The Extractive Metallurgy of Zirconium By the Electrolysis of Fused Salts

III. Expanded Scale Process Development of the Electrolytic Production of Zirconium from K₂ZrF₆[1]

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ABSTRACT

The electrolysis of K_2ZrF_6 in an electrolyte of NaCl to produce ductile zirconium metal has been expanded from the laboratory scale into a larger scale operation. An electrolytic cell capable of producing 3–4 lb of zirconium metal per run was designed and operated. Following successful operation of this unit, a cell capable of producing 30–40 lb of zirconium metal per run was used to evaluate the process on a scale 50 to 60 times the laboratory scale.

Electrolytic zirconium powder of high purity has been reproducibly obtained in good yields and at commercially acceptable current efficiencies. Upon consolidation, the metal shows fabricating properties comparable to those exhibited by Kroll sponge zirconium. The present larger electrolytic cell produces zirconium metal at a rate approaching that of the original commercial Kroll sponge producing reactors. Further expansion to larger scale operation should be entirely feasible.

INTRODUCTION

Two preceding papers (1, 2) on the extractive metallurgy of zirconium by the electrolysis of fused salts have discussed historical and theoretical aspects of this process, operational procedures, operational variables affecting the production of zirconium metal by the electrolysis of the double fluoride of zirconium, and the application of this process in producing high quality zirconium metal powder. The process can be summarized as being the electrolysis of fused potassium zirconium fluoride in molten sodium chloride in a purified argon atmosphere. The zirconium is deposited as dendritic crystalline metal in a matrix of salts from which it can be separated readily by water leaching. The over-all cell reaction is

$$K_2ZrF_6 + 4NaCl \rightarrow \underline{Zr} + 2\overline{Cl}_2 + 2KF + 4NaF \quad (I)$$
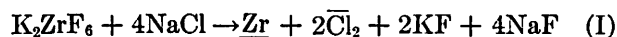
In this paper, the expansion of the process from a laboratory unit capable of producing 200 g of zirconium per run to a cell in which 3–4 lb (1.3–1.8 kg) of zirconium metal per run can be made is described. This paper also describes the further expansion from this 3–4 lb cell, to a cell capable of producing 30–40 lb (13.5–18.0 kg) of zirconium metal per cathode at a rate of 4–6 lb/hr (1.3–2.7 kg/hr).

The zirconium metal produced in this expanded scale equipment has been evaluated by chemical analysis and by physical metallurgical procedures, and the results are presented.

FOUR POUND PRODUCING UNIT

Experimental Work

Equipment.—An electrolytic cell capable of producing 3–4 lb of zirconium in one 8-hour day by the electrolysis of K_2ZrF_6 in NaCl was designed and constructed at Horizons Incorporated. This cell represents approximately a tenfold increase in productive capacity over the laboratory cells previously described (2). It resembles the smaller cell in materials of construction and consists essentially of a graphite crucible and anode, a thermally insulated shell in which an inert atmosphere of argon can be maintained, and an operating head through which solid cathodes can be inserted into the molten bath. The cell is heated by a graphite resistance element. The cathode is comprised of a nickel rod to which a steel cathode is welded. The nickel rod is protected by a graphite sleeve within the cell and at the bath surface.

