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THE PRODUCTION OF ZIRCONIUM BY FUSED
SALT ELECTROLYSIS

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S U M M A R Y

A further study concerning the feasibility of producing zirconium metal by electrolysis of fused salt bath has been made. Indications have been that higher temperatures and perhaps current densities will be required, and this work has followed that pattern.

New baths were developed for use at 2000°F. These did not yield significantly different results than those of previous work. It was also determined that current density, electrode distance, and type of bath had little effect on the results under the conditions of electrolysis employed.

Plating a cathode repeatedly to increase the size of plate was attempted, but this was unsuccessful. The original plate was completely dissipated.

A series of runs was next made at 2700° to 2900°F using a new series of highly refractory oxide-fluoride baths. These show some promise of yielding metallic zirconium. Also, it seems very probable that this can be achieved at the melting point of zirconium.

The most significant results thus far obtained have been with the use of an agitated cathode in the original $\text{NaCl-K}_2\text{ZrF}_6$ bath. This has yielded a substantial deposit of zirconium metal on the cathode (up to 0.025" thick). In no case was a significant amount of black powder found in the bath where agitation was employed.

THE PRODUCTION OF ZIRCONIUM BY FUSED SALT ELECTROLYSIS

I. INTRODUCTION

A comprehensive study has been undertaken to determine the feasibility of producing metallic zirconium by electrolysis of fused salt baths. From the preliminary phases of the work, it was found that a plate of zirconium metal could be obtained from $\text{NaCl-K}_2\text{ZrF}_6$ baths at temperatures above 1580°F , the transition temperature of zirconium. These were obtained principally on copper and to a lesser extent on molybdenum, nickel, and titanium.

The second phase of the work entailed an investigation of actual amounts of the zirconium metal so produced with respect to weight and plate thickness. This was studied with variation of time, cathode material, temperature, and current density. Variations in amount of zirconium plated out were small in all cases, and the maximum thickness produced was 0.004 to 0.006 inches. It was noted that current efficiency dropped off rapidly with increasing time. There were also indications that better yields and brighter plates were produced at maximum current density and temperature.

Obviously the chief limitation of the previously disclosed methods is in the small thickness of zirconium produced. It is evident from previous work that higher temperatures, and perhaps higher current densities, were desirable. It is the object of the present phase of the investigation to carry out similar electrolyses at temperatures of 2000°F

and higher. For this work, new salt baths were developed and a number of questions regarding the process, itself, answered.

Agitation of the cathode area has been considered for some time. This has also been carried out in this phase of the work and has yielded the best results to date.

II. EXPERIMENTAL EQUIPMENT

With the exception of the furnace, the equipment used in previously reported work was again employed. The power supply was a 12 ampere, 24 volt selenium rectifier unit; this was regulated by a current control unit, and connected to the electrolytic cell through a micromax controller fitted to record voltage, amperage, or temperature. (See Report No. I).

A gas fired furnace was designed and built in this laboratory to operate above 2000°F. This was constructed of fire brick and fitted with a gas-compressed air burner. The furnace is of circular design and holds a 3-1/2" crucible in the center flush against a fire brick cover. Temperature was manually controlled and constant temperature within $\pm 25^\circ$ was possible.

Special zircon-mix crucibles were made to withstand the conditions of the gas furnace. These held about 350 grams of material.

For temperatures of operation at 2700° to 2900°F, an Ajax Northrup high frequency converter with induction coil was used. Temperature control was manual and measured by use of an L and N optical pyrometer.

III. EXPERIMENTAL WORK

A. High Temperature Electrolysis: 2000°F.

The trend of the present phase of the project has been in the direction of higher temperatures and consequent variation of bath composition for satisfactory work at these higher temperatures. The first temperatures of operation were generally around 2000°F. Preliminary studies were made with a number of bath compositions to determine those best suited for the work with respect to temperature of fusion, degree of fuming, weight loss per unit time, and stability. Electrolyses were then run on the best of these compositions and the results were compared with each other and with the previous runs. The gas fired furnace was used for all runs of this type. Cathode material was generally nickel or titanium for the high temperature runs. Results of this work are shown in Table I.

The $\text{CaCl}_2\text{-K}_2\text{ZrF}_6$ bath was not found to be satisfactory beyond 1750°F. Over this temperature, heavy fuming takes place. Below 1750°F, however, plates are obtained comparable to those in an NaCl bath.

Adding ZrO_2 to the $\text{NaCl-K}_2\text{ZrF}_6$ bath produced no noticeable change in the character of the electrolysis or the resultant plate. Only a small amount of ZrO_2 is soluble in the bath, the majority of the material settling out in the bottom of the crucible.

