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BETTIS PLANT

PITTSBURGH, PA.

Operated for the U. S. Atomic Energy Commission by
Westinghouse Electric Corporation

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THE EFFECT OF HOT WORKED THICKNESS ON THE CORROSION
BEHAVIOR OF ATMOSPHERE-MELTED ZIRCALLOY-2

S. KASS

WAPD

Zircaloy-2 strip is purchased in the dimensions required for the end use of the material. Thus, strip intended for cladding is rolled to 160 - 190 mils thickness, end support stock is fabricated to 220 - 260 mils thickness, and other component stock may be fabricated to 400 - 500 mils thickness. Strip-acceptance coupons and quality-determination corrosion coupons are generally prepared by machining approximately 10 - 20 mils from each major surface. Their thicknesses, therefore, are approximately the same as the as-received material.

A cursory examination was made of Bettis 14-day, 750°F, 1500-psi steam corrosion test data from coupons of strip fabricated from ingots atmosphere-melted by Allegheny Ludlum and Firth Sterling with U. S. Bureau of Mines and Carborundum sponge. This examination showed that either the corrosion weight gains tend to increase with increasing strip or sample thickness, or the corrosion properties of atmosphere-melted Zircaloy-2 improve with increasing hot-work. Inasmuch as prior experiments demonstrated that the corrosion of Zircaloy-2 is not influenced by specimen thickness per se, it was postulated that the effects noted were the result of increased hot-working.

A review of the long-term corrosion behavior of argon-atmosphere-melted Zircaloy-2 was undertaken to confirm the trends of improved corrosion resistance with increased hot-work. It was felt that if the trends were substantiated, it would be mandatory to redefine the corrosion acceptance weight gain ($28 \pm 10 \text{ mg/cm}^2$) with respect to the fabricated strip thickness, since the standard value was obtained from material fabricated by hot-work to 90 - 160 mils thickness.

MATERIALS AND COUPONS

The corrosion data included in the review represent Zircaloy-2 ingots melted at the Allegheny Ludlum Steel Corp. and Firth Sterling Inc. from sponge zirconium produced at the U. S. Bureau of Mines and the Carborundum Metals Co. The coupons were machined from the as-received stock to a 63-rms finish. Most of them were either 1.5-in. x 1.0-in. x thickness, or 1.0-in. x 0.5-in. x thickness.

Also included in the review were coupons representing fuel elements fabricated from ingots supplied by the above sponge producers and alloy melters. The fuel element coupon surfaces were not machined.

TESTING PROCEDURE

Corrosion tests were performed in 750°F steam at 1500 psi and in 680°F water according to Bettis Plant specifications (Ref. 1). Upon completion of each test cycle, the coupon weight gains were obtained, and the coupons were returned to test without disturbing or removing the surface oxide films.

DATA ANALYSIS AND RESULTS

The evaluation of the life-test data included the computations of the mean weight gain in mg/dm^2 and standard deviation (σ) for each classification of coupon thickness after 14, 28, 56, 84, 112, and 140 days exposure in 750°F steam.

The results of a statistical analysis of the data thus obtained are presented in Table I. Several interesting items should be noted:

1. After a 14-day exposure to 750°F steam, the 95% confidence interval for the average for dimension C includes the 95% confidence interval for dimension D, while the confidence intervals for dimensions A and B are distinct from each other and from C and D. This indicates that, statistically, it is relatively safe to assume that the averages of A, B, and C, when combined with D, are different, although an exact probability of statement is not available.
2. After continued exposure in 750°F steam, (for a minimum of 56 days) the confidence interval for A includes B, the interval for C continues to include D, and the intervals A-B and C-D are distinct from each other. Therefore, the averages of weight gains from thickness ranges of atmosphere-melted Zircaloy-2 less than 200 mils thick and from 200 - 500 mils thick will differ.

The weight gain and range values of atmosphere-melted Zircaloy-2 raw materials conform to the following table:

Strip Thickness* (mils)	Nominal Weight Gain (mg/dm ²)	Range (mg/dm ²)
less than 125	25	20 - 30
126 - 200	28	18 - 38
201 - 500	31	19 - 43

On the basis of this investigation, consideration is being given to incorporating the effect of strip thickness on corrosion weight gain in the specifications for Zircaloy-2.

ACKNOWLEDGMENT

The author would like to thank A. S. Covert for performing the statistical analysis.

REFERENCE

1. S. Kass, "Corrosion Testing of Zircaloy-2 and Zircaloy-3," WAPD-TM-97, October 1957.

* As obtained by hot-work.