Normal operation consists of a charge melting period, a pre-electrolytic period, and the electrolysis. The cell and cathodic deposit are allowed to cool overnight to room temperature, and a 1-hr period at the beginning of the next cycle is used to remove the cathode and the crucible and to prepare for the subsequent run.
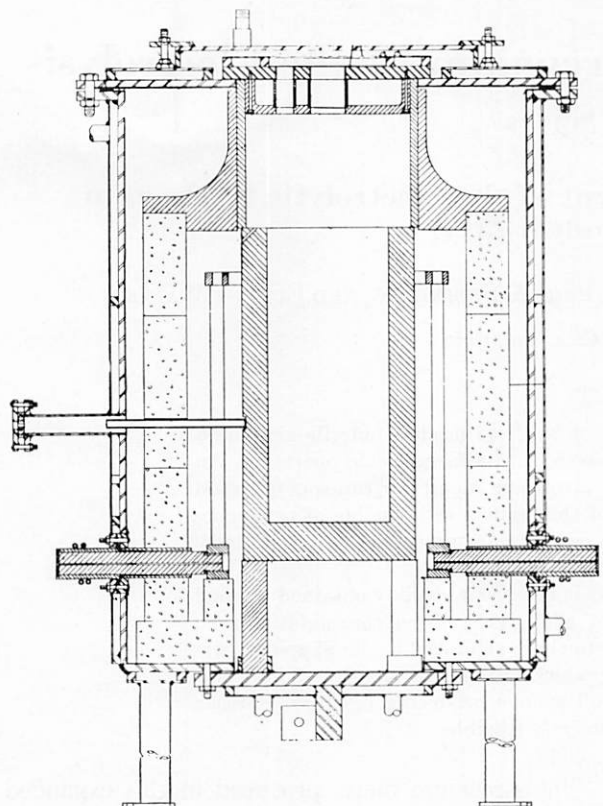
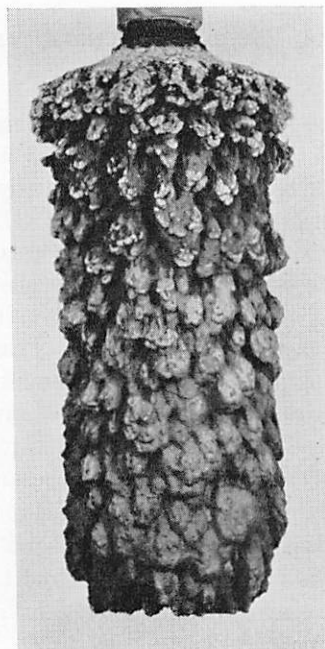Fig. 1. Electrolytic cell. ▨▨▨ graphite; ▢▢▢ K-28 firebrick; ▨▨▨ steel, nickel sheathed.

Fig. 2. Typical zirconium "carrot" on removal from electrolytic cell. ⅕ normal size before reduction for publication.

Cell Operation

The electrolytic cell is cleaned and assembled as shown in Fig. 1, and the crucible is charged with granular sodium chloride. The salt is melted under an argon atmosphere in about 2 hr with an a-c power input of about 24 kw. Dry potassium fluozirconate is then added to the molten sodium chloride through the charging hole and is rapidly melted. A normal starting charge is 10 lb of K_2ZrF_6 and 20 lb of NaCl. The bath temperature is controlled at 830°–850°C. A graphite cathode is immersed in the bath and a low voltage pre-electrolysis bath purification is performed. A small direct current starting at 1.5–1.8 v is passed through the bath for about 30 min, during which time the voltage increases to 2.8 v indicating removal of metallic impurities and water. At this voltage zirconium begins to deposit on the cathode and chlorine is evolved at the anode. The pre-electrolysis is continued for another 30 min at 2.8 to 3.1 v d.c. as a precautionary measure. A small amount of zirconium metal deposits out on the graphite rod. After this pre-electrolytic purification step, the bath is ready to be electrolyzed.

Upon removal of the pre-electrolytic cathode, a steel cathode is then immersed completely in the fused salt bath with a small d-c voltage impressed upon it. When the cathode reaches bath temperature (in about 5 min), the voltage is increased to 5 to 6 v d.c. to pass enough current to establish the initial current density at 300 to 400 amp/dm². When the cell polarizes, additional K_2ZrF_6 and NaCl are charged into the crucible. By this means, production of zirconium can be maintained at a consistently high rate.

When the predetermined number of ampere hours has been put through the electrolyte, the cathode is raised from the bath. The cathode is held above the bath, but in the argon atmosphere, and the entire unit is allowed to cool to room temperature.

Fig. 2 shows a typical cathode and cathode deposit after removal from the cell. Fig. 3 shows the deposit broken open to reveal the zirconium metal and the customary outer salt-metal layer.

Both crucibles and cathodes are reused; normal life for a crucible is 20 electrolyses or more and for a cathode, 100 runs. Cathodes are protected at the bath interface and in the chlorine atmosphere above the bath by graphite sleeves. These sleeves are replaced after each run.