The 2216 series of runs was generally not satisfactory. Weights and changes in thickness were not obtained because of cathode fractures and washing difficulties. Some plating was obtained in all cases except in 2216-E-1. In 2216-C-2, heavy volatilization of the bath was encountered. As a result of this, only the tip of the nickel cathode remained in the

TABLE I

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VARIATION OF BATH COMPOSITIONS

Run	2214-A-1	2214-A-2	2214-A-3	2215-A-1	2216-A-1	2216-C-1	2216-C-2	2216-C-3
Time (mins.)	27	30	60	60	60	60	18	60
Temp. (°F)	1640	1640	1640	1640	1650	1950	1950	1640
Bath) Composition) %	60 CaCl ₂ 40 K ₂ ZrF ₆	60 CaCl ₂ 40 K ₂ ZrF ₆	60 CaCl ₂ 40 K ₂ ZrF ₆	10 ZrO ₂ 30 K ₂ ZrF ₆ 60 NaCl	65 NaCl 35 K ₂ ZrF ₆	60 CaCl ₂ 40 K ₂ ZrF ₆	65 NaCl 35 K ₂ ZrF ₆	65 NaCl 35 K ₂ ZrF ₆
Cathode	1/4" Cu	1/4" Cu	1/4" Cu	1/4" Cu	1/4" Cu	0.022" Ni	0.022" Ni	0.022" Ni
Δ Wt. Cathode (g.)	—	—	+0.1445	+0.1586	—	—	—	—
Δ d Cathode (ins.)	—	+0.004	+0.003	+0.002	—	—	—	—
Av. Voltage	4.5	4.0	3.3	4.1	4.3	4.2	4.8	5.7
C. D. (amp./dm ²)	50	50	25	50	50	50	50	50
Current Eff.	—	—	2.6	2.86	—	—	—	—
Run	2216-E-1	2217-A-1	2220-C-1	2220-C-2	2220-B-1	2220-D-1	2220-D-2	
Time (mins.)	10	60	8	30	35	30	30	
Temp. (°F)	2000	1800	2000	2000	2000	2000	2000	
Bath) Composition) %	65 NaCl 35 K ₂ ZrF ₆	60 BaCl ₂ 40 K ₂ ZrF ₆	30.6 CaF ₂ 29.4 MgF ₂ 40 K ₂ ZrF ₆	30.6 CaF ₂ 29.4 MgF ₂ 40 K ₂ ZrF ₆	30.6 CaF ₂ 29.4 MgF ₂ 40 K ₂ ZrF ₆	30.6 CaF ₂ 29.4 MgF ₂ 40 K ₂ ZrF ₆	30.6 CaF ₂ 29.4 MgF ₂ 40 K ₂ ZrF ₆	
Cathode	0.010" Zr	0.010" Cu	0.022" Ni	0.022" Ni	0.010" Mo	0.025" Ti	0.025" Ti	
Δ Wt. Cathode (g.)	—	—	—	+0.1475	—	—	—	
Δ d Cathode (ins.)	—	—	—	+0.004	—	—	—	
Av. Voltage	5.0	4.5	4.5	5.5	4.6	4.6	4.8	
C. D. (amps/dm ²)	50	50	50	50	50	50	50	
Current Eff. %	—	—	—	—	—	—	—	

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bath. This in effect produced a high current density of about 400 to 500 amps/dm². The cathode tip had a heavy metallic coating about 1/16" thick. This presumably was because of formation of an Ni-Zr eutectic mixture.

Photomicrographs of sections of this plate are shown in Figures No. 1, No. 2, and No. 3. The temperature of electrolysis was 1950°F and from the photomicrographs was above the Ni-Zr eutectic temperature. Figure No. 3 shows that a heavy diffusion into the nickel grain boundaries has occurred with a resulting low melting point eutectic having formed. In addition, a pearlite type of transformation must have occurred also as a product of a eutectoid decomposition since a large amount of a pearlite structure is present in this area. The thick coating obtained on the nickel is a mixture of two phases resembling that obtained in a cast structure and is probably a compound of Ni and Zr and a Zr-rich solid solution containing Ni. In 2216-C-3 a small 1-3/8" crucible was used as a cathode compartment inside the larger 3-1/2" crucible. The black powder was almost entirely contained in the small crucible, but no change in the plate was noted, the run using a Zr cathode at 2000°F. 2216-E-1 was interrupted because of a sudden drop in current capacity. The Zr cathode was found to have disintegrated to a black powder similar in nature to the usual cathode deposit.

