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THE PRODUCTION OF ZIRCONIUM BY FUSED SALT ELECTROLYSIS

by

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SUMMARY

Investigations have been undertaken to further elucidate the nature of a previously disclosed process (Reports No. 1 and 2) for obtaining zirconium metal by fused salt electrolysis. The primary concern of this present work was to determine variation in results with changing time, current density, and cathode material.

Using a standard electrolytic set-up with facilities for current and temperature control as previously described (Report No. 1), a variety of runs were made with a bath of 35% K_2ZrF_6 and 65% NaCl. Temperature, time, current density, and cathode materials were in turn taken as variables. ^{1/2 2}

Previous conclusions were verified in that copper cathodes at temperatures above 1600°F are necessary for satisfactory plating of zirconium metal. Plating of varying slight degree was obtained on nickel, zirconium and titanium cathodes. Electrolyses were attempted using copper plated cathodes of iron, titanium and nickel. Only the copper plated nickel was satisfactory giving results much like that using pure copper cathodes.

In temperature variation, no plating is obtained at temperatures below 1580°F, the transition point of zirconium. There ^{was} seems to be some increase in yield of plated material with temperature increase. Time ^{had} has little effect on ^{the} amount of plating obtained; current efficiency drops ^{and} appreciably as time of electrolysis ^{was} is increased.

Current density appears ^{ed} to affect the plating yield somewhat. In general higher current densities ^{have} yielded the best results, both in amount and type of plate obtained.

Metallographic examinations were made on representative cathodes from each series of runs. These studies verified the presence of a zirconium plate on copper and to a lesser extent on other metal cathodes used. A discussion of the

nature of the plates from the metallographic evidence is given.

A supplemental study was made to determine the feasibility of depositing zirconium from non-aqueous solutions. (See Appendix I), electrolysis was carried out using a solution of $ZrCl_4$ in N-ethyl pyridinium bromide. A metallic plate was in evidence prior to organic decomposition, and further work on this aspect of the problem is in progress. *end*

Production of Zirconium
by
Fused Salt Electrolysis

I. INTRODUCTION

A method whereby zirconium metal can be obtained by electrolysis of a fused salt bath has been previously disclosed in work reported to the Atomic Energy Commission (Report No's I and II dated November 1, 1949 and November 10, 1949, respectively).^(1,2) In this process, continuous, adherent, bright, metallic deposits of zirconium metal have been produced on a copper cathode by electrolyzing a fused salt bath mixture containing 35% K_2ZrF_6 and 65% NaCl at a temperature above 1580°F, the temperature at which zirconium undergoes a phase transformation from the HCP crystal structure to a BCC crystal structure. Cathode current densities ranging from 10 to 100 amperes/dm² were investigated and deposits were obtained in all cases, the only variation being in the thickness and crystal size of the deposit obtained.

The present work being reported has been undertaken to determine (1) the characteristics of the zirconium so produced, and (2), the feasibility of utilizing fused salt electrolysis as a means of producing zirconium metal commercially.

This work has been divided into two phases, the first of which is covered in this progress report. In determining the characteristics of the electrolytic process for producing zirconium, the immediate objectives of this work were to determine the effects of (1) variation in time of electrolysis, (2) cathode material, and (3) current density on the type and amount of zirconium produced. This study has been supplemented by a spectrographic and metallographic examination of the plated zirconium.

II. EXPERIMENTAL EQUIPMENT

The experimental work has been accomplished using the same equipment as

described in detail in Report No. 1. A nichrome wire wound resistance furnace is used fitted with a Leeds and Northrup Micromax controller utilizing a chromel-alumel thermocouple for constant temperature control.

The current source for the electrolysis is a selenium rectifier operating through a current controller unit designed in this laboratory. The unit is capable of delivering a constant amperage or voltage to the electrodes. A Micromax controller has been modified so that it will record either current or voltage.

Graphite rods have been used as the anodes throughout. The rods are protected with ceramic protection tubes of zircon slip as produced in this laboratory. The thermocouple and cathode are protected by use of similar tubes, otherwise severe corrosion takes place at the air-salt interface.

All runs are made in a hood since toxic fumes and some volatilization of the salt mixture are given off in the electrolytic process.

III. EXPERIMENTAL RESULTS

A. Work at Constant Current and Temperature

1. With Copper Cathode

A number of fused salt electrolyses were run at 50 amps/dm² and 1640°F using copper cathodes in an effort to determine any differences in amount of plate obtained with increasing time. In the first set 0.010" copper sheet was used as the cathode. A 1 in.² piece was used giving 2 in.² (0.0654 dm²) of surface. This required 6.45 amperes to give a current density of 50 amps/dm².

In all runs, the bath ingredients (35% K₂ZrF₆, 65% NaCl) were ground together in a mortar and dried overnight in an oven at 125°C. A total of 105 g. of salt mixture was used in each case. Any water remaining was electrolyzed at the start of the run through use of graphite electrodes below the decomposition potential of K₂ZrF₆ (1.3V). This electrolysis was done at 1450°F. Following this the temperature was raised to 1640°F, the current raised to 6.45 amps, and the plating process carried on for varying lengths of time.