Materials.—The cell, after any maintenance work or an extended shut-down, is made anhydrous by evacuation at 900°C at 50–100 μ. The K_2ZrF_6 is vacuum dried at 90°C and 150 μ for 2 hr before being charged into the cell. The sodium chloride used in this large unit is AR granular grade NaCl, supplied in 100-lb drums, and is used after drying in air at 120°C overnight. Melting the salts is carried out under a purified argon atmosphere.

In this work, three grades of potassium fluozirconate have been used: a C.P. grade K_2ZrF_6, 99+ % in
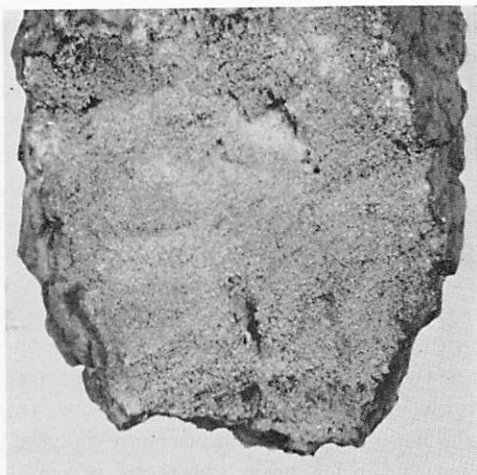
F<small>IG</small>. 3. Zirconium cathode "carrot" after breaking away part of the deposit showing the coarse zirconium powder, as deposited during electrolysis, and the outer salt layer.

purity, available commercially; double recrystallized K_2ZrF_6, an anhydrous salt available commercially; and double recrystallized K_2ZrF_6 produced in the authors' laboratory from commercial grade K_2ZrF_6.

Double recrystallized K_2ZrF_6 is required as the proper starting raw material for the production of low hardness zirconium metal. However, workable zirconium metal can be produced from commercial grade potassium zirconium fluoride. These conclusions are justified by the results of runs made in this unit. These results are shown in the tabulation of typical experimental runs given below.

Table I is a summary of a number of electrolyses in this larger scale unit. Three runs from each grade of K_2ZrF_6 used are summarized. All runs were made using a starting composition of 33% by weight of the fluozirconate and 67% by weight of sodium chloride.

In Table I, runs 1, 2, and 3 are typical of 29 electrolytic runs made with commercial grade K_2ZrF_6. Zirconium produced with this material ranged in hardness from Rockwell A 57 to Rockwell

A 64 (Brinell 205 to 275). Current efficiencies are good, averaging 55–60%, but extremely wide variations were found in the chemical analysis, particularly in oxygen contents. The product is washed with more difficulty than that obtained from purer starting materials and, upon melting, fumes appreciably.

Per cent yield figures in runs 3–9 are lower than those obtained in strictly batch operations because of a change in operational procedure. Excess K_2ZrF_6 was added to the salt bath as the predetermined number of ampere hours were approached to keep the concentration of zirconium salt high. This cell ran for a predetermined number of ampere hours and the bath was not depleted of available zirconium.

Runs 4, 5, and 6 represent 17 runs made in the 4-lb cell using K_2ZrF_6 recrystallized in the laboratory and vacuum dried at 150°C. Consistently good quality zirconium, low in oxygen content, can be made with this salt as a starting material. The current efficiencies obtained in the electrolyses are somewhat lower, 45–55%, as are the over-all yields. The hardness of the zirconium is consistent at R_A 50–52 (Brinell 150–170). Oxygen contents of zirconium produced from this material range from 0.06 to 0.10%.

Runs 7, 8, and 9 represent 12 electrolytic experiments in which commercial anhydrous double recrystallized K_2ZrF_6 was used as the zirconium raw material. The electrolysis of this fluozirconate produces zirconium metal with Rockwell hardnesses from R_A 47 to R_A 51 (Brinell 145 to 170). Current efficiencies average 55–65%. The purity of the zirconium metal made in these experiments is very high. Oxygen contents range from 0.03 to 0.07% and carbon from 0.02 to 0.03%. Nitrogen contents, in nearly every run in this cell, average about 0.0035%.

