BATTELLE MEMORIAL INSTITUTE

THE TRANSFER OF IMPURITIES IN
ZIRCONIUM PREPARED BY THE DE BOER PROCESS

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SUMMARY

Approximately 50 pounds of iodide-deposited zirconium were produced in an 8-inch-diameter Hastelloy B de Boer bulb for use in preparing feed materials of controlled composition. Twelve pounds of this metal had good corrosion resistance throughout the entire length of the hairpin. The four initial runs in this unit produced material which was high in titanium (up to 4800 ppm.) and was not corrosion resistant. Iodide-deposited titanium had been prepared in this unit prior to its use in this work, and although care was taken to clean it out thoroughly before it was used to prepare zirconium, some residual titanium-bearing material was undoubtedly left in the unit. With continued use of the unit, the corrosion resistance of the resulting zirconium crystal bars increased.

The transfer of iron, titanium, aluminum, nitrogen, carbon, silicon, nickel, and chromium from the feed stock to the crystal bar by the de Boer process was studied. The feed materials were prepared by making binary alloys of these elements with iodide-deposited zirconium from the 8-inch-diameter de Boer bulb. In addition to these alloys, high-carbon sponge zirconium and high-temperature vacuum-sintered sponge zirconium were also used in the experiments described here.

Noncorrodible zirconium was also used as feed stock to determine the effect of redeposition on the purity and corrodibility of the product. Several runs produced zirconium of good corrosion resistance and the purity of the product was essentially the same as that of the starting material.

Experiments were made using sponge zirconium with various additions of iodine on the deposition of zirconium. It was shown that the rate of deposition of zirconium and the transfer of impurities were not affected by the iodine concentration.

INTRODUCTION

This report summarizes results of an investigation conducted during the period from December 1, 1949 to December 15, 1950, of the transfer of impurities in the de Boer process for the preparation of zirconium crystal bar.

In studying the factors influencing the transfer of impurities, known amounts of metallic and nonmetallic impurities normally present in sponge zirconium were added to iodide-deposited zirconium by arc and induction-melting techniques.

The resultant alloys were then used as feed materials in preparing small crystal bars to determine the carry-over of various impurities.

Since iodide-deposited zirconium was in short supply, it was necessary to prepare the material required for this work. This metal was produced in an 8-inch-diameter de Boer unit.

EXPERIMENTAL WORK

Equipment and Experimental Procedures

The iodide-deposited zirconium required for this investigation was prepared in a metal de Boer bulb, constructed of Hastelloy B,

nickel-molybdenum-iron alloy produced by the Haynes-Stellite Corporation. The bulb is 54 inches long and 8 inches in diameter and is capable of producing two "hairpin" crystal bars, each 8 feet long.

In the study with feed materials of controlled composition, small Pyrex de Boer bulbs were used. These bulbs were 4 inches in diameter and 12 inches long and produced a single crystal bar, 20 inches in over-all length. A schematic diagram of one of these bulbs is shown in Figure 1.

The feed materials are held in the annular space formed by the bulb shell and a perforated molybdenum-sheet cylinder. The zirconium metal is deposited on fine tungsten wire in these de Boer bulbs.

Once the feed stock is charged into the bulb and the starting filament is attached to the electrodes, the bulb is heated to 480-540°C., and evacuated to remove residual gases. It is then cooled, and a small amount of iodine is admitted into the bulb. The bulb is then heated to 170°C. at which temperature the iodine and zirconium react to form zirconium tetraiodide. After the iodide is formed, the temperature of the bulb is raised to 300-425°C., the operating temperature range. Current is then passed through the filament until it is hot enough to decompose the zirconium tetraiodide. The filament temperature is regulated by keeping constant the product of the potential in volts and the cube root of the current in amperes.

Deposition on the heated filament is then continued until the desired filament size is reached. The bulb is cooled, and argon or helium is admitted into the bulb before removing the crystal bar.

FIGURE I. EXPERIMENTAL PYREX DE BOER BULB

Preparation of Zirconium in the
8-Inch-Diameter de Boer Bulb

A total of 40 pounds of metal was made in the 8-inch-diameter de Boer bulb for use in preparing feed materials of controlled compositions. The zirconium was in the form of hairpins, 8 feet in over-all length, and was deposited on 0.007-inch-diameter tungsten wire. Chemical and spectrographic analyses were run on material taken from these deposits, and samples were removed from various locations along the length of the hairpins, and subjected to two weeks' corrosion tests in 600°F. water. Table 1 contains the results of these tests and the analysis of the crystal bars.