The following results were obtained:

TABLE I (0.01" Copper Cathode)

<u>Run No.</u>	<u>2203-A-1</u>	<u>2203-A-2</u>	<u>2203-A-3</u>	<u>2203-A-4</u>
Time (mins.)	15	30	61	120
Wt. Cathode + Plate	1.9906	2.0185	1.9291	2.0986
Wt. Cathode	1.8856	1.9040	1.8020	1.8449
Wt. Plate (g)	0.1050	0.1145	0.1271	0.2537
Thickness Plate (in.)	0.0015	0.0025	0.0035	0.0045
Av. Voltage	4.2	4.2	4.5	4.3
Current Density (amps/dm ²)	50	50	50	50
Current Eff. %	9.43	4.17	2.28	2.27

Several runs were also made where weighings were not obtained. The thickness of the plates checked quite closely. Two hour runs were attempted, but the cathode material disintegrated in that length of time at the point where the cathode was fastened to the holder.

After the plating process, the copper cathode became very brittle. To determine whether this was due to reaction with the electrolyte, a run was made below the K_2ZrF_6 decomposition potential to determine any change in the cathode material. The copper was found to retain its original characteristics aside from some corrosion.

The plates obtained have a bright metallic character and do not peel off after 3 weeks time. They may be removed by treatment with 10% HNO_3 . In all cases a large amount of black powdery material surrounds the cathode. Some of this immediately adjacent to the cathode is very black and pyrophoric, presumably Zr metal.

Since difficulty was encountered using the 0.010" copper sheet as a cathode material, other runs were made using 1/4" copper strip. The same bath

composition and conditions were retained.

Results of the runs were as follows:

TABLE NO. II (Heavy Copper Cathode)

<u>Run No.</u>	<u>2205-A-2</u>	<u>2206-A-1</u>
Time (mins.)	60	120
Wt. Cathode + Plate	22.4201	22.5586
Wt. Cathode	22.2204	22.3376
Wt. Plate (g)	0.1997	0.2210
Thickness Plate (ins.)	0.003	0.003
Av. Voltage	4.0	4.5
Current Density (amps/dm ²)	50	50
Current Eff. %	3.6	1.99

These plates had the same general appearance and character as those previously prepared. The thickness and weight of the plate were of approximately the same magnitude for the one and two hour runs. The one hour run has a larger apparent weight, but this is probably due to incomplete washing since the thickness is comparable to that previously obtained. The plates in 2206-A-1 and also in 2203-A-3 were stripped with 10% HNO₃ and then filtered and dissolved in aqua regia. Subsequent treatment with ammonia precipitates the zirconium quantitatively. In both cases, a very light blue color remained after the precipitation indicating presence of a small amount of copper in the plate. Samples of the plate were too small for a quantitative treatment and further analysis was obviously in error.

2. Work with other Cathode Materials

a. Nickel

Plating was attempted with 0.022" nickel using 50 amps/dm² current for one hour. This gave a total increase in thickness of 0.006 - 0.008 ins. or 0.003 - 0.004 ins. for the plate. However, the plate did not have the metallic

appearance of that on copper and appeared more like an oxide coating.

TABLE NO. III (Nickel Cathode)

<u>Run No.</u>	<u>2210-C-1</u>	<u>2202-C-1</u>
Time (mins.)	60	60
Wt. Ni + Plate	5.5129	
Wt. Ni	5.3997	
Wt. Plate (g)	+ .1132	
Δd Cathode (ins)	+ .003	+ .004
Av. Voltage	4.8	4.6
Current Density (amps/dm ²)	50	50
Current Eff. %	2.04	

b. Molybdenum

Runs were carried out using 0.010 ins. molybdenum as a cathode.

These were also done at 50 amps/dm² for one hour. A plate about 0.002 in thickness was obtained. This had the same general appearance as that obtained on copper except that it was a coarser grained structure.

c. Titanium

These were run under 50 amps/dm² also using 0.010" Ti. The following results were found:

TABLE IV (Titanium Cathode)

<u>Runs</u>	<u>2207-D-1</u>	<u>2207-D-2</u>	<u>2207-D-3</u>
Time (mins.)	90	60	60
Wt. Cathode + Plate		2.6160	2.3055
Wt. Cathode (g)		2.5862	2.5753
Wt. Plate		0.0298	-.2698
Thickness Deposit (ins.)	0.002	0.002	+ .0025
Voltage -- Av.	3.9	4.2	4.4

TABLE NO. IV (continued)

<u>Runs</u>	<u>2207-D-1</u>	<u>2207-D-2</u>	<u>2207-D-3</u>
Current Density (amps/dm ²)	50	50	50
Current Eff. %		0.54	

This plate did not have the bright metallic characteristics found with copper cathodes. The gain in weight is also found to be much less. It appears as a rough oxide coating rather than a plate. Weight was not obtained in 2207-D-1 because of a fractured cathode. Titanium also becomes brittle on long exposure to the salt bath.

d. Zirconium

Zirconium metal (0.010") as supplied by the Foote Mineral Company was tried as a cathode material. This reacts with the bath quite readily and it is difficult to get successful runs in which weights of deposited material can be ascertained.