Conditions of bath temperature and initial current

TABLE I. *Summary of runs made in 3–4 lb zirconium cell*

Run	Reference No.	Grade of K₂ZrF₆	Bath temp, °C	Current density amp/dm²	Curren efficiency	% yield	As-cast Rockwell hardness	Analysis		
								% O	% N	% C
					%					
1	92–69	Commercial CP	850	370	70	78.5	R_A 62	0.22	0.0027	0.037
2	92–77	Commercial CP	850	390	65	85.0	R_A 58	0.130	0.0031	0.051
3	92–103	Commercial CP	850	330	62	52.5	R_A 58	0.229	0.0028	0.056
4	92–121	Commercial CP Horizons recrystallized	850	325	47	59.0	R_A 52	0.080	—	0.017
5	92–123	Commercial CP Horizons recrystallized	850	340	45	44	R_A 52	0.088	0.0034	0.062
6	92–171	Commercial CP Horizons recrystallized	840	370	59	58	R_A 51	0.062	0.0099	0.028
7	92–173	Commercial double recrystallized	830	340	53	62	R_A 51	0.035	0.0008	0.024
8	92–177	Commercial double recrystallized	830	330	70	49	R_A 49	0.034	—	0.026
9	92–179	Commercial double recrystallized	835	370	61	56.5	R_A 48	0.042	—	0.025

TABLE II. *Typical screen analyses of electrolytic zirconium powder*

(USS Tyler Standard Sieves)

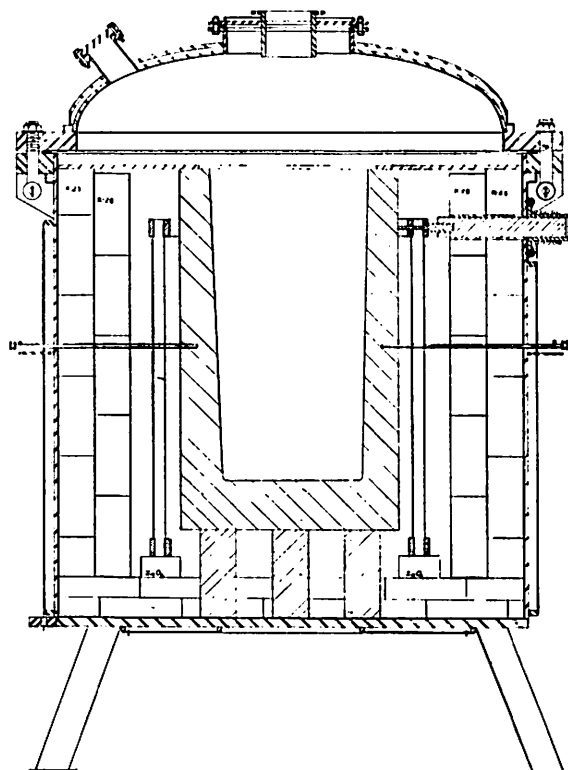| Run No.	+35	−35 +100	−100 +150	−150 +200	−200 +325	−325
92–96	0.4	30.2	24.0	18.2	20.2	7.0
92–103	1.0	15.8	12.2	20.4	34.2	16.4
92–123	7.8	17.8	12.4	17.2	27.8	17.0
92–177	0.2	20.2	14.8	26.4	25.6	12.8
92–179	0.2	31.4	14.4	29.8	18.0	6.2

Fig. 4. Large scale electrolytic cell. ▨ graphite; ▦ K-28 firebrick; ▨ steel, nickel sheathed.

density used in the 9 runs summarized in Table I have been established as the most desirable ones, not only in this larger scale equipment, but also in the small scale work previously reported (1, 2). In this 4-lb/run electrolytic cell, the electrolyses differ from the small scale operation in that additions of K_2ZrF_6 and NaCl were made during the electrolysis in order to avoid polarization and to keep the concentration of zirconium salts nearly constant in order to assure a supply of available zirconium. This cell is run, therefore, for a specified number of ampere hours. Hence, current efficiencies remain high, averaging about 55%, and are comparable to results obtained in the 200 gram cells with similar raw materials. However, the material yields are lower since this particular unit was operated as a batch unit and the bath was never run to exhaustion.