The BaCl₂-K₂ZrF₆ bath was found to be extremely corrosive, completely dissolving the Cu cathode. Excessive fuming also takes place. Of all the various baths tried, the K₂ZrF₆-CaF₂-MgF₂ composition seemed to be the most satisfactory at 2000°F. In 2220-C-1 and C-2, the Ni-Zr eutectic formation was again observed. There was no evidence of a plate using an Mo cathode. Interesting results were obtained using Ti cathodes

FIGURE NO. 1

Specimen No. : 2216-C-2
Etchant : None
Magnification: 75X

FIGURE NO. 2

Specimen No. : 2216-C-2
Etchant : None
Magnification: 75X

FIGURE NO. 3

Specimen No. : 2216-C-2
Etchant : None
Magnification: 150X

however. Here fairly heavy bright plating was noted. This was separated from the Ti cathode by a thin salt layer. This, however, was difficult to reproduce and presumably was due to impurities introduced into the bath by the electrode holders or from the leaching of the crucible.

B. High Current Density Work

Because of the interesting results obtained on nickel when exposed to a high current density, several runs were made using small copper cathodes yielding a high current density. Representative results are given in Table II.

TABLE II
USE OF HIGH CURRENT DENSITY

Run	2218-A-1	2218-A-2
Time (mins.)	30	50
Temp. °F	1800	1640
Bath Composition) %	65 NaCl 35 K ₂ ZrF ₆	65 NaCl 35 K ₂ ZrF ₆
Cathode	1/4" x 1/4" Cu	1/4" x 1/4" Cu
Δ Wt. Cathode (g.)	--	+0.0430
Δ d Cathode	--	+0.0015"
Av. Voltage	4.6	6.0
Current (amp.)	9.0	12.0
C. D. (amps/dm ²)	300	400

A large amount of very black powder was obtained in all high current density experiments, but the character of the actual plate was not as good as obtained at lower current densities. Considerable difficulty was encountered with anodic polarization in this work.

C. Use of Zirconium Anode

Attempts were made to substitute zirconium metal for carbon as anode material. It was thought that this might improve the efficiency of the bath. Results are shown below:

TABLE III

USE OF ZIRCONIUM ANODES

<u>Run</u>	<u>2219-E-1</u>	<u>2219-E-2</u>
Time (mins.)	15	20
Temp. (°F)	1640	1640
Bath Composition) %	60 NaCl 40 K ₂ ZrF ₆	60 NaCl 40 K ₂ ZrF ₆
Δ Wt. Cathode (g.)	-0.1072	--
Av. Voltage	4.4	4.5
Current (amps.)	1.6	6.45
Current density (amps/dm ²)	13	50

Zirconium metal (0.010") obtained from the Foote Mineral Company was used as anode and cathode with the anode about 50% larger than cathode. The anodes disintegrated in both cases burning off at the stem and forming black powder throughout the bath. This powder is highly pyrophoric. No evidence of plating was detected on the cathode.

D. Use of Lower Melting Baths

A number of experimental runs were made using semi-refractory substances with lower melting points. Such a bath would be desirable from a convenience standpoint if a satisfactory deposition of zirconium

could be obtained. In addition, a conducting salt that is not an alkali or alkaline earth halide is used. This will prevent any secondary reaction from occurring in the electrolyte whereby the alkali or alkaline earth metal produced at the cathode reacts with the K_2ZrF_6 in the bath yielding the black powder always found dispersed in the electrolyte. The following preliminary results were obtained:

TABLE IV
Semi-Refractory Baths

No.	gms. K_2ZrF_6	gms. $PbCl_2$	gms. $ZnCl_2$	gms. $(KPO_3)_x$	E Volts	I Amps	Remarks
1	8	12			5	2	Solid Pb and Pb powder around cathode.
2	12	8			5	1	Black Pb powder around cathode.
3	16	4			5	1	Same as 2.
4	10		10		5	1	Zn plate on cathode.
5	10			10	5	1	Black Zr powder throughout bath and around cathode.

Runs of approximately 5 minutes duration at 650° to 950°F were accomplished. Copper strips, 1/8" x 1/4", were used as cathode materials and 1/4" diameter carbon rods were used as anodes.

Since the work of this type showed some promise, more accurate runs were made using a higher $PbCl_2$ concentration. It was thought at that time that the black powder obtained on the cathode might be zirconium powder.