Following are the best results obtained:

TABLE V (Zirconium Cathode)

<u>Run</u>	<u>2208-E-1</u>	<u>2208-E-2</u>	<u>2208-E-3</u>	<u>2208-E-5</u>
Times (mins.)	15	32	60	30
Wt. Cathode + Plate	1.3162	1.3434		1.3413
Wt. Cathode	1.3882	1.4274		1.4042
Δwt. cathode (g)	-0.0720	-0.0840	(loss)	-.0629
Thickness (Plate) ins.	.0005	0.0005	0.001	.001
Av. Voltage	4.2	4.2	4.1	4.2
Current Density (amps/dm ²)	50	50	50	50

An apparent plate is obtained in each case since a slight increase in thickness is obtained and the surface has the appearance of a plate. However,

there is a weight loss in the zirconium cathode apparently due to reaction with the bath. The Zr metal appears very porous under the microscope after the electrolysis. No runs were complete for longer than 32 minutes due to attack on the cathode. 2208-E-5 was run at 1450°F and gave the same apparent results as at 1640°F.

e. Iron

The following runs were made using .040" iron as the cathode material.

TABLE VI (Iron Cathode)

<u>Run</u>	<u>2211-F-1</u>	<u>2211-F-2</u>
Time (mins.)	60	60
Cathode + Dep.	7.3715	7.2357
Wt. Cathode	7.3888	7.2392
Wt. Deposit	-.0173	-.0035
Δd Cathode	-.001	-.001
Av. Voltage	4.4	4.3
Current	50	50

A very large amount of black pyrophoric powder is obtained at the cathode. No apparent plate is noted, and the iron suffers considerable attack by the bath. The surface appears badly corroded, and a loss in weight and thickness is obtained.

B. Variation of Current Density

Runs were made using copper cathodes at varying current densities to determine what effect the current had on the amount of plate. Other conditions were kept constant. 1/4" Cu strip was used as cathode. Results are given below:

TABLE VII (Cu Cathode - Variation of Current Density)

<u>Run</u>	<u>2209-A-3</u>	<u>A-4</u>	<u>A-5</u>	<u>A-6</u>	<u>A-7*</u>	<u>2205-A-1</u>
Time (mins)	60	60	60	60	30	60
Wt. Cathode + Plate	22.2724	21.5102	22.3275		21.4349	21.9224

*Interrupted by anodic polarization

TABLE NO. VII (continued)

Run	2209-A-3	A-4	A-5	A-6	A-7	2205-A-1
Wt. Cathode	22.1815	21.3900	22.2410		21.2745	21.7912
Wt. Plate (g)	.0909	0.1202	0.0865		0.1603	0.1312
Thickness plate (ins.)	0.0015	0.0015		0.003	0.002	0.0015
Av. Voltage	3.4	3.1	2.2	6.5	6.7	4.7
Current Density	25	25	10	100	100	100
Current Eff%	3.27	4.38	3.15		2.88	1.18

Plates obtained in all cases were of approximately the same character.

The amount seems to increase with applied current. 2205-A-1 apparently partially shorted out. Here large (1/2") anode rod was used. In 2209-A-6 and A-7, 1/4" rod was used and appeared to give better results because of greater electrode spacing.

The plate obtained in 2209-A-6 stripped off spontaneously on washing. At first it appeared to consist of two layers, the outer one peeling off. A rough analysis for copper on the strip showed no characteristic blue color.

Yield of zirconium plate seems to increase somewhat with current density as well as with time. It is thought the electrode spacing is quite significant in this respect also. Where smaller anode rods were used allowing greater spacing between the electrodes, the amount of plate generally was somewhat larger. In addition, the amount of pyrophoric zirconium powder surrounding the cathode is notably increased. This burns on contact with a flame. In most previous work, the cathode material burned only after repeated aqueous extraction and screening of the residue.

It is noted that current efficiency drops off as the time of a run is increased. This presumably indicated that most of the plate is formed during the first minutes of a run.

C. Use of Copper Plated Cathodes

Several runs using copper plated cathodes were made to determine whether

a plate could be obtained over the copper as on a copper cathode. Plating was done using a CuSO_4 bath at 0.5A and 4.0V.

The electrolytic procedure was carried out as in all other runs with results as follows:

TABLE NO. VIII (Copper Coated Cathodes)

<u>Run</u>	<u>2213-AC-1</u>	<u>2213-AF-1</u>	<u>2213-AD-1</u>
Cathode	Cu on Ni	Cu on Fe	Cu on Ti
Time (mins.)	60	60	60
Wt. Cathode + Dep.	5.7532	5.9099	2.5335
Wt. Cathode	5.6198	5.9260	2.5676
Wt. Deposit	+.1334	-.0161	-.0341
Δ l Cathode	+.002	+.002	+.001
Av. Voltage	4.1	4.3	4.3
Current d	50	50	50
Current eff.	--	--	--

A bright plate was obtained on the Cu-Ni with a heavy coating around the edge. The Cu, however, was found to have been dissipated in the plating bath. The Cu-Fe and Cu-Ti showed no signs of the typical plate appearance, but appear a dull grey to black.

IV. EXAMINATION AND EVALUATION OF ZR PLATES OBTAINED

In order to evaluate the zirconium plates produced on the various cathode materials, a metallographic examination of all cathodes and their deposits was made. A check on the zirconium plate thickness could also be made by examination of the cathode and plate cross-section at a suitable magnification.