Yields reported in Table I should be considered in the light of this explanation.

Table II shows typical particle size distributions of the zirconium produced in this large laboratory electrolytic cell. No specific correlation has been made between particle size distribution and hardness for the zirconium powder, but, as a generalization, the coarser deposits tend to result in slightly softer metal upon melting. In some runs, the finer material has been found to result in harder ingots, but in other runs there has been no difference in the hardness of the consolidated metal. Coarse powder is preferable, however, since its recovery from the cathode deposit is easier and there is less loss in handling and in leaching. The metal is recovered by water leaching followed by air drying.

FORTY POUND PRODUCING UNIT

Experimental Work with 40-lb per Run Electrolytic Cell

Equipment.—A large scale electrolytic cell was designed (Fig. 4) to produce 30–40 lb of zirconium metal per run.[2] The design was based upon the laboratory electrolytic cell and the larger unit discussed above, with some modifications. Additional design features were incorporated, because of the increased physical size, in order to provide flexibility of operation, although it was not the intention to arrive at a prototype of a commercial cell.

This unit consists of a nickel-sheathed mild steel shell and is constructed on the interior much like the smaller units. It is completely water jacketed and is heated with a sectioned graphite heating element. The unit is insulated with refractory insulating brick on its sides and bottom. A machined graphite piece is both crucible and anode and can accommodate a 250–350 lb charge of molten salts. The cathode consists of jointed steel and graphite sections, the section upon which the zirconium metal is electrodeposited being mild steel. This section is threaded into a solid graphite rod which extends out of the cell through a nickel-sheathed operating head. The cell can carry up to 5000 amp direct current if desired. The unit operates in an argon atmosphere.

Cell operation.—Prior to its initial run, this unit was evacuated for eight hours at 900°C at a pressure of 35–125 μ. If any extended shut-down for maintenance or observation takes place between runs, the cell is again evacuated at a lower temperature before subsequent use. For these subsequent evacuations, a temperature of 200°C is adequate.

The crucible is brought up to 830°–850°C operating temperature in about five hours, at which time the sodium chloride, about 170 lb, is charged. Analytical

Reagent grade NaCl is used without predrying. Double recrystallized potassium zirconium fluoride, about 50 lb, is then added to the molten sodium chloride and is rapidly melted.

No pre-electrolysis is carried out in this large unit.

The steel cathode (including an additional 2–3 in. of graphite) is completely immersed in the fused salt bath with a small d-c voltage impressed upon it. The current is slowly increased until a current density of 260–300 amp/dm² is established on the cathode. When the bath polarizes, additional K_2ZrF_6 and NaCl are charged into the bath. Normally, a 50-50 mixture of K_2ZrF_6 and NaCl is used for the charge. By this means, the initial high production rate of zirconium metal can be maintained.

When a predetermined number of ampere hours has been passed through the electrolyte, the cathode is raised from the bath. The cathode is suspended above the bath, but in the argon atmosphere, and the entire unit is allowed to cool to room temperature.

Typical cathode deposits are shown in Fig. 5 and 6.

Some difficulty was experienced in this cell with crucible leakage and cathode breakage. Other graphite and nickel-clad parts appear to be satisfactory for reasonable service; that is, no gross attack has been observed in eight complete electrolytic cycles.

Table III is a summary of the runs made in this unit. As in the smaller unit, all runs were made using a starting composition of 33 % by weight of the fluozirconate in the sodium chloride.

Metal recovery of electrolytic deposits.—Electrolytic deposits from the electrolysis of K_2ZrF_6 in fused sodium chloride average about 30 % by weight of zirconium metal, the remainder being a mixture of soluble zirconium and sodium halides. The cold deposit is chipped away from the steel cathode by an air hammer and is then jaw crushed to about ¼ in. sized chunks. These lumps are then pulverized to about −80 mesh powder.

The crushed and pulverized cathode deposit is then leached in a continuous cone washer in which the metal is fluidized by an upward movement of water as the soluble salts are leached away and removed in the overflow. This unit represents, therefore, an approach to a continuous counter-current leaching operation.