Twelve pounds of this material was judged to be of good corrosion-resistant quality over the entire length of the hairpins. The corrosion resistance of the balance of the material varied from good to poor over the length of the hairpins. This material was considered to be of questionable quality for use in preparing feed materials of controlled compositions by either arc or induction-melting techniques.

Transfer of Impurities

A study of the transfer of impurities from the feed to the crystal bar was made using controlled composition feed materials. These feed materials were prepared by alloying iron, titanium, nitrogen, aluminum, silicon, nickel, and chromium successively with iodide-deposited zirconium. Other types of feed materials used in this study were high-carbon induction-melted sponge zirconium and high-temperature vacuum-sintered sponge zirconium. Table 2 summarizes the results of these experiments and indicates the run

9

TABLE 1. SUMMARY OF RESULTS ON THE PREPARATION OF ZIRCONIUM
IN THE 8-INCH-DIAMETER METAL DE BOER UNIT

BMI Run No.	Results of Chemical and Spectrographic Analysis of Feed Materials and Crystal Bars*, Determinations - Parts Per Million									Results of Standard Corrosion Tests on Crystal Bars (Two Weeks' Exposure in 600°F. Water)	Remarks ⁽¹⁾
	Ti	Al	Fe	Mg	Na	Ca	Si	C	N		
Bureau of Mines sponge zirconium, Lot No. 1	5	100	110	8000	40	<10	—	—	—	—	—
4989-3(2)	1600- 4800	100	130- 170	10- 30	20- 40	<10	—	—	—	Poor	Equipment formerly used to prepare titanium metal; titanium products were apparently not completely removed.
4989-11(2)	795- 1300	<1- 300	9- 68	<5	<25	—	30	—	10- 22	Poor	Metal showed improvement by heat-tint tests; titanium content lower.
4989-14(2)										Poor	Oil leak developed during run, stopping deposition and ruining feed material.
Bureau of Mines sponge zirconium, Lot No. 2	830	680	1100	5000	30	—	700	—	—	—	—
4989-18(3)	290	150	900	42	50	—	400	—	—	Poor	First run on new feed.
4989-21(3)	55	50	200	21	100	40	70	—	—	Poor	Second run on this feed.
4989-24(3)										Poor	Filament burned out at 115 amperes and was left in bulb while deposition took place on second filament.
4989-25(3)										—	Bulb was not opened after first filament burned out. This filament burned out at 94 amperes.
4989-27(3)										Poor	Slight oil leak developed during run. Filament burned out at 160 amperes.
4989-32(3)	90	100	100	20	<20	60	150	170	<20	Poor	Feed material was removed from bulb and washed thoroughly with water before this run was made.
4989-34(3)	80	50	100	—	<20	60	150	900	<20	Good	Seventh run on same feed.
4989-36(3)	90	50	100	—	<20	60	20	200	<20	Poor	Eighth run on same feed.
4989-39(3)	120	50	100	—	<20	60	80	200	<10	Good	Ninth run on same feed.
4989-42(3)	100	100	450	80	<20	—	350	200	10	Good	Tenth run on same feed.
4989-44(3)	100	100	200	20	30	—	20	200	20	Poor	Eleventh run on same feed.
4989-45(3)	100	100	150	20	<20	—	20	200	<10	Poor	Twelfth run on same feed.

TABLE 1. (Continued)

10

BMI Run No.	Results of Chemical and Spectrographic Analysis of Feed Materials and Crystal Bars*, Determinations - Parts Per Million									Results of Standard Corrosion Tests on Crystal Bars (Two Weeks' Exposure in 600°F. Water)	Remarks (1)
	Ti	Al	Fe	Mg	Mn	Ca	Si	C	N		
Foots Mineral Company's sodium-reduced sponge zirconium, Lot No. 912-S-5-S	50	350	4500	250	<20	—	500	—	—		
4989-51(4)	10	50	300	10	<20	50	80	300	10	Good	First run on this feed.
4989-57(4)	30	10	1500	10	10	10	100	200	40	Poor	Second run on same feed.
4989-59(4)	50	70	2275	25	<10	40	90	300	40	Good	Third run on same feed.
4989-62(4)	50	75	2500	40	<10	35	90	300	10	Good	Fourth run on same feed.
4989-66(4)	30	90	850	40	<10	100	80	200	10	Good	Feed washed with water and additional feed from same lot added to bulb before this run was made.
4989-67(4)	40	90	1025	30	<10	30	100	300	<10	Good	Second run on washed feed.
4989-68(4)	25	75	1340	30	<10	40	100	200	10	Good	Third run on washed feed.
4989-69(4)	30	70	1100	45	<10	70	110	400	20	Poor	Fourth run on washed feed.