A. Specimen Preparation

To prepare the thin cathode specimens for metallographic examination, steel bar clamps were prepared for holding the specimens. The clamps protected the edges

of the specimens and maintained them within five degrees to the perpendicular. To aid in the preservation of the edges, the specimens were sandwiched between two thin sheets of copper.

A flat surface was produced by grinding on a well worn grit belt grinder followed by the customary grinding on successively finer emery paper through the 3/0 grit. The polishing operation was started on a broadcloth covered wheel charged with No. 1 polishing alumina. When all of the scratches produced by the emery paper were removed, the specimen was given a rather deep etch to remove any burred edges and any metallic particles that might have been caught between the specimen and the clamp. Polishing was continued on microcloth using No. 2 polishing alumina. Repeated etching and polishing was used to remove any flowed material. When a satisfactory surface had been produced, the specimen was given a final polish with microcloth charged with shamo. During the entire polishing operation the clamp was constantly rotated to prevent the formation of "tails" at inclusions and voids.

The following etchants were used for the various cathode materials:

TABLE IX

<u>Cathode Material</u>	<u>Etchant</u>	<u>Application</u>
Copper	<u>A</u> 10 parts: 50% NH_4OH 3 parts: 3% H_2O_2	Fresh solution is prepared each time. Applied with cotton swab for 5-10 sec.
Nickel	<u>B</u> 5 gms. 4% HF 2 ml. conc. HCl 99 ml. Ethyl Alcohol	Applied with cotton swab 3-4 mins.
Titanium and Zirconium	<u>C</u> 4% HF (48%) 2% HNO_3 (conc) 94% H_2O <u>D</u> 6 parts glycerin 2 parts HF (48%) 1 part HNO_3 (conc)	Rubbed vigorously with cotton swab to remove oxidation products, 1-2 sec. Applied with cotton swab, 30-60 sec.

The specimens were carefully washed in H_2O and alcohol and dried in warm air. It is essential to remove all moisture from the capillary cracks between specimen and clamp, since this moisture will seep out and stain the specimen if not removed.

B. Metallographic Examination

1. Copper Cathodes: the copper cathodes coated with zirconium and described in Table I were prepared for metallographic examination as described above. They were examined unetched and then etched to reveal the copper structure. Figure No's. 1, 2, and 3 show copper cathode, run No. 2203-A-1 electrolyzed for 15 minutes.

Figure No. 1, unetched, shows an adherent continuous coating of zirconium on a copper base. A general corrosion at the grain boundaries in the interior of the copper has taken place in this short interval of time.

Figure No. 2 magnification of 75X, is a photomicrograph of the same specimen cross-section etched to reveal the copper structure. No recrystallized zone, or new phase is evident at the Zr-Cu interface at this magnification. Figure No. 3 shows the same cross-section of the specimen at 150X, again etched to reveal the copper structure. No new structure is evident. However, a slight diffusion of zirconium into the copper is indicated. Just below the Zr-Cu interface a thin light zone is present in the copper grains. These copper grains are continuous, and no recrystallized zone is shown, indicating that the very thin light zone of the copper grains must be a solution of zirconium into copper.

As previously described all of the thin copper cathodes, coated with zirconium were brittle and from the photomicrographs this brittleness must, for the greater part, be due to the corrosion that has taken place at the copper grain boundaries.

The copper cathodes plated for 30 minutes (Specimen No. 2203-A-2) shows a much heavier deposit of zirconium and also a much greater corrosion of the copper (Figure No's. 4, 5, 6). The photomicrograph of the unetched cathode cross-section at 100X, Figure No. 4, reveals that a reaction has taken place at the Zr-Cu interface, and a new phase can be discerned in Figure No. 5, the etched specimen, shown at 75X.

Fig. 1—Specimen No. 2203-A-1. Etchant, none.
75X

Fig. 2—Specimen No. 2203-A-1. Etchant, NH_4OH
+ H_2O_2 . 75X

Fig. 3—Specimen No. 2203-A-1. Etchant, NH_4OH
+ H_2O_2 . 150X

Fig. 4—Specimen No. 2203-A-2. Etchant, none.
75X

Fig. 5—Specimen No. 2203-A-2. Etchant, NH_4OH
+ H_2O_2 . 75X

Fig. 6—Specimen No. 2203-A-2. Etchant, NH_4OH
+ H_2O_2 . 150X

This band is more plainly seen in Figure No. 6 at 150X. A diffusion band, revealing a new phase, probably Cu_3Zr is now present between the copper cathode base and the zirconium plate. This intermediate phase should contain about 32% Zr.

The plate of zirconium on a copper cathode obtained after electrolyzing the fused salt bath for 1 hour is shown in Figure No's. 7, 8, and 9.

In Figure No. 7, of the unetched specimen (2203-A-3), the intermediate phase appears in the plate obtained on the copper cathode after electrolysis of 1 hour. It is brought out in greater detail in the photomicrograph of the etched specimen in Figure No. 8 and in Figure 9, which shows the structure at 150X.