When the zirconium metal is free of all soluble salts, it is removed from the water, filtered, and air dried.

Properties of Electrolytic Zirconium

Physical Properties

The electrolytically deposited zirconium metal, in the form of dendritic crystals, is consolidated first . by pressing into dense compacts 1 in. in diameter
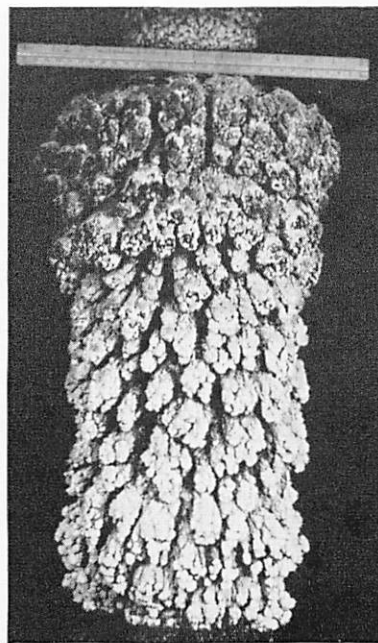

Fig. 5. Typical zirconium cathode deposit produced in the large scale electrolytic cell.
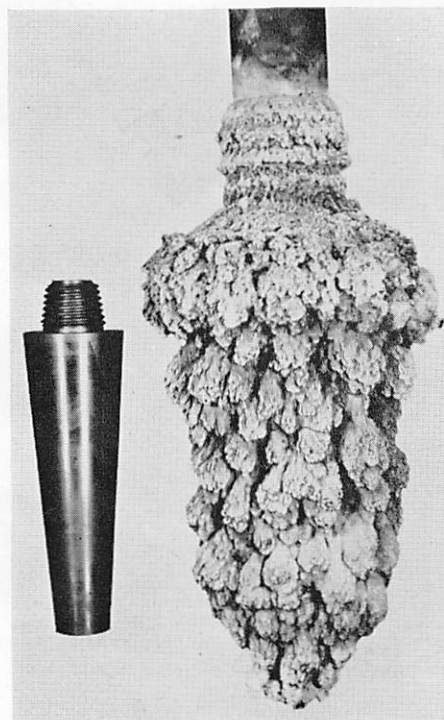

Fig. 6. Zirconium cathode deposit compared with typical mild steel cathode.

and ¼ in. to ⅜ in. in height. These compacts are then arc melted in a tungsten-arc, water-cooled, copper hearth furnace under a quarter of an atmosphere of argon. Fig. 7 shows typical zirconium metal dendritic crystals as produced in the large scale electrolytic cell. Fig. 8 shows uncompacted electrolytic zirconium, a compact of 20 grams of this powder, and an arc melted compact.

TABLE III. *Summary of electrolytic runs made in large scale electrolytic cell*

Run No.	Bath temp., °C	Initial current density, amp/dm² on cathode	Current density amp/dm² on anode	Current efficiency	Rate of production, lb Zr/hr of electrolysis	As-cast Rockwell hardness	Remarks
				%			
1	835	330	55	62	5.0	R_A 61	$O_2 = 0.320\%$; $C = 0.015\%$
2	870	330	45	67	5.5	R_B 90	$O_2 = 0.108\%$; $C = 0.045\%$
3	870	290	40	60	5.0	R_B 91	$O_2 = 0.061$; $C = 0.067\%$
4	820	330	45	65	5.3	R_B 87	
5	855	370	50	64	5.3	R_B 93	
6	840	270	37	53	3.8	R_B 88	

All runs made with starting concentration 33% K_2ZrF_6 by weight.
Salt additions made during electrolysis, at bath polarizations.
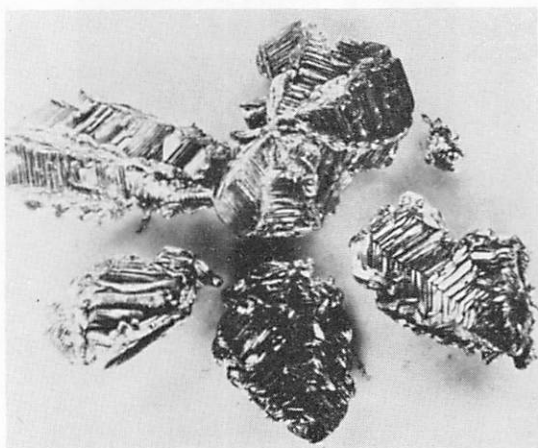