TABLE V

 $\text{PbCl}_2\text{-K}_2\text{ZrF}_6$ Baths

Run	2226-A-1	2226-A-2
Time (mins.)	30	30
Cathode	1/8" Cu	1/8" Cu
Δ Wt. Cathode (g.)	+0.0028	+0.0082
Δ d Cathode (ins.)	-0.001	+0.001
Av. Voltage	12.0	11.5
Current (amps)	6.45	6.45
C. D. (amps/dm ²)	50	50
Bath Composition) %	20 K_2ZrF_6 80 PbCl_2	20 K_2ZrF_6 80 PbCl_2
Temp. (°F)	950	950

The bath fuses to a brown liquid at 850° to 900°F. It carries the current quite readily and a gray material is deposited on the cathode. A thorough washing with water to dissolve the salt showed most of the deposit to be salt. To determine the composition of the plate, the lead was precipitated as the sulfate and filtered off. The residual solution showed no test for zirconium metal.

E. Evaluation of Certain Factors in the Electrodeposition Process

A number of experiments were run in an effort to answer certain pertinent questions concerning the fused salt electrolytic process. These were as follows:

1. Effect of electrode distance on amount of plated zirconium obtained.

This question was answered through use of circular copper cathodes with anodes of varying size inserted in the center. Representative results are given below.

TABLE VI
VARIATION OF ELECTRODE DISTANCE

Run	2221-A-1	2221-A-2
Time (mins.)	60	60
Temp. (°F)	1640	1640
Bath Composition) %	25 NaCl 35 K_2ZrF_6	65 NaCl 35 K_2ZrF_6
Cathode	1-1/8" Cu ring	1-1/8" Cu ring
Anode	5/16" C	1" C
Δ Wt. Cathode (g.)	+0.0689	+0.0663
Δ d Cathode (ins.)	+0.0025	+0.003
Av. Voltage	4.7	4.5
Current (amps.)	6.45	6.45
C. D. (amps/dm ²)	50	50

Bright plates of Zr of the usual type were obtained in about equivalent amounts regardless of the electrode arrangement. Apparently under these conditions, electrode distance has little or no effect on the character of the deposit.

2. Will zirconium from bath dissolve in a molten metal cathode? Use of molten metal cathodes has previously been postulated. Several runs were made using Sn and Cu cathodes in the molten state to determine the extent of dissolution of zirconium in the cathode and whether any metallic zirconium would be plated on the cathode.

TABLE VII

USE OF MOLTEN METAL CATHODES

Run	2222-G1-1	2222-A1-2
Time (mins.)	60	80
Temp. (°F)	1640	2050
Cathode	Sn (1)	Cu (1)
Anode	5/8" C	3-5/8" C
Bath	65 NaCl	30.6 CaF ₂
Composition)	35 K ₂ ZrF ₆	29.4 MgF ₂
		40.0 K ₂ ZrF ₆
Approx. wt. (g.)	—	2.7
Av. Voltage	5.2	6.5
Current (amps.)	6.45	9.68
C. D. (amps./dm ²)	50	75

Zirconium dissolved in the tin quite readily, particles being easily detected in metallographic examinations (Figure No. 4). The cathode also sparked in contact with a grinding belt showing presence of pyrophoric zirconium. Particles of either Zr or a compound of Zr and Sn are shown scattered throughout the tin matrix. Approximately 5% Zr was detected in the copper cathode also. Figure No's. 5, 6, and 7 show the photomicrograph obtained after solidification of the liquid copper cathode. A fine precipitate presumably obtained on cooling a Cu-rich Zr solid solution is evident together with some larger primary crystals of Cu₃Zr in Figure No. 6. Primary particles of a compound of Cu and Zr are shown in Figure No. 5. Figure No. 7 at 330X shows several phases present in the Cu matrix in which a precipitate of Cu₃Zr is present.

FIGURE NO. 4

Specimen No. : 2222-GL-1
Etchant : None
Magnification: 75X

FIGURE NO. 5

Specimen No. : 2222-GL-1
Etchant : None
Magnification: 330X

FIGURE NO. 6

Specimen No. : 2222-A1-2
Etchant : $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2$
Magnification: 75X

FIGURE NO. 7

Specimen No. : 2222-A1-2
Etchant : $\text{H}_2\text{O}_2-\text{NH}_4\text{OH}$
Magnification: 330X

These structures could presumably be the result of a eutectoid reaction that has taken place in a zirconium-rich region of the ingot, resulting in the formation of two phases showing in this region. Neither metal showed any sign of metallic zirconium on or near the surface. A considerable amount of black powder was found adjacent to the cathodes in all cases.

3. What changes are there in a second electrolysis of a bath?

A run was made using old bath material containing considerable zirconium in the form of finely divided black powder. A 1/4" copper cathode was used and a current of 50 amps/dm² employed. The usual type of plate was obtained. Most of the black material which had been dispersed throughout the old bath material settled out at the bottom of the crucible. No appreciable change either in amount or character of the old bath material was detected.