TABLE I
SUMMARY OF STATISTICS

Dimension			Days of 750°F Test					
			14	28	56	84	120	140
1. Under 125 mils	A	n	22	17	26	23	19	22
		$\bar{x}$	25.3	33.3	49.9	66.0	74.8	86.4
		L	24.6	32.3	48.1	64.9	76.7	87.9
			26.0	34.4	51.3	67.1	76.7	87.9
		S	1.5	2.1	3.6	2.5	3.9	
2. 126 to 200 mils	B	n	355	280	46	31	29	
		$\bar{x}$	28.1	37.7	50.5	66.4	75.6	
		L	27.8	37.1	48.7	64.1	72.9	
			28.5	38.3	52.2	68.6	78.4	
		S	3.5	5.1	5.9	6.0	7.3	
3. 201 to 300 mils	C	n	116	103	58	69	62	
		$\bar{x}$	31.0	41.1	53.2	70.6	83.3	
		L	30.3	39.6	51.0	69.1	80.2	
			31.7	42.5	55.5	72.2	86.3	
		S	3.7	7.5	8.6	6.2	12.0	
4. 301 to 500 mils	D	n	56	71	20	22	26	
		$\bar{x}$	31.1	44.8	52.8	71.7	84.4	
		L	29.9	42.6	48.8	67.9	78.4	
			32.3	47.0	56.9	75.5	90.4	
		S	4.4	9.3	8.7	8.6	14.8	

n = number of samples per observation

$\bar{x}$ = mean weight gain, mg/dm²

L = 95% confidence interval for average

S = standard deviation

HYDROGEN PICKUP UPON ETCHING OF ZIRCALLOY-2 AND ZIRCALLOY-3

E. HILLNER

WAPD

An experiment was conducted to determine if there is any appreciable hydrogen pickup when samples of Zircaloy-2 and Zircaloy-3 are etched.

Fifty-two samples, measuring approximately 0.25-in. x 0.25-in. x 0.15-in., were prepared from recently fabricated material, etched, and then vacuum degassed for 24 hr at 950°C. Several control samples were sent directly for hydrogen analysis. Other control samples were abraded to remove at least 2 mils from each surface and then sent for analysis. The remaining specimens were immersed in a 5% HF, 35% HNO₃, 60% H₂O etching solution, and two samples were removed every 20 seconds. One was washed, dried and sent for hydrogen analysis; the other was washed, dried, and abraded until 2 mils were taken off each surface

prior to being sent for analysis. This procedure was followed so that the results obtained from both types of samples could be compared to determine whether hydrogen pickup was concentrated within a thin layer beneath the surface. The final samples were subjected to 200 sec in the etching bath.

All of the control samples, abraded and unabraded, had hydrogen levels of approximately 4 ppm. The hydrogen content of etched samples was found to be independent of etching time and abrading and equal to the value of that found for the control samples. It is concluded that there is no appreciable hydrogen pickup upon etching of recently produced Zircaloy-2 and Zircaloy-3 material.

HYDROGEN CONTENT AS A FUNCTION OF TIME IN ETCHING BATH

Time in Etching Bath (sec)	Condition	H ₂ Concentration (ppm)	
		<u>Zircaloy-2</u>	<u>Zircaloy-3</u>
0	Unabraded	4	3
0	Abraded	4	8
20	Unabraded	2	3
20	Abraded	4	3
40	Unabraded	2	3
40	Abraded	3	2
60	Unabraded	3	2
60	Abraded	3	3
80	Unabraded	3	2
80	Abraded	5	3
100	Unabraded	4	2
100	Abraded	5	5
120	Unabraded	3	4
120	Abraded	2	2
140	Unabraded	3	4
140	Abraded	5	4
160	Unabraded	4	4
160	Abraded	4	6
180	Unabraded	3	4
180	Abraded	3	3
200	Unabraded	3	-
200	Abraded	3	5

PROPERTIES OF VACUUM-CAST ZIRCALOY-2

C. V. ZABIELSKI AND L. S. RUBENSTEIN

WAPD

The April issue of Zirconium Highlights (WAPD-ZH-6) outlined a program for the comprehensive evaluation of vacuum-skull-melted reactor components which were

cast from suitable reactor-grade scrap (Ref. 1). This article presents a summary of some mechanical and corrosion properties of the cast product. Typical casting configurations are shown in Fig. 1.

The mechanical test data obtained from tensile and impact specimens removed from each wall of two square-walled castings are summarized in Table I. Typical, acceptable tensile and impact values of wrought Zircaloy-2 are included for comparison. In Table II, 56-day, 750°F, 1500-psi steam corrosion data are presented from both surface and interior specimen. In addition to corrosion test specimens, four castings were subjected to the same test conditions for three days in the as-machined condition. These yielded the continuous black lustrous film commonly associated with good corrosion resistance.

A review of dimensional, chemical, metallographic, radiographic, and weldability data showed the castings to be acceptable for reactor use.