(1) Metal deposited on 0.007-inch-diameter tungsten filament in all runs.

(2) Crystal bar prepared from Bureau of Mines sponge zirconium, Lot No. 1.

(3) Crystal bar prepared from Bureau of Mines sponge zirconium, Lot No. 2.

(4) Crystal bar prepared from Foots Mineral Company's sodium-reduced sponge zirconium, Lot No. 912-S-5-S.

*Analyses of crystal bars for other determinations in parts per million are:

Hf - 7100 to 27,000; Mn - <1 to 70; Cu - 3 to 218; Cd - <1 to <10; B - <0.1 to 5; Sn - <5 to 10; Mo - <1 to 10.

TABLE 2. SUMMARY OF EXPERIMENTS ON THE TRANSFER OF IMPURITIES
FROM THE FEED TO THE CRYSTAL BAR IN THE PIREX DE BOER
BULBS

BMI Run No.	Feed Material ⁽¹⁾	Results of Chemical and Spectrographic Analysis ⁽²⁾ Determinations - Parts per Million									Filament Constant ⁽³⁾ , $K = EI^{1/3}$, Per Inch of Filament Length	Bulb Temp., °C.	Results of Standard Corrosion Tests, (Two Weeks' Exposure)	Remarks ⁽⁴⁾
		Ti	Al	Fe	Mg	Bi	Cr	Si	C	N				
4989-84	Arc-melted iodide zirconium plus 2900 ppm. (0.25%) titanium	2500	50	750	10	<10	5	200	110	130	1.8	320-350	Poor	The arc-melted alloy was machined into chips and charged into the bulb.
		2100	80	200	<10	80	<10	170	210	<10				
5319-12	Ditto	3700	50	300	<10	5	15	50	210	<20	1.25	215-230	Poor	Second run on this feed.
5319-17	"	2400	50	60	10	<5	10	10	180	<10	2.4	305-325	Poor	Third run on this feed.
5319-25	"	2400	40	70	10	<5	10	80	190	<20	1.6	210-230	Poor	Fourth run on this feed.
4989-99	Arc-melted iodide zirconium plus 1000 ppm. (0.10%) iron	90	50	1230	10	<10	5	200	70	210	1.5	300-330	Poor	The arc-melted ingot was machined into chips and charged into the bulb.
		170	50	290	10	<5	10	50	90	<10				
5319-6	Ditto	380	180	250	10	<5	10	150	150	<10	1.5	300-310	Poor	Second run on this feed.
5319-15	"	110	120	370	10	<5	<10	100	220	30	1.7	200-225	Good	Third run on this feed.
5319-26	"	60	30	260	10	<5	<10	80	280	20	2.1	200-220	Good	Fourth run on this feed.
4989-86	Induction-melted iodide zirconium plus 1000 ppm. (0.10%) nitrogen	140	280	300	100	20	<20	150	1600	1200	1.5	290-310	Poor	Nitrogen was added to zirconium crystal bar by thermal diffusion and then induc- tion melted in a graphite mold. The ingot was machined into chips.
		30	50	110	12	<5	20	50	100	80				Second run on this feed.
4989-94	Ditto	65	80	100	15	<5	10	80	80	<10	1.5	310-340	Poor	
5319-10	Arc-melted iodide zirconium plus 1000 ppm. (0.10%) aluminum	130	1100	>500	10	30	50	150	150	<10	1.4	315-325	Poor	The arc-melted ingot was machined into chips.
		380	800	50	<10	<5	<20	150	160	<20				
5319-16	Ditto	130	800	60	10	<5	<10	120	210	<10	1.4	200-240	Poor	Second run on this feed.
5319-20	"	110	800	150	10	20	50	30	320	<10	1.9	305-320	Poor	Third run on this feed.
5319-23	"	190	700	280	10	10	60	300	520	<10	1.2-1.9	200-220	Poor	Fourth run on this feed.

TABLE 2. (Continued)

