERFICIAL				BRINELL	
	A	B	C	30T	30N	15T	15N	500 Kg	3000 Kg
250	-	-	30.0	-	-	-	-	-	221.0
240	-	-	26.5	81.5	45.5	93.0	71.0	168.0	215.0
230	60.0	100.0	23.0	81.0	43.5	92.5	70.0	164.0	209.0
225	59.5	99.5	21.5	80.5	42.5	92.0	69.5	162.0	206.0
220	59.0	99.0	20.0	80.0	41.5	-	68.5	160.0	203.0
215	58.5	98.0	18.5	79.5	40.5	91.5	68.0	157.5	200.0
210	58.0	97.0	17.0	79.0	39.0	91.0	67.5	155.0	197.0
205	57.0	96.0	15.5	78.5	38.0	-	67.0	152.0	193.5
200	56.5	95.0	14.0	78.0	37.0	90.5	66.0	149.5	190.0
195	56.0	94.0	13.0	77.0	35.5	90.0	65.5	146.5	187.0
190	55.0	93.0	11.5	76.5	34.5	89.5	64.5	144.0	183.5
185	54.5	92.0	10.5	76.0	33.0	89.0	64.0	140.5	180.0
180	54.0	90.5	9.0	75.0	32.0	-	63.0	137.0	176.0
175	53.0	89.5	8.0	74.0	30.5	88.5	62.0	134.0	172.5
170	52.5	88.0	6.5	73.0	29.0	88.0	61.5	130.5	169.0
165	51.5	87.0	5.5	72.0	27.5	87.5	60.5	127.0	165.0
160	51.0	85.5	4.0	71.0	26.0	87.0	59.5	124.0	161.0
155	50.0	84.0	3.0	70.0	24.5	86.0	58.5	120.5	157.5
150	49.5	82.0	2.0	69.0	23.0	85.5	57.5	117.0	153.5
145	48.5	80.0	-	67.5	21.5	85.0	57.0	113.5	149.5
140	47.5	78.0	-	66.0	20.0	84.0	56.0	110.0	145.0
135	46.5	76.0	-	64.5	18.0	83.5	55.0	106.5	141.0
130	45.5	74.0	-	63.0	16.5	82.5	53.5	103.0	136.5
125	44.5	72.0	-	61.5	14.5	82.0	52.5	99.0	132.0
120	43.0	69.5	-	59.5	12.5	81.0	51.0	95.5	127.5
115	41.5	67.0	-	57.5	10.5	80.0	50.0	92.0	123.0
110	40.0	64.0	-	55.5	8.5	79.0	48.5	88.0	118.0
105	38.5	61.0	-	53.5	6.0	78.0	47.0	84.0	113.0
100	36.5	57.0	-	51.0	3.5	77.0	45.0	80.0	108.5
95	34.5	53.0	-	48.5	1.0	76.0	43.5	77.0	104.0
90	32.0	48.0	-	46.0	- 1.5	75.0	41.5	73.0	99.0
85	30.0	42.5	-	43.5	- 5.0	73.5	39.5	69.0	94.0
80	27.5	36.0	-	40.5	-	72.0	37.5	65.0	88.0
75	24.5	29.0	-	37.5	-	70.5	35.5	61.0	83.0
70	22.0	21.0	-	34.5	-	69.0	33.5	57.0	77.5
65	-	-	-	31.5	-	67.0	31.5	53.0	72.0
60	-	-	-	28.5	-	65.0	29.0	-	-
55	-	-	-	-	-	-	-	-	-
50	-	-	-	-	-	-	-	-	-

All relative values are averages of tests on annealed zirconium and various alloys.

TENSILE CREEP SPECIMEN

FIG.1

WAFD-T-46

21-5410-20

Fig. 5-260°C Strengths vs. Hardness