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THE PREPARATION OF LARGE-DIAMETER
ZIRCONIUM CRYSTAL BAR BY THE DE BOER PROCESS

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SUMMARY

Zirconium crystal bars, 8 feet in over-all length and up to 1.68 inches in diameter, have been produced in a 16-inch-diameter, Hastelloy B, de Boer unit, specially constructed for use in this work. Twelve experimental runs were made, producing a total of approximately 220 pounds of large-diameter zirconium crystal bars.

Results of this work have shown that large-diameter crystal bars can be successfully produced in a conventional de Boer apparatus, and that corrosion-resistant metal can be prepared if suitable precautions are taken to avoid contamination of the feed material prior to deposition.

The power consumption in the preparation of large-diameter crystal bar was not considered excessive. Analysis of the data obtained in preparing a crystal bar with an average diameter of 1.62 inches showed that it should be possible to produce such bars at a current consumption of 80-90 kw./hr./pound. Since the power consumption in present commercial practice is 40-60 kw./hr./pound, the additional power consumption does not seem unreasonable in view of other economies that result from use of the large bars in selected operations.

INTRODUCTION

In normal de Boer process operation, crystal bars from 0.25-0.5 inch in diameter were being produced at the time this investigation was initiated. Progress has been made in the preparation of larger bars, however, and, in current practice, bars up to 0.8 inch in diameter are being produced.

The diameter to which the crystal bar is "grown" governs not only the weight of metal which is produced in a given run, but also the size of sheet and other shapes that can be obtained directly from the crystal bar.

The preparation of larger diameter bars presented numerous problems. The most significant of these were associated with the high currents required to heat the bars. These problems included the development of suitable electrode connections, providing adequate power dissipation, and avoiding excessive bowing of the filaments. However, the preparation of larger diameter bars appeared attractive because it offered the possibility of substantial economies in production by reducing the frequency of loading, outgassing, sponge cleanup, and other auxiliary operations, and, in addition, held promise as a means of simplifying fabrication problems.

An investigation of the preparation of crystal bars up to 1.0 to 1.5 inches in diameter was therefore undertaken to determine whether or not the production of the larger diameter bars was feasible.

A 16-inch-diameter de Boer unit was specially constructed for this investigation to provide adequate surface area for dissipating the power required to heat the larger diameter bars and to provide adequate clearance to accommodate unavoidable distortion of the filaments.

EXPERIMENTAL WORK

Equipment

A 16-inch-diameter de Boer bulb, designed to produce zirconium crystal bars in the form of hairpins up to 8 feet in over-all length, and up to 1-1.5 inches in diameter, was constructed for these experiments. A photograph of

this unit is shown in Figure 1, and a schematic diagram of the bulb is shown in Figure 2.

The bulb is constructed of Hastelloy B, a nickel-molybdenum-iron alloy produced by the Haynes-Stellite Company. It is 16 inches in diameter, and 60 inches long. The flange and head sections are made from 1-inch-thick plate, and the body of 1/8-inch sheet. Two 0.8-inch-diameter tungsten electrodes are fastened to the head plate by electrode caps made of Hastelloy B, and are insulated from the head plate with Teflon gaskets. Water-cooled copper couplings are attached to the electrode caps to conduct current to the electrodes from the power supply.

A vacuum seal is obtained in the bulb by using a lead gasket between the head plate and the flange. The head plate and Teflon gaskets are kept intact at the operating temperatures of 300°C. to 425°C. by surrounding the head plate with a water-cooled oil reservoir.

The bulb is connected to the vacuum system through a bellows-type valve. The body and seal of the valve are constructed of Hastelloy C and the bellows of Monel metal.

The unit is heated to operating temperature in a fused-salt bath, and the temperature of the salt is maintained by automatic control.

The power supply for this unit consists of manually adjusted variable transformers, providing voltage regulation from 0 to 100 volts with an ultimate current capacity of about 3000 amperes at 13 volts.

Experimental Procedures

The feed material, usually sponge zirconium, is held in the annular space formed by the bulb shell and the perforated molybdenum retainer. The

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FIGURE 1. PHOTOGRAPH OF THE 16-INCH-DIAMETER HASTELLOY B
deBOER BULB

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FIGURE 2. SCHEMATIC DRAWING OF THE 16-INCH -
DIAMETER HASTELLOY B DE BOER BULB

filaments or "hairpins" on which the zirconium is deposited can be either tungsten or zirconium wire.