The photomicrographs of the 2 hour run are shown in Figure No's. 10, 11, and 12. Again, the thickness of plate has been increased, and an intermediate band of compound Cu_3Zr is evident. The columnar grains of the plate are shown in Figure No. 10 and evidence of diffusion of Zr into the cracks at the copper grain boundaries is clearly brought out. Also, the copper grains, stained in this photomicrograph have grown to such a size that the original copper cathode is now about one copper grain thick.

In order to overcome the difficulty encountered using the electrolytic copper sheet as a cathode, phosphorous deoxidized copper bar stock was substituted for the cathode material. The bar stock was 1/4 inch in thickness and was much easier to handle both for electrolysis and metallographic examination. The severe corrosion encountered with the electrolytic copper is due to the fact that this type of copper contains quite a bit of copper oxide. When the electrolysis is conducted any H_2O present is decomposed to oxygen which reacts at the anode with the carbon and H_2 which goes to the cathode. The H_2 diffuses very rapidly through the cathode material, reacts with the copper oxide which is predominately at the grain boundaries and forms H_2O which is insoluble in the copper and cannot diffuse out. It therefore expands and cracks the copper along the grain boundaries, causing the embrittlement obtained in all of the cathodes made from this electrolytic copper. As previously

Fig. 7—Specimen No. 2203-A-3. Etchant, none.
75X

Fig. 8—Specimen No. 2203-A-3. Etchant, NH_4OH
+ H_2O_2 .
75X

Fig. 9—Specimen No. 2203-A-3. Etchant, NH_4OH
+ H_2O_2 .
150X

Fig. 10—Specimen No. 2203-A-4. Etchant, NH_4OH
+ H_2O_2 .
75X

Fig. 11—Specimen No. 2203-A-4. Etchant, NH_4OH
+ H_2O_2 .
150X

Fig. 12—Specimen No. 2203-A-4. Etchant, NH_4OH
+ H_2O_2 .
75X

described when a cathode of this copper is immersed in the bath and held at 1640°F for one hour without current flowing there is no effect on its ductility.

The cathode 2205-A-2, made from this phosphorous deoxidized copper was electrolyzed for 1 hour at 1640°F. After washing, the plated cathode was sectioned so that a vertical-section and a cross-section could be examined metallographically. Figure No's. 13 and 14 show the vertical section at 35X. Figure No. 15, this same section at 75X, and Figure 16 the section at 150X. No corrosion of the copper is evident. A smaller grain size of the base copper is present just above the Zr-Cu interface. This is undoubtedly due to recrystallization of the copper cold-worked by the cutting operation to form the cathode. A gradation of color is present in these copper grains, denoting a slight diffusion of Zr into Cu in solid solution. An interface is present with a band of a new phase, Cu_3Zr , then another interface or boundary, and then the zirconium plate. This plate is continuous and adherent, and is bright and shiny on examination. The results obtained are similar to those obtained with the 0.010" thick electrolyte copper sheet except that no corrosion at the grain boundaries is noted. The photomicrographs of the cross-section are similar.

2. Nickel Cathodes

Only a slight increase in weight and thickness of plate was obtained in the fused salt electrolysis of the mixture of NaCl and K_2ZrF_6 utilizing a nickel cathode.

Figure No. 17 shows the microstructure of the as-received nickel. The nickel cathode, after electrolysis of 1 hour duration is shown in Figure No. 18. Grain growth of the base nickel has occurred and only a very thin deposit of plate can be detected at 75X. At 335X (Figure No. 19), this thin plate is evident. Its character and appearance is not like the deposit obtained on copper as it lacks the shiny metallic luster previously encountered.

Fig. 13—Specimen No. 2205-A-2. Etchant, NH_4OH + H_2O_2 . 35X

Fig. 14—Specimen No. 2205-A-2. Etchant, none. 75X

Fig. 15—Specimen No. 2205-A-2. Etchant, NH_4OH + H_2O_2 . 150X

Fig. 16—Specimen No. 2205-A-2. Etchant, NH_4OH + H_2O_2 . 150X

Fig. 17-Specimen No. as received Ni sheet.
Etchant, Compello's reagent. 75X

Fig. 18-Specimen No. 2202-C-1. Etchant,
Compello's reagent. 75X

Fig. 19-Specimen No. 2202-C-1. Etchant,
Compello's reagent. 335X

3. Molybdenum and Iron Cathodes

No discernable deposits or gain in weight were in evidence with use of either a molybdenum or iron cathode.

4. Titanium Cathodes

In searching for cathode materials for deposition of zirconium from a fused salt bath, the use of titanium as a possible cathode material was investigated. In the Ti-Zr system an uninterrupted series of solid solutions is indicated. Both of these metals belong to the same group in the periodic system and have an HCP lattice structure at room temperature. In this series, a solid solution can have a transition temperature at which the crystallographic transition $\alpha \rightleftharpoons \beta$ takes place, several hundred degrees lower than that of either zirconium or titanium, although both of these pure metals transform at almost the same temperature from the HCP to the BCC modification.