4. Is there an increase in weight with repeated washing and replating of the same cathode?

A 1/4" copper cathode and NaCl-K₂ZrF₆ electrolyte were used in the usual fashion. A 30 minute run was made and the cathode removed and washed. This was then replaced in the bath and replated, this process being repeated a number of times. Results are shown in Table VIII.

TABLE VIII

REPEATED PLATING OF SAME CATHODE

Time (mins.)	30	30	35	10
Temp. °F	1640	1640	1640	1640
Wt. Cathode (g)	+0.1214	-0.1164	-0.1904	-0.1461
Av. Voltage	5.8	6.6	—	6.8
C. D. (amps./dm ²)	50	50	50	50

The usual type of plate was obtained in the first plating. After this initial run, a distinct loss in weight was noted in each successive run. The original plate was completely dissipated and the copper attacked by the bath.

5. Is the plate character and size improved by using a minimum Zr ion concentration in the electrolyte?

Runs were made using a low Zr ion concentration to determine any changes in character of the plate. In many instances, particularly with the more noble metals, low concentrations are essential for successful electrodeposition. A sample run is given in Table IX.

TABLE IX

USE OF LOW Zr CONCENTRATION

Run	2227-A-1
Time (mins.)	60
Temp. (°F)	1640
Bath Composition) %	90 NaCl 10 K ₂ ZrF ₆
Δ wt. Cathode	+0.1565
Δ d Cathode	+0.004
Av. volts	4.3
C. D. (amps/dm ²)	15.5

No significant changes in results were observed. Variation of current density with these baths also had little effect. Copper cathodes and carbon anodes were used in these runs.

Since the work done at 2000°F has shown little improvement over previous electrolyses, the one alternative seemed to be still higher temperatures. Electrode distance, cathode material, etc., seemed to have little effect in improving the deposit considering all work done to date, the temperature of electrolysis seemed to be the most significant factor. Therefore, a number of electrolysis runs have been made at temperatures of 2700° to 2900°F. This work is described and reported on in Appendix I.

6. Agitation of Cathode Area?

Agitation has been considered as a possible means of achieving a more adherent metallic deposit. It is well known that agitation promotes the growth of more uniform deposits in many cases of electrodeposition. This also permits the use of much higher current densities than normally are used.

The same equipment set-up was employed as in the original investigation except that a stirring motor fitted with a carbon stirring paddle was inserted in the center of a ring type cathode. The electrolyte in the center of the ring was constantly agitated during the electrolysis. Speeds were approximately 150 to 300 RPM. After the first two runs a larger nichrome current furnace was substituted permitting the use of 3-1/2" crucibles. Copper, nickel, and molybdenum were tried as cathode materials.

Results are very encouraging as substantial deposits of zirconium metal were found on the cathodes. The most significant item of all is the lack of black powder in the bath or adjacent to the cathode. The following results have been obtained to date.

TABLE X

RESULT OF ELECTROLYSIS WITH AGITATION OF BATH

Run	2231-A-1	C-1	C-2	C-3	2234-B-1	B-2
Time (mins.)	30	30	40	30	30	25
Temp. (°F)	1640	1640	1500	1650	1350	1350
Δ d Cathode	-0.015	+0.020*	--	+0.020**	+0.002	+0.003
Av. Voltage	2.7	Ca.12	4	2.5	2.5	3
Current	6.45	Ca.0.5	5.5	2.5	6.45	6
Current Density	50	5.9	43	19	50	46
Cathode	Cu	Ni	Ni	Ni	Mo	Mo

Bath Composition: 35% K_2ZrF_6 , 65% NaCl

The copper cathodes (2231-A-1) were found to readily dissolve in the bath on agitation so nickel was substituted as a cathode material. The plate obtained in 2231-C-1 was the most interesting of the series. The coating was bright, metallic, and reasonably ductile. It was somewhat uneven and porous, but this can undoubtedly be remedied through an adjustment of conditions. The plate varied from a thickness of 0.004 to 0.025" for the 30 minute run. A fairly high current efficiency was indicated. There was no evidence of black powder adhering to the cathode and only a slight amount in the bath immediately adjacent to the cathode.

Figure No's. 8 through 10 are photomicrographs of different cross-sections of this plated cathode. As can be seen in Figure No. 8, the thick deposit obtained is highly porous and may be due in part to the stirring effect in which some of the gases from the anode area are stirred into the cathode area and entrapped. Large dendrites are

FIGURE NO. 8

Specimen No. : 2131-C1
Etchant : Carapello's Reagent
Magnification: 150X

FIGURE NO. 9

Specimen No. : 2131-C1
Etchant : Carapello's Reagent
Magnification: 150X

FIGURE NO. 10

Specimen No. : 2131-C1
Etchant : Carapello's Reagent
Magnification: 150X

evident in the deposit and particles of a phase other than Zr or Ni are present at the plate-cathode interface. Figure No. 9 shows this interface in greater detail and mutual solution of Ni and Zr is evident. Figure No. 10 at 330X brings out this interface in greater detail and shows it to be continuous. It is probably an intermetallic compound of Zr and Ni, Ni_4Zr .