In preparing zirconium crystal bars, the following procedures are used:

1. The sponge zirconium, as received, is admitted to the bulb.
 2. The starting filament is attached to the tungsten electrodes, and the bulb is sealed.
 3. The bulb is heated to 480-540°C. and evacuated to remove residual gases.
 4. The bulb is cooled and iodine is vaporized into the bulb from a container attached to the bulb. The iodine container is kept cold with dry ice during the outgassing operation.
 5. The evacuated bulb is sealed and then heated to 175°C., where the iodine and zirconium react to form zirconium tetraiodide.
 6. When the formation of iodide is complete, the bulb is heated to the operating temperature of 300-425°C.
 7. Sufficient voltage is applied to the electrodes to provide the filament current required to heat the filament to 1300-1500°C., and deposition takes place on the heated filament. The filament temperature is controlled by keeping constant the product of the potential in volts and the cube root of the current in amperes. As metal is deposited on the filament, the current increases with a constant applied voltage. This constant, referred to as the deposition K, varied from 140-165 with an 8-foot filament, i.e., from 1.46-1.72 per inch of filament. The applied voltage is progressively reduced by manual adjustment of the transformers. Deposition is continued until the desired filament size is reached.
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8. The bulb is cooled, and helium or argon is admitted to the bulb. The bulb is then opened to remove the crystal bar.

Results and Discussion

Twelve experimental runs were made in the 16-inch-diameter unit which produced about 220 pounds of zirconium crystal bar. Table 1 summarizes the results of these runs and indicates the run number, feed material weight, and diameter of the crystal bars prepared. As can be seen from the table, the most successful run produced a 45.3-pound crystal bar, 8 feet in over-all length and 1.62 inches in average diameter. Figure 3 is a photograph of this crystal bar.

The growth of large-diameter bars presented some problems not normally encountered in the production of iodide-deposited zirconium. One of these was the large amount of heat radiated from the large-diameter crystal bars. This overheated the Teflon gaskets used to insulate the bulb shell from the electrodes, and permitted leakage into the evacuated bulb. A better design of the electrode assembly provided additional cooling of these gaskets and improved the operation of the equipment.

Tapered connections consisting of molybdenum strip and wire were used to fasten the starting filament to the electrodes. These molybdenum strip and wire connections failed to support the weight of the heavy crystal bars. Zirconium adapters (shown on the ends of the crystal bar in Figure 3), were machined from Bureau of Mines ingots to replace the molybdenum strip and wire connections. The adapters were screwed onto the ends of the electrodes, and the starting filament was welded onto these adapters. This method of

TABLE 1. CRYSTAL BARS DEPOSITED IN THE 16-INCH-DIAMETER METAL UNIT

EMI Run No.	Description of Feed Material	Size of Crystal Bar		Selected Chemical Analysis (Parts per Million)										Results of Standard Corrosion Tests, Two Weeks' Exposure ⁽¹⁾	Observations and Remarks
		Weight, Pounds	Average Diameter, Inches	Ti	Al	Fe	Mg	Ni	Cr	Si	O	N			
4989-78 ⁽²⁾	Bureau of Mines sponge zirconium, EMI Lot No. 3	3-3/4	0.5	25	400	150	5	5	<10	120	200	17	Poor	First run in unit. Filament operated at too high a temperature and burned out at 600 amperes.	
4989-79 ⁽²⁾	Ditto	14-3/4	0.9	15	110	150	10	<5	<10	100	100	8	Poor	Run was stopped because of oil leakage into bulb.	
4989-82 ⁽²⁾	"	20	1.1	10	225	100	10	<5	<10	100	300	10	Poor	Oil leakage into bulb also occurred in this run.	
4989-88 ⁽²⁾	"	23-5/8	1.2	<30	40	90	<10	<5	<10	40	150	7	Poor	Tapered leads from electrodes failed to support weight of crystal bar.	
4989-96 ⁽³⁾	Foots Mineral Company, sponge zirconium, Lots Nos. 001-S-10 and 004-5-6	4-1/3	0.5	<30	<20	190	<10	<10	<10	200	130	4	Poor	Filament burned out at electrodes; this was apparently caused by depletion of crude near top of bulb.	
4989-98 ⁽³⁾	Ditto	7-3/4	0.75	<30	<20	190	<10	<5	20	40	170	6	Good	Additional crude charged; filament burned out at electrodes.	
5319-3 ⁽³⁾	"	3-1/8	0.43	<30	<20	320	20	<5	30	60	160	7	Poor	Filament also burned out at electrodes.	
5319-14 ^(3,4)	Bureau of Mines sponge zirconium, EMI Lot No. 5	17	1.0	90	50	130	<10	20	<10	50	110	5	Good	Crystal bar slipped off tungsten electrode, thereby ending the run. Unit modified to permit introduction of iodine without opening bulb to air.	
5319-19 ⁽³⁾	Ditto	8-1/2	0.7	100	80	110	<10	5	<10	90	260	7	Good	After initial run on this feed, bulb was partially depleted of crude near the top. Supply of this feed was exhausted; to avoid contamination, no other crude was added. Five corrosion samples considered good; one sample from electrode end of bar showed oxide-filled cracks.	
5319-29 ⁽³⁾	Bureau of Mines sponge zirconium, Odd lots	27	1.2	No data available.								Poor	Run was stopped to add more crude. Crystal bar was firmly attached to electrodes and deposition on this bar was attempted. Thermal strain in heating bar up to operating temperature was enough to pull the bar away from the electrodes.		
5319-32 ⁽³⁾	Ditto	18	1.0	No data available.								No data available.	Tapered leads from electrodes to filament broke because of weight of the bar.		
5319-33 ⁽³⁾	"	29	1.3	No data available.								No data available.	Zirconium adapters used in place of tapered leads to fasten the filament to the electrodes. Filament pulled apart at the adapter.		
5319-51 ⁽³⁾	Bureau of Mines sponge zirconium up to 1-inch diameter. Titanium Alloy Manufacturing Company sponge zirconium from 1-inch to 1.6-inch diameter	45-1/3	1.62	No data available.								No data available.	Modified design of zirconium adapters was used. Rate of deposition using TAM feed was considerably slower than when the Bureau's feed was used.		