BMI Run No.	Feed Material ⁽¹⁾	Results of Chemical and Spectrographic Analysis ⁽²⁾ Determinations - Parts per Million									Filament Constant ⁽³⁾ $K = EI^{1/3}$ Per Inch of Filament Length	Bulb Temp., °C.	Results of Standard Corrosion Tests, (Two Weeks' Exposure)	Remarks ⁽⁴⁾
		Ti	Al	Fe	Mg	Ni	Cr	Si	C	N				
4989-100	High-carbon (0.29%) Bureau of Mines zirconium ingot	53	35	415	10	<5	15	50	2900	35	1.4	305-325	Poor	Ingot was machined into chips for use as feed material.
		60	80	160	10	<5	10	50	60	<10				
5319-5	Ditto	140	200	50	10	<5	10	80	140	<10	1.1	305-325	Poor	Second run on same feed stock.
5319-13	"	80	100	130	<10	5	15	50	120	15	1.1	195-225	Good	Third run on same feed stock.
5319-18	"	80	50	170	10	<5	<10	30	310	<10	1.5	205-215	Good	Fourth run on same feed stock.
5319-42	Arc-melted iodide zirconium plus 1000 ppm. (0.1%) chromium	<10	40	140	<10	10	about 1000	60	260	<20	1.75	360-390	—	Alloy prepared by arc-melting corro- sion-resistant crystal bar with chromium. Ingot was machined into chips.
		<10	100	110	10	5	20	200	80	<10				
5319-47	Ditto								<50	<5	1.7	360-390	—	Duplicate run.
5319-44	Arc-melted iodide zirconium plus 1000 ppm. (0.1%) silicon	<10	60	120	<10	10	<10	230	320	<20	1.75	360-390	—	Same as 5319-42 except silicon was added.
		50	80	120	10	10	20	170	80	<5				
5319-49	Ditto								<50	<5	1.75	369-390	—	Duplicate run.
5319-46	Arc-melted iodide zirconium plus 1000 ppm (0.10%) nickel	<10	40	170	<10	about 1000	<10	80	310	10	1.75	360-390	—	Same as 5319-42 except nickel was added.
		50	90	110	<10	10	20	160	100	25				
5319-50	Ditto								<50	2800	1.75	360-390	—	Bulb leaked air at end of run.
5319-43	Arc-melted iodide zirconium plus 1000 ppm. silicon, 1000 ppm. iron, and 1000 ppm. aluminum	<10	950	1080	20	10	20	1100	370	20	1.6	360-390	—	Same as 5319-42 except silicon, iron, and aluminum were added.
		<10	810	130	20	5	10	130	70	<10				
5319-48	Ditto								<50	<5	1.7	360-390	—	Duplicate run.
4989-89	High-temperature vacuum-sintered sponge zirconium (D-38) obtained from Argonne	10	200	340	550	10	50	300	200	340	3.0	300-340	Poor	—
		29	200	80	10	<5	10	—	100	40				
4989-97	Ditto	<30	30	160	10	<5	15	100	60	10	1.6	300-320	Poor	

Footnotes appear on the following page.

TABLE 2. (Continued)

Footnotes:

- (1) The intended composition of arc-melted feed materials are listed in this column, and the compositions as determined by analysis are shown in the adjacent column.
- (2) Analyses of samples for other determinations in parts per million are: Hf - 7100 to 27,000; Mn - <1 to 140; Cu - <5 to 50; Cd - <1 to <10; B - <1 to 10; Sn - <5 to 10; Mo - <10 to 200.
- (3) The filament temperature was controlled by keeping constant the product of the potential in volts and the cube root of the current in amperes and dividing by the filament length in inches. Accurate measurements of the filament temperature were not available but it is estimated that a "K" of 1.25 corresponds to a filament temperature of roughly 1100°C., and a "K" of 4.00 to a filament temperature of roughly 1700°C. under the conditions of these experiments.
- (4) Zirconium deposited on 0.003-inch-diameter tungsten filament.

number, feed materials, operating conditions, and chemical and spectrographic analyses of the feeds and the deposits.

The analytical results show that the de Boer process for preparing zirconium is an effective method of lowering the amount of certain impurities. Only small amounts of nickel, chromium, and nitrogen were transferred from the feed to the crystal bar. Nickel was reduced in amount from 1600 ppm. in the feed to 10 ppm. in the deposit, chromium from 1000 ppm. to 20 ppm., and nitrogen from 1100 ppm. to 3-82 ppm. The elements which were "reduced" to a lesser extent were: carbon (2900 ppm. to 60-310 ppm.), silicon (1100 ppm. to 130 ppm.), iron (1200 ppm. to 280-390 ppm.), and aluminum (1100 ppm. to 700-800 ppm.). No reduction in the titanium content took place in any of the experiments, and in one case there was actually a higher concentration in the deposit than in the feed.

In addition to those elements which were especially investigated, analytical data disclosed that magnesium is not carried over to the deposit, and that the calcium, copper, and manganese contents are lowered to a certain extent. (Oxygen content is known to be lowered, but oxygen analyses are not included here.)

A zirconium alloy containing 0.1 per cent iron, 0.1 per cent aluminum, and 0.1 per cent silicon was prepared to determine whether the presence of these impurities in larger amounts than those normally present in sponge zirconium would influence their mutual transfer to the deposit. The results show that these elements were carried over to the crystal bar to the same extent as they had been from the binary alloys.