The titanium sheet material used was commercially pure titanium obtained from the Remington Arms Company, Inc. A microsection of this titanium is shown in Figure No. 20. Figure No's. 21 and 22 show the microstructure of the titanium cathode and the plate obtained at 75X and 150X, respectively. The microstructure of the base titanium has a structure which resembles that of commercial titanium quenched from above the transformation temperature, the rate of transformation of the $\beta \rightleftharpoons \alpha$ being influenced by the impurities present, particularly oxygen and nitrogen. The microstructure reveals the Widmanstatten character of the transformation. The plate obtained is evident in both Figure No's. 21 and 22 and there is no evidence of interfaces appearing between the plate and the base titanium. The one hour run with a titanium cathode, again shows a plate obtained (Figure No. 23) with no evidence of an interface. As was disclosed in Table No. V a slight loss of weight with an increase in thickness was measured in the third run (Specimen No. 2207-D-2) with a titanium cathode. No explanation has been found as yet for this

Fig. 20—Specimen No. As received commercial titanium. Etchant, 4% HF, 2% HNO₃, 94% H₂O.
75X

Fig. 21—Specimen No. 2207-D-1. Etchant, 20% HF, 1% HNO₃.
75X

Fig. 22—Specimen No. 2207-D-1. Etchant, 20% HF, 1% HNO₃.
150X

Fig. 23—Specimen No. 2207-D-2. Etchant, 4% HF, 2% HNO₃, 94% H₂O.
150X

fact other than the fact that a slight solution of the titanium in the electrolyte must take place on insertion of the cathode into the bath.

5. Zirconium Cathodes

An ideal starting cathode would be one composed of pure zirconium so that any plate of zirconium deposited would not have to be removed for the recovery of the zirconium produced by electrolysis. A photomicrograph of the zirconium sheet, obtained from the Foote Mineral Company, and used as cathode material is shown in Figure No. 24. Some cracks and porosity are evident in this material. In all of the runs with zirconium an increase in cathode thickness and decrease in weight was obtained, the decrease in weight being due to corrosion of the cathode by the molten electrolyte as is evident from the photomicrographs. It is felt that since there was porosity to begin with, the molten electrolyte must have flowed into the cracks and pores and dissolved some of the cathode material and enlarged these cracks and pores, with a resultant total loss in weight for the cathode and plate.

Figure No's. 25 and 26 are photomicrographs of the zirconium with plate after an electrolysis run of 32 minutes, shown at 75X and 150X respectively.

Figure No. 27 shows the cross-section of a zirconium cathode and plate at 150X after 1 hour of electrolysis at 1640°F (Specimen No. 2208-E-3). A thin plate is in evidence but as yet we have not determined its characteristics or properties. The zirconium base metal has recrystallized and the grains have grown to a much larger size than was evident in the as-received zirconium or the electrolysis run of 32 minutes duration.

6. Copper-plated Cathodes

Copper was plated out on cathodes of iron, nickel and titanium to determine the effect of a Cu plated cathode on the amount and type of zirconium that could be obtained by electrolysis of a fused salt bath. Only the copper-plated nickel cathode yielded encouraging results.

Figure No's. 28 and 29 are the photomicrographs of the cathode cross-section

Fig. 24—Specimen No. As received zirconium.
Etchant, 4% HF, 2% HNO₃, 94% H₂O. 150X

Fig. 25—Specimen No. 2208-E-2. Etchant, 4%
HF, 2% HNO₃, 94% H₂O. 75X

Fig. 26—Specimen No. 2208-E-2. Etchant, 4%
HF, 2% HNO₃, 94% H₂O. 150X

Fig. 27—Specimen No. 2208-E-3. Etchant, 4%
HF, 2% HNO₃, 94% H₂O. 150X

of specimen No. 2213-AC-1 at 335X and 500X respectively. As can be seen from the photomicrographs several reactions have occurred. Mutual diffusion of the copper and nickel has occurred so that there is now a solid solution region of Ni-Cu continuous with the nickel and also with copper. Adjacent to the remaining copper plate is a mixture of the Cu (solid solution)- Cu_3Zr eutectic with some large areas of Cu_3Zr at the Cu interface. A band of what appears to be Zr is present adjacent to this eutectic region. The reason for this 2 phase band, rather than a one phase band of Cu_3Zr must be that the porous copper electrodeposit had allowed the Zr to diffuse rapidly into the pores and reaction has taken place throughout the material rather than through an interface.

7. Copper Cathodes at Various Current Densities

As has been previously discussed, the effect of current density on the character and amount of the zirconium plate produced on a copper cathode was investigated. Figure No's. 30 and 31 are photomicrographs of copper cathodes with zirconium plates obtained at a current density of 100 amperes/dm² for a time of electrolysis of 60 minutes and 30 minutes respectively. As can be seen an interface and a band of Cu_3Zr is evident between the copper and the zirconium. The deposit obtained is much like those obtained at lower current densities.

V. CONCLUSIONS

Limited data previously obtained on the production of zirconium by fused salt electrolysis have been repeated and enlarged. The use of a copper cathode at temperatures over 1600°F is requisite before a zirconium plate is obtained. Plates of zirconium, to a lesser extent, have been obtained on nickel, titanium and zirconium at 1640°F.

In the use of a copper cathode, it is necessary that OFHC or phosphorous deoxidized copper be used, since small amounts of oxides present in the copper are reduced by hydrogen which diffuses rapidly into the cathode to form H_2O . This H_2O is insoluble in the copper and causes embrittlement and cracking of the cathode.