Footnotes appear on the following page.

- (1) Data given are for samples machined to provide a uniform surface for corrosion testing. Tested in 600°F. water.
- (2) Zirconium deposited on a 0.007-inch-diameter by 8-foot tungsten filament.
- (3) Zirconium deposited on a 1/4-inch-diameter by 8-foot zirconium filament prepared by cold rolling and swaging sections of crystal bar prepared in earlier runs.
- (4) The unit was modified to permit the introduction of iodine without opening the bulb to air after outgassing the sponge zirconium.
- (5) Tested in 600°F. water.

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FIGURE 3. PHOTOGRAPH OF 45-POUND ZIRCONIUM CRYSTAL BAR, 8 FEET OVER-ALL LENGTH BY 1.6 INCHES IN DIAMETER WITH ZIRCONIUM ADAPTERS ON ENDS

attaching the filament proved satisfactory, as is shown by the performance of the adapters in the run in which the 45.3-pound crystal bar was produced.

The experimental work has shown that large-diameter zirconium crystal bars can be produced successfully in conventional de Boer type units. This metal can be fabricated into sheet or rod by forging and hot rolling, using a steel jacket on the bar. The metal is ductile enough to be cold rolled, but there are some cracks in the crystal bar which do not knit together under cold working.

Corrosion Resistance of Large-Diameter Zirconium Bars

In this investigation, primary attention was directed toward the preparation of large-diameter crystal bars, and the corrosion resistance of these bars was of secondary importance. No special precautions were taken in the earlier experiments to prepare noncorrodible metal. The unit was then modified to prepare corrosion-resistant crystal bars by introducing iodine without opening the bulb to air after outgassing the sponge zirconium used as feed material.

Data on the chemical and spectrographic analysis and the corrosion resistance of the iodide-deposited zirconium prepared in the 16-inch-diameter de Boer unit are also contained in Table 1. It should be noted that, after precautions were taken to avoid contamination of the feed material prior to deposition, the corrosion resistance of the crystal bars was considerably improved.

Some difficulty was encountered at this stage of the work in obtaining suitable feed material for the operation of the unit. To continue the preparation of large-diameter bars, it was necessary to use odd lots of sponge
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zirconium, including some of doubtful pedigree, a factor which undoubtedly affected the corrosion resistance of the deposits. It was found that the runs had to be stopped to charge additional feed material in order to grow crystal bars over 1 inch in diameter. A reduction in the diameter of the perforated molybdenum-sheet retainer to increase the space available for the zirconium feed stock would have eliminated the necessity for recharging the unit. However, this change in design was not required, since runs were customarily interrupted to observe the nature of the filament growth, and the bulb could be recharged at that time.

Zirconium Feed Materials

Sponge zirconium produced by the Bureau of Mines, the Foote Mineral Company, and the Titanium Alloy Manufacturing Company was used as feed material in the 16-inch-diameter unit. No attempt was made in this investigation to evaluate the feed zirconium obtained from these sources to produce corrosion-resistant crystal bars. Instead, the suitability of these feed materials for preparation of large-diameter zirconium crystal bars was evaluated as described in this section.

In de boer bulbs, feed materials are held in the annular space formed by the bulb shell and the molybdenum-sheet retainer. It is desirable to charge as much feed material as possible into this space to avoid depletion of the crude near the top of the bulb. In the latter event, filament burn-out at the junction with the electrodes usually results. The bulb density of sponge zirconium received from the Bureau of Mines and the Titanium Alloy Manufacturing Company was greater than that of the feed stock supplied by the Foote Mineral Company. The former two feed materials could therefore be charged more efficiently.

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Only one run was made using TAM's sponge zirconium in this study. It reacted much more slowly with iodine than the other two and, as a result, the deposition of zirconium proceeded more slowly. On this basis, the Bureau of Mines sponge zirconium gave the best results when large-diameter crystal bars were prepared.

(The data contained in this report

(The original data are contained in BMI Record Books Nos. 4989, pp. 78 to 98, and 5319, pp. 3 to 51. This covers the period from December 1, 1949, to December 2, 1950.)

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