The utilization of castings in reactor cores will reduce core production costs through the use of additional scrap and increased yields.

TABLE I

COMPARISON OF TENSILE AND IMPACT PROPERTIES OF CAST AND WROUGHT ZIRCALOY-2

<u>Tensile Properties</u>						
	<u>Test Temp. (°C)</u>	<u>No. of Specimens and Direction</u>	<u>0.2 Yield Strength (psi)</u>	<u>Tensile Strength, (psi)</u>	<u>% Elong. in 2-in.</u>	<u>R.A. (%)</u>
Cast	R.T.	15	55,500	74,500	21.6*	29.3
	260	13	30,100	42,100	25.5*	45.2
Wrought	R.T.	Long.	35,000	60,000	14.0	23.0
	R.T.**	Trans.	51,000	57,000	15.0	31.0
	260	3, Long.	20,700	34,800	36.0	64.0
	260	3, Trans.	25,500	34,100	32.5	49.5
<u>Impact Properties</u>						
	<u>Test Temp. (°C)</u>	<u>No. of Specimens and Direction</u>	<u>ft/lb</u>			
Cast	R.T.	16	6.6			
	260	16	24.2			
Wrought	R.T.	3, Long.	5.2			
	R.T.	3, Trans.	2.0			
	260	3, Long.	22.8			

* Elongation, % in 3/4-in.

** Suggested Values for MIL-Z-19859, (revised)

Fig. 1 Typical Vacuum-Cast Zircaloy-2 Configurations

TABLE II

56-DAY, 750°F, 1500-psi STEAM CORROSION DATA

<u>Two Lower Brackets</u>	<u>No. of Coupons</u>	<u>Average Weight Gain (mg/dm²)</u>	<u>Range (mg/dm²)</u>
As-cast surface	4	63	61 - 64
15 mils removed from surface	4	62	59 - 65
30 mils removed from surface	4	62	58 - 67
45 mils removed from surface	4	59	56 - 58
As-cast, 150 mils thick	16	62	58 - 74
<u>Two Upper Brackets</u>			
As-cast, 150 mils thick	8	57	46 - 69

ACKNOWLEDGMENT

Some of the information on forged Zircaloy-2 bar was derived from work done by W. H. Friske and C. V. Zabielski of Bettis Plant.

REFERENCE

1. C. V. Zabielski, "A Program for Evaluation of Zircaloy-2 Castings," Zirconium Highlights, WAPD-ZH-6, April 1958, pp. 8-9.

FABRICATION OF SPECIAL SHAPES

D. ZUCKER

WAPD

During fiscal 1958 a study was initiated to determine methods of fabricating Zircaloy special shapes to required geometric and dimensional tolerance for use in reactor applications. These development products were to be shapes other than common hot-rolled strip or plate requiring subsequent machining. This investigation conformed with the continuous Bettis effort to reduce costs. These shapes which are required for a variety of applications in the Bettis development program fall into two major categories: 1) complex shapes which were fabricated by extrusion and either cold-drawing or simple stretch-straightening, and 2) rectangular shapes with precision tolerances fabricated by cold-rolling and slitting, Turk's head rolling, and cold-drawing. Figure 1 presents some typical configurations formed by these methods with the desired tolerances.

TYPICAL EXTRUDED SHAPES

RECTANGULAR SHAPES BEING PRODUCED BY THE METHODS INDICATED BELOW EACH DRAWING;
ALL UNIFORMLY $0.102 \text{ IN.} \pm 0.002 \text{ IN.}$ THICK

Fig. 1 Typical Special Shapes

ZIRCONIUM DATA SHEET

HARDNESS CONVERSION CHART FOR ANNEALED ZIRCONIUM AND ZIRCONIUM ALLOYS

(Source: Ref. 1)

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	--	--	--	--	--	--	--	--	--

Hardnesses were obtained on 30 different zirconium base alloys, the most highly alloyed containing only 5 w/o of the additive element. All specimens were machined flat and parallel to a fine finish and were then annealed at 800°C (1470°F) for 45 min 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.

REFERENCE

1. W. L. Mudge, Jr., "The Mechanical Properties and Microstructure of Annealed Zirconium," WAPD-T-46, June 1953.

MISCELLANY

Individuals of contributing organizations are encouraged to comment on the articles published in Zirconium Highlights by presenting a written discussion for inclusion in the Miscellany Section.

Contributing organizations are encouraged to submit titles of recent papers on the technology of zirconium and zirconium alloys which are unclassified and available through commercial sources or O.T.S. for listing in Zirconium Highlights.

A Recent Publication Available Through O.T.S.

E. B. Friedl, W. E. Berry, P. D. Miller, F. W. Fink, "The Nitric Hydrofluoric Acid Pickling of Zircaloy-2," BMI-1270, June 11, 1958.