Fig. 28—Specimen No. 2213-AC-1. Etchant,
none. 335X

Fig. 29—Specimen No. 2213-AC-1. Etchant,
none. 500X

Fig. 30—Specimen No. 2209-A-6. Etchant,
 $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. 150X

Fig. 31—Specimen No. 2209-A-7. Etchant,
 $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. 150X

The H_2 formed at the cathode is due to electrolysis of small amounts of H_2O present in the electrolyte.

It is evident from the work reported that a reaction of copper and zirconium occurs to form a compound Cu_3Zr which is present between the copper base and the plate. This diffusion band is bounded by two interfaces.

There is little information available on the Cu-Zr binary system, particularly on the Zr-rich end of the Cu-Zr phase diagram. The solid solubility of Zr in Cu appears to be very low. Microscopic examination has shown it to be some tenths of 1% at the most. (3,4) Electrical resistance measurements even make it very doubtful whether there is any formation of solid solution of Zr with Cu. (3) In the case of copper it appears that the specific resistance increases linearly with the Zr content in alloys from 0 to 6% Zr. With very small quantities of Zr, the specific resistance remains practically constant. The tensile strength, however, increases considerably, even with these small quantities. (3)

Zirconium forms a compound with copper the composition of which cannot be stated with absolute certainty but it may probably be represented by the formula Cu_3Zr . This compound forms a eutectic with the "solid solution" poor in Zr, having the following co-ordinates: Cu- Cu_3Zr , temperature of eutectic $964^\circ C$ ($1767.2^\circ F$) at 12.3% Zr.

The compound Cu_3Zr would have a composition of 32.35% Zr. The tentative phase diagram up to this composition is shown in Figure No. 32.

The extent of solid solubility of Zr in Cu and Cu in Zr and the number and types of compounds that may form can be hypothesized by a consideration of the Hume-Rothery Rules. The extent of solid solubility of one element in another is generally conceded to depend on several factors which include:

- (a) the relative lattice types and atomic size of the solute and solvent metals,
- (b) the chemical affinity of one for the other and,
- (c) the relative valency effect.

Cu-Zr Copper-Zirconium

Fig. 32

Zr occurs in two allotropic forms: the alpha modification at room temperature is HCP and the beta form is BCC at $863\pm 3^{\circ}\text{C}$ (1585°F). Copper is face-centered cubic in symmetry. Thus a dissimilar crystal structure exists between the two elements. The atomic size factor consideration shows zirconium and copper to differ by 20% so that on this consideration no solubility of Cu in Zr or Zr in Cu should appear. Zirconium appears on the left side of the second long period of the periodic table included in the group of transition elements considered electropositive. Copper occurs in the first long period but is to the right of zirconium and is therefore electronegative with respect to Zr. Thus a difference exists between Zr and Cu as regards their chemical affinity since the more electropositive the solute and the more electronegative the solvent, or vice versa, the greater is the tendency to restrict solid solubility and to form intermetallic compounds.

Also a metal of lower valency tends to dissolve a metal of higher valency more readily than vice versa. In the case of copper, it dissolves decreasing amounts of a solute as the valency of the solute increases. Zr is generally considered tetravalent and as such its solubility in copper can be expected to be limited.

Considering the reverse of this, or the solubility of copper in zirconium, it would appear that even less copper would dissolve in zirconium than vice versa. The general rule that in a binary system the solubility in a higher melting metal is greater than in a low melting metal would thus appear to be an exception in this case as well. Rather, a strong tendency is indicated to form stable intermediate compounds at the expense of primary solid solutions, zirconium being strongly electropositive with respect to copper would be expected to exhibit this tendency.

There is no information available in the literature concerning the type of compounds occurring in the Cu-Zr system. However, Laves and Wallbaum⁽⁵⁾ have analyzed the compounds formed in the ~~Cu-Ti~~ system and their analysis can be used to give some indication of what is to be expected in the Cu-Zr system. According to

Laves and Wallbaum, in copper alloys of low Ti content, the compound Cu_3Ti is formed which has a deformed hexagonal structure while a high Ti content produced an isomorphous compound CuTi_2 which has a face-centered structure with 96 atoms per cell, apparently a complex phase. The former would correspond to an " ϵ " phase with an electron-atom ratio of $7/4$ while the latter with its large cell suggests a " δ " phase although CuTi_2 does not correspond to an electron-atom ratio of $21/13$ according to the ratios for the various intermediate phases as postulated by Hume-Rothery. The crystal structures found in structurally analogous phases that seem to follow the " ϵ " type show a HCP arrangement for an electron-atom ratio of $7/4$ while the " δ " type with a $21/13$ electron-atom ratio shows a complex cubic structure. The Cu-Ti compounds seem to follow these analogous structures and therefore it is expected that the Cu-Zr system should be similar with the compounds Cu_3Zr , and CuZr_2 present in this system.

However, in the work completed to this date no evidence of the phase CuZr_2 has been disclosed in the electrolysis of Zr using a Cu cathode at the temperatures utilized.