Effect of Iodine Concentration on
the Deposition of Zirconium

A 1200-gram lot of Bureau of Mines sponge zirconium was charged into a Pyrex de Boer unit and crystal bars were prepared in three successive runs utilizing increasing amounts of iodine, i.e., 5, 25, and 50 grams.

The analyses of the starting material and the deposits made in these experiments are given in Table 3. These results show that the amount of impurities transferred to the crystal bar is not affected by the quantity of iodine used in preparing the metal. No noticeable increase or decrease in the rate of deposition of zirconium with increasing iodine concentration was observed in these experiments.

Redeposited Zirconium Crystal Bars

Corrosion-resistant zirconium prepared in the 8-inch-diameter de Boer bulb was used as feed material in the Pyrex bulbs to determine the effect of redeposition on the purity and the corrodibility of the product. The feed material was machined into chips to provide increased surface area for the reaction and was distributed among three bulbs. Small crystal bars were prepared under similar conditions of operation. The analyses and corrosion results obtained from these experiments are listed in Table 4.

Noncorrodible metal was prepared in several runs, although the first run in each bulb produced material of poor corrosion resistance. This was probably due to a slight contamination of the feed material in the machining operation rather than by the lower filament temperatures used in the first experiments.

TABLE 3. EFFECT OF IODINE CONCENTRATION ON THE DEPOSITION OF ZIRCONIUM

EMI No.	Feed Material	Determinations - Parts per Million ⁽¹⁾									Filament ⁽²⁾ Constant, K per Inch of Filament Length	Bulb Temp., °C.	Remarks ⁽³⁾
		Ni	Al	Fe	Ag	Si	Cr	Si	C	N			
5319-40	Bureau of Mines sponge zirconium, B I Lot No. 5B	<10	190	150	7300	10	<10	30	200	25	1.4	360-390	Weight ratio of iodine to sponge zirconium was 1 to 250.
		<10	40	140	10	5	10	30	170	<10			
5317-41	Ditto	<10	100	100	20	5	10	200	170	45	1.4	340-370	Weight ratio of iodine to sponge zirconium was 1 to 50.
5319-45	"	10	90	120	10	10	10	200	30	45	1.5	365-395	Weight ratio of iodine to sponge zirconium was 1 to 25.

(1) See Footnote (2) in Table 2.

(2) See Footnote (3) in Table 3.

(3) Zirconium deposited on 0.003-inch-diameter tungsten filament.

17

TABLE 4. SUMMARY OF EXPERIMENTS ON REDEPOSITED Zr CRYSTAL BAR

Bulb Run No.	Feed Material	Determinations - Parts per Million ⁽¹⁾									Filament ⁽²⁾ Constant K per Inch of Filament Length	Bulb Temp., °C.	Results of Standard Corrosion Tests, Two Weeks' Exposure	Remarks ⁽³⁾
		Ti	Al	Fe	Mg	Ni	Cr	Si	C	N				
5319-27	Corrosion-resistant iodide zirconium, BMI Runs Nos. 4969-51 and -66	10-	50-	300-	10-				200-					
		30	90	850	40	--	--	80	300	10				First run in Bulb A
		(Crystal Bar)												
		40	40	100	10	<5	<10	90	190	15	1.4	295-315	Poor	
5319-34	Ditto	60	60	150	50	<5	<10	100	320	10	2.1	305-320	Good	Second run in Bulb A
5319-39	"	10	40	170	10	10	10	100	70	15	2.5	305-330	Poor	Third run in Bulb A
5319-31	"	130	40	90	20	10	<10	80	280	10	1.4	305-315	Poor	First run in Bulb B
5319-36	"	120	40	130	10	10	<10	90	370	<10	2.3	310-330	Poor	Second run in Bulb B
5319-37	"	90	40	180	10	10	10	90	340	5	2.1	305-315	Good	Third run in Bulb B
5319-28	"	500	50	90	<10	10	<10	90	180	15	1.4	305-325	Poor	First run in Bulb C
5319-35	"	40	40	150	10	40	40	100	330	10	2.1	305-320	Good	Second run in Bulb C

(1) See Footnote (2) in Table 2.

(2) See Footnote (3) in Table 3.

(3) Zirconium deposited on 0.003-inch-diameter tungsten filament.

The iron contents of the redeposited crystal bars are lower than the amounts present in the starting material. Titanium analyses of these materials, although erratic, generally show higher amounts in the deposits than in the feed stock. With the exception of these two elements, the purity of the deposits is about the same as that of the original metal, and redeposition does not lead to a reduction in the amount of impurities in the metal finally produced.