A series of tests indicated the plate to be zirconium metal. It sparks readily on the grinding wheel. It is inert to all concentrated acids except HF and aqua regia. On dissolution in aqua regia and subsequent precipitation with concentrated NH_4OH , the white hydrated oxide $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$ is found.

The other runs in Table XI consisted of slight variations of the conditions. In 2231-C-2 and C-3 a larger crucible was used with larger anodes to offset polarization difficulties. The cathode dissolved in C-2 and no plate was obtained. In C-3 the temperature was lowered and a plate much like C-1 obtained.

The photomicrographs of this plate at various sections are shown in Figure No's. 1 through 15. The unetched section, shown in Figure No. 11, indicates a very heavy continuous deposit of Zr. The etched specimen, Figure No. 12, shows black inclusions scattered throughout the deposit. Etching this specimen with 50% HNO_3 , 50% Glacial acetic acid indicates that an interface rich in Ni is present, probably Ni_4Zr , and that small particles of this compound are scattered throughout the deposit. The grain structure of the deposit is also disclosed. The particles scattered throughout the deposit could conceivably be due to the fact that the rapid stirring of the bath caused some erosion of the

FIGURE NO. 11
Specimen No. : 2231-C3
Etchant : None
Magnification: 75X

FIGURE NO. 12
Specimen No. : 2231-C3
Etchant : Carapello's Reagent
Magnification: 75X

FIGURE NO. 13
Specimen No. : 2231-C3
Etchant : 50% HNO_3 ,
50% Glacial
Acetic Acid
Magnification: 75X

FIGURE NO. 14
Specimen No. : 2231-C3
Etchant : Carapello's Reagent
Magnification: 400X

FIGURE NO. 15
Specimen No. : 2231-C3
Etchant : 50% HNO_3 , 50% Glacial
Acetic Acid
Magnification: 400X

Ni₄Zr compound that formed and that later these particles were retained or trapped in the plate. Figure No. 14 at 400X clearly indicates that at this section of the plate and cathode two bands have formed presumably the two compounds Ni₄Zr and Ni₃Zr. On these layers a heavy deposit of Zr metal has formed. Figure No. 15, at 400X, again shows a few particles of Ni-Zr compound which have been eroded from the plate and are present in the heavy Zr layer. Again the grain structure of the layer is evident.

Plating was tried on Mo cathodes (2234-B-1 and B-2) but results were not as good as with Ni. There was evidence of a plate but not in as large an amount. Under these conditions, there was still no evidence of the usual Zr powder. Another observation was that plating may take place below 1580°F, whereas it was previously thought temperatures above 1580°F, the Zr transition point, were necessary for plating.

IV. CONCLUSIONS

The most significant information obtained in this phase of the work has been the use of agitation as a means of getting an adherent plate through electrolysis of fused salt baths. With further work to determine the optimum conditions for plating with respect to cathode material, stirring speed, and electrode positions, it is believed a commercially feasible process for production of zirconium metal can be evolved.

The other work with high temperature baths also shows promise as a method of producing zirconium metal. It seems highly probable that the pure metal can be obtained in electrolytic baths at the melting

point of zirconium. It is quite possible that results may be obtained below this high temperature.

It has been shown in this work that such things as current density, electrode distance, and so on have little effect on the plating results with former procedures. However, it might be well to re-evaluate these factors in an agitated bath.

A method of producing solutions of zirconium in copper and tin through use of molten initial cathodes has been shown. Metals separation problems make this an undesirable means of obtaining pure Zr however.

Electrolytic baths other than alkali or alkaline earth halides do not seem to be useful in this work. There is invariably contamination from other metals as was shown in work with PbCl_2 and ZnCl_2 baths.

At the present time, it seems that two possible solutions to the problem are at hand, one through use of high refractory baths at temperatures around 3630°F (2000°C) and the other a lower temperature bath with cathodic agitation. The work remaining will consist of an evaluation of factors in the plating process in order to determine the best conditions for the desired results. A certain amount of work is needed on the physical set up of the agitated baths since some difficulty has been had with the cathodes dissolving in the bath. The 2700°F baths investigation will take the course of finding better baths and go toward a 3600°F (2000°C) electrolysis. If this is successful, it will then be necessary to determine which is the superior method from the standpoints of operation and results obtained.