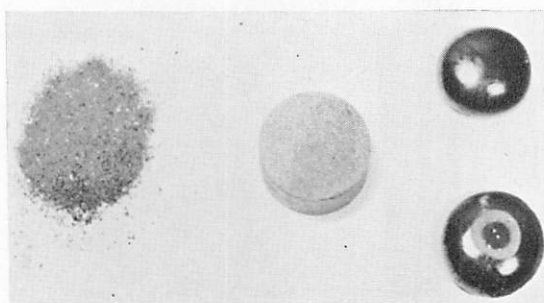FIG. 7. Typical zirconium metal dendritic crystals

FIG. 8. Recovered zirconium powder, compacted zirconium powder, and small arc-melted zirconium ingots.

The arc furnace uses a tungsten electrode mounted in a water-cooled copper tube which is flexibly mounted in a copper head through a bellows assembly. The hearth is water-cooled copper, to take advantage of the fact that molten zirconium does not wet cold copper. The outer shell of this furnace is a cylindrical piece of Pyrex glass. Auxiliary equipment consists of an argon purification train of P_2O_5 and heated titanium sponge, a vacuum pump and cold trap, a manometer, and a 400 amp d-c Hobart welder for the power source. It is similar to many which have been described in the literature.

Metal Evaluation

Rockwell hardnesses are taken on these arc melted pellets and this hardness becomes the primary means of product evaluation. Although hardnesses are customarily determined on the Rockwell B scale, a conversion from Rockwell A to Rockwell B scale was made since the hardness of zirconium alloys cannot always be made in the Rockwell B scale. This conversion between Rockwell A, Rockwell B, and Brinell is shown in Fig. 9.

Various melted pellets of 20–60 g and ingots of 100–150 g have been hot and cold reduced by rolling to determine the workability of the electrolytic zirconium. All of the metal produced can be hot worked to strip at 700°–800°C. Zirconium as-cast ingots or pellets, Rockwell B 85–92, can be cold rolled but are more successfully worked with successive anneals at 850°C (in air) after moderate
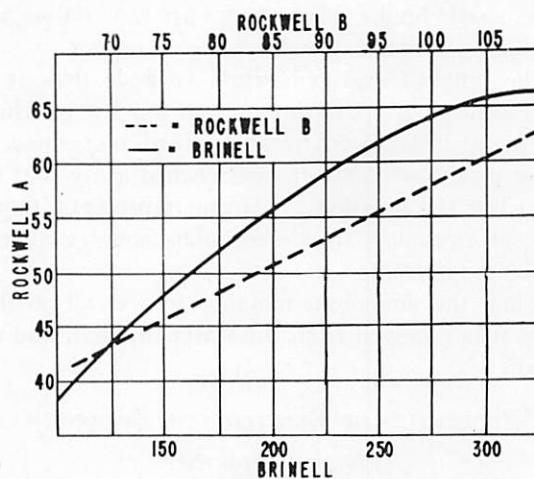

FIG. 9. Conversion from Rockwell "A" to Rockwell "B" and Brinell for zirconium.
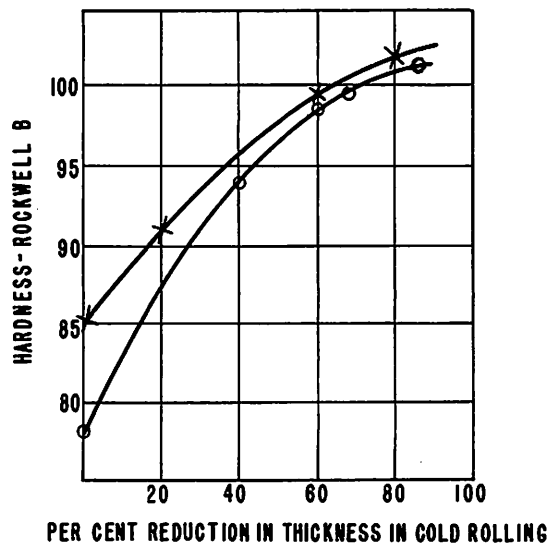
Fig. 10. Effect of cold rolling on the hardness of electrolytic zirconium.