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V. APPENDIX I

PRODUCTION OF Zr METAL BY HIGH TEMPERATURE
FUSED SALT ELECTROLYSISI. INTRODUCTION

The purpose of the following experiments was to determine whether or not it is possible to obtain a Zr plate or mass of Zr metal on or near carbon electrodes, utilizing temperatures of electrolysis higher than fused salt electrolyses are normally conducted, namely, 1400° to 1600°C. An attempt was also made to conduct the electrolysis above the melting point of Zr (1830°C), but met with little success because of the difficulty of developing an electrolytic bath which would not react too violently with carbon above 1600°C.

II. EXPERIMENTAL WORK

The experimental work consisted of setting up a suitable induction furnace with a cover which would exclude as much as possible the entry of air and prevent oxidation of the carbon crucible and electrode leads. This was done by inserting a 3-1/4" O.D. silica tube with a transite bottom cemented in place into a 3-3/8" I.D. induction furnace and packing "Norblack" around a 2" O.D., 3-1/4" long, 1/4" wall thickness, flat bottom carbon crucible, the top of the crucible being flush with the silica tube which was flush with the transite top of the furnace. The heat loss of this system to the induction coil at 2000°C was calculated to be 4 to 5 calories/sec. The rate of flow of water through the induction coil was 12 ml/sec., which was ample for the purposes intended. Sil-O-Cel was then sprinkled on the transite furnace top and a piece of fire brick with a 3" diameter x 1-1/2" depth cavity was

pressed into place. In this piece of fire brick, $1/2$ " diameter, 1 " diameter, and $5/16$ " diameter holes were drilled to receive the $1/2$ " carbon anode, the sight hole, and a $5/16$ " diameter carbon cathode rod. This cathode rod was pointed at one end to fit in a countersink in the lip of the crucible which served as the cathode.

The carbon electrode leads and the anode were protected from oxidation by ceramic tubing approximately $1-1/2$ " long, slipped over the carbons and resting on the firebrick roof. A mirror placed at 45° , 6 " above the 1 " sight hole, was then lined up with an optical pyrometer to observe temperatures. A small piece of firebrick kept the sight-hole covered when the temperature was not being read.

The High Frequency Converter used was a 6 KW, 20,000 cycle unit, 2.5-3 KW being sufficient for equilibrium conditions at 1700°C .

The two selenium rectifiers used were 13.5 volt 50 amp. plate rectifiers, which were estimated to develop a 25 to 30% A.C. component. They were connected in parallel and the D.C. output was adjusted by a variac which controlled the A.C. 110 V. input line.

The usual procedure of operation was to preliminarily calcine the salt and oxide in a silicon carbide resistance furnace at 2000° to 2100°F . This material was then crushed to a coarse grain size and placed in the previously "Norblack" packed crucible in the furnace. Sil-O-Cel was sprinkled on the transite and the firebrick cover placed in position. The $5/16$ " carbon lead was inserted and the $1/2$ " carbon partially inserted. The bath was melted and the $1/2$ " carbon immersed to the correct depth. The direct current was applied, and on completion of the run, the $1/2$ " carbon partially withdrawn. The crucible and furnace were then allowed

ELECTROLYSIS AT

No.	Bath Composition						Approx. M.P. °C	Temp. of Oper. °C	Polarity of Elec.	Starting Wgt. of Bath gm.
	% Al ₂ O ₃	Weight CaF ₂	Weight MgF ₂	Weight ZrO ₂	Weight BaZrO ₃	% (NaF) ₃ AlF ₃				
2228 H-1	—	25.5	24.5	—	50	—	1450	1475-1520	Crucible is cathode	140
2228 H-2	—	25.5	24.5	—	50	—	1450	1500-1570	Crucible is cathode	140
2232 H-1	—	25.5	24.5	—	50	—	1450	1500	1/2" carbon rod is cathode	140
2232 H-2	5	70	—	25	—	—	1450	1500-1550	Crucible is cathode	140
2232 H-3	15	55	—	30	—	—	1380	1500-1600	Crucible is cathode	99.5
2233 H-1	10	55	—	30	—	5	1300	1300-1600	Crucible is cathode	104
2233 H-2	15	55	—	30	—	—	1380	1500-1250*	Crucible is cathode	100
2236 H-1	5	70	—	25	—	—	1450	1400-1550	Crucible is cathode	130

* This temperature (below 1380°) could be accounted for by a change in bath composition.

1250° to 1600°C

No.	Measured Wgt. loss from fuming gm.	Degree of fuming during elec.	V.	A.	Time Mins.	Cur- rent Den- sity ² A/dc	Total Time of Elec. Min.	Comments
2228 H-1	Not measured	Great	3-1/2 4	9 10	60	6.3 7.0	60	Some evidence of carbide form- ation in area adjacent to cathode.
2228 H-2	Not measured	Great	7 13-1/2 13-1/2	40 16 60	3 11 1	28 11.2 42	15	Cathode reveals nothing of sig- nificance except small amount of carbide formation. Anode effect was apparent
2232 H-1	Not measured	Great	7	55	30	275	30	Large lump of material remained on cathode on its removal. Metal- lograph and microscope reveals metallic-looking deposits in mater- ial surrounding cathode and in bath remaining in crucible.
2232 H-2	Not measured	Great	3 3-1/2	18	17	12.6	17	Metallic-looking deposits in bath and on the walls of the crucible.
2232 H-3	8	Great	2 3-1/2	8 16	15 5	5.6 11.2	20	Metallic-looking deposits in bath and on the walls of the crucible.
2233 H-1	Not measured	Great	2 2-1/2	10	17	7	17	Metallic-looking deposits in bath and on the walls of the crucible. Some voltage tests conducted after run was finished, showed 10-12 V. A.C. pickup from converter.
2233 H-2	Not measured	Great	5 6	35	7	24.5	7	Metallic-looking deposits from crucible wall test positive for Zr by the aqua-regia-NH ₄ OH pptn. test.
2236 H-1	Not measured	Great	5	30	10	21	10	Heaviest metallic-looking deposits obtained from all the runs. Total time of this run was 17 minutes and the converter was turned off while electrolysis was being run.

to cool prior to dismantling.

Results in general indicated that current efficiencies were very low because of the small quantities of black metallic-looking material obtained. Best results were obtained in run No. 2233 H-2, where the D.C. electrolyzing current was not used while the H.F. unit was in operation. The D.C. and H.F. were used intermittently, because it was found that the H.F. converter was inducing a 10-12 volt alternating current into what was supposed to be only a D.C. circuit; however, even this could not be completely overcome by this procedure because the D.C. itself had an A.C. component of approximately 25 to 30%.

One qualitative analysis was made of the carefully scraped metallic-looking material adjacent to the crucible cathode. The analysis was positive for the element Zr by the aqua-regia, NH_4OH pptn. test. Most likely the material is Zr carbide.

Significantly enough, if a run is made without applying a D.C. voltage, only a very thin layer of the black material is formed lining the crucible; however, under conditions of electrolysis, a very thick layer (up to $1/16''$) of the material is formed (Run No. 2233 H-2 being the best example) showing that ZrO_2 is being decomposed electrolytically. Metallographic and microscopic study shows the layer to have a metallic appearance.

Fuming was very apparent in all of the runs, especially during electrolysis, because of the high D.C. voltages used. This was probably also due to the induced A.C. from the H.F. converter and the inherent A.C. from the rectifiers which would have caused wide variations in the voltage. The end result was a very low current efficiency. Decrease

in the diameter of the anode in all of the runs ($1/16''$ to $1/8''$) showed that CO gas was liberated. However, the large volume of gases coming from the anode and from the bath in general must have been for the most part F_2 because of the strongly acidic nature of the gas when moist pH paper was exposed for a moment over the sight-hole.

It was soon decided from the initial experiments to eliminate all materials from the bath which had a lower decomposition potential than ZrO_2 . This excluded $BaO \cdot ZrO_2$ so ZrO_2 alone was used as a source of Zr. MgF_2 , which is a little too close in decomposition voltage to ZrO_2 , was also eliminated. Below are listed calculated decomposition potentials at $2000^\circ K$ for some of the materials used.

CaF_2	0.60 volts
ZrO_2	0.43 volts
Al_2O_3	1.09 volts

At first it was hoped that when CaF_2 or Al_2O_3 are also decomposed because of the relatively high voltages, the Ca or Al would ppt. Zr from the ZrO_2 , but because of the high temperatures, these metals apparently boil off so readily that they do not even have time to react. This results in white clouds of material which are given off by the bath during electrolysis.

Future suggestions then on order would be:

1. The use of a carbon resistance furnace.
2. So far as laboratory work is concerned, the use of a storage battery with a suitable rheostat to control the voltage within narrow limits for the D. C. source.

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3. Elimination of CaF_2 because of its low decomposition potential.

A 60% ZrO_2 - 40% Al_2O_3 mixture which melts at approximately 1900°C would be more suitable.

4. Suitable crucible or crucible lining for the ZrO_2 - Al_2O_3 bath.

5. A plot of amperes versus volts in the above-mentioned bath to determine where irregularities in the curve would exist to attain optimum operating voltage of the cell.

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