TABLE IV. *Spectrographic analyses of typical electrolytic zirconium powder and of rolled arc melted zirconium made from this powder*

	Powder	Strip
Zr	Major	Major
Si	0.003	0.002
Fe	0.01	0.03
Al	0.01	0.007
Hf	1.5	1.5
Cu	0.0005*	0.0007
Ti	0.05	0.05
Ca	0.005*	0.005*
Mg	0.001*	0.001*
Mn	0.001*	0.001*
Pb	0.001*	0.001*
Mo	0.001*	0.001*
Ni	0.004	0.003
Cr	0.003	0.002
Sn	0.001*	0.001*
W	—	—

* Less than.

(20–40%) cold working. Fig. 10 illustrates typical hardness change with per cent reduction in thickness obtained in cold rolling of electrolytic zirconium. It can be seen that the hardness approaches R_B 100 during cold rolling before edge cracking, regardless of the initial as-cast hardness.

Spectrographic analyses of typical electrolytic zirconium powder as produced in the two electrolytic cells described above and of arc melted buttons made from this powder are given in Table IV. Typical oxygen analyses of such powder range from 0.06 to 0.09%, nitrogen from 0.003 to 0.009%, and carbons from 0.02 to 0.06% (see Table I).

CONCLUSIONS

The process development of the electrolysis of potassium fluozirconate in sodium chloride has been successfully expanded from the laboratory bench scale through a development-sized electrolytic cell capable of producing 3-4 lb to an electrolytic unit capable of producing 30–40 lb of zirconium metal per run. The process has been demonstrated to operate at commercially acceptable current efficiencies and yields and to produce good quality zirconium metal at a rate of about 4–6 lb/hr, which is equivalent to the production rate of the original Kroll sponge reactor. Results indicate that further expansion of the scale of operation will present no unsurmountable technical difficulties.

The zirconium metal, produced at this near-commercial rate of 4–6 lb/hr, has been evaluated, as as-cast metal, to have a hardness of Rockwell B 80 to Rockwell B 83 (Brinell Hardness Number 150 to 165), if recrystallized potassium zirconium fluoride is used as starting material. Such K_2ZrF_6 is readily available from commercial manufacturers.

Zirconium metal produced by the process, consolidated by arc melting, can be either hot or cold worked to sheet, foil, or wire. The oxygen content of this metal ranged from 0.06 to 0.09%; nitrogen averages 0.003%; and carbon 0.02 to 0.06%.

Comparison with Kroll Process

The operating schedule to produce 220 lb of zirconium by the Kroll magnesium reduction process (magnesium reacted with zirconium tetrachloride) is 41 hr and 30 min. The vacuum distillation of the yield of the reduction requires 42 hr and 10 min (3). Thus the 220 lb of zirconium are produced in 83 hr and 40 min. This is an over-all production rate of 2.6 lb of zirconium per hour for the Kroll process.

The electrolytic process time schedule, as obtained in the operation of its largest scale unit, is as follows for the production of 135 lb of zirconium: heat-up and melting of salt charge, 11 hr; electrolysis, 30 hr; metal recovery, 13 hr; total time, 54 hr. This is an over-all production rate of 2.5 lb of zirconium per hour, comparing favorably with the production rate obtained with the magnesium reduction process.

Another comparison between the two processes is possible. Excluding vacuum distillation time, the Kroll process requires 5.3 hr to produce 1 lb of zirconium. The electrolytic process produces zirconium at the rate of 3.3 lb of zirconium per hour, including cell heat-up time. However, more than one run can be made in a cell which is equipped with facilities for cathode removals without cooling-down

periods. If the initial 11-hr cell heat-up period is excluded, therefore, a production rate of 5.5 lb of zirconium per hour is achieved.

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