From the diffusion band disclosed in the photomicrographs only one phase, the Cu_3Zr compound, is evident. Preliminary spectrographic and gravimetric analysis, as described in the report, has shown the copper content of the outer layer to be small or not present in some cases, and below that which would be necessary for a CuZr_2 compound to have formed. Impurities of Hf, Zn, Ti, and Al are present however.

From these results it can be concluded that zirconium forms at the surface of the cathode and diffuses to a fraction of a percent, the limit of solid solubility. With increasing amounts of zirconium formed at the cathode a reaction occurs and a band of Cu_3Zr is formed with an interface between the $\angle$ -Cu solid solution. The rate of diffusion of Cu through this compound is extremely low as compared to the rate of plating of Zr. Hence in the time limits of electrolysis investigated to date, the diffusion of Cu through the Cu_3Zr band into the Zr plate is not of sufficient

rate for a concentration of Cu to build up to form a CuZr_2 band if such a compound exists. The rapidity in which a Zr plate initially builds up may be due to the fact that Zr is wetted very rapidly by Cu. This wettability has been well established in the case of Cu-Ti coatings.^(6,7) The reasons for this wettability have as yet not been established.

In the case of Ni cathodes, no diffusion band has as yet been identified, as the plate thicknesses reported on in this report have not been excessive. The hypothetical Ni-Zr diagram proposed⁽⁸⁾ shows two compounds, Ni_4Zr and Ni_3Zr , at 27.98% Zr and 34.13% Zr respectively. Electrolysis at 1950°F with a nickel cathode and a high current density indicates that much larger amounts of Zr and thickness of plate can be obtained with Ni cathodes. These data will be reported on in the near future.

It is felt, also, that higher temperature and higher current densities are needed to increase the yields using Ti and Zr cathodes. In all cases much more Zr is produced than appears as a plate. This Zr stays in the bath as a black powder, generally adjacent to the cathode. Side reactions are producing some of this black powder and are the reasons for the low current efficiency to date. Work in progress, now, is aimed at increasing the yield and the current efficiency.

VI. WORK IN PROGRESS

It is felt that substantial temperature and current density increases are necessary in the fused salt electrolysis process for the production of zirconium, in order to make the process more attractive. Consequently, more refractory baths are being investigated at temperatures in the neighborhood of 2000°F at much higher current densities. Greater electrode spacing is also being utilized to cut down on the loss in current efficiency because of side reactions and possible reactions of the zirconium at the cathode with the gases flowing to the anode. Alkaline earth halides are being used to prevent excessive fuming of the bath. The possibility of dissolving

ZrO₂ in the electrolyte and making the process semi-continuous is also being investigated. This work will be reported on at the next reporting date.

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VII. Appendix I

THE ELECTRODEPOSITION OF ZIRCONIUM FROM NON-AQUEOUS SOLUTIONS

I. INTRODUCTION

There is no significant information in the literature concerning the electrolysis of zirconium salts in non-aqueous solutions. Because of the very strong hydrolytic tendency of zirconium metal in aqueous solution, use of non-aqueous solvents would appear to be a logical step to take. Electrolysis of aqueous solutions have generally yielded only the hydrous oxide.

If zirconium metal could be obtained from such solutions, this would be a highly desirable process, as opposed to the use of fused salt electrolysis. Less complex equipment would be involved, and operating conditions would be much easier to maintain. Notable among these advantageous conditions would be the low temperature of electrolysis which would not be far above room temperature.

Hurley and Wier¹ have recently claimed successful deposition of aluminum from non-aqueous solutions. They obtained metallic aluminum in varying forms from white to lustrous depending on current density, successfully plating aluminum on copper, iron, nickel and tin. They employed N-alkyl pyridinium halides in which aluminum chloride was dissolved to form the electrolyte, the molar ratio of the pyridinium halide to aluminum chloride being about 1 to 2.

Runs were made using 0.3 - 1.0 amps/dm² current density under an e.m.f. of 1-3 volts. Temperature was maintained at around 125°C. The electrolyte was used alone and in a benzene or toluene mixture in which the hydrocarbon formed a surface layer protecting the bath from the atmosphere. They also reported an improved plate through superimposition of an A.C. current across the electrodes. Several patents cover the aluminum process. (2,3,4,) Reference has previously been made to the work in AEC Report No. 1

II. EXPERIMENTAL

The N-ethyl pyridinium bromide was prepared for use as the solvent.

Equimolar amounts of pyridine and ethyl bromide are ~~used~~ in the simple addition reaction:

The ethyl bromide is added to the pyridine in small amounts over a period of about 45 minutes. The reaction is carried out in a reflux flask fitted with water-cooled condenser, separatory funnel and a motor driven stirrer. Temperature is maintained at 120-40°C., but little heating is required since the reaction is exothermic. As the final amount of ethyl bromide is added, the mixture solidifies to a fine white solid, melting at near 100°C. The product may be contaminated with some pyridinium hydrobromide as the following reaction is also possible:

This should not lead to complications in the electrolysis since both possible products are quaternary ammonium salts and would possess ionic properties for conducting a current.

Zirconium tetrachloride was added to the molten pyridinium salt and was found to be soluble in significant amounts. This formed a dark brown liquid presumably due to formation of some sort of complex between the zirconium and the pyridinium molecule. A mixture of about 35% ZrCl_4 and 65% $\text{C}_5\text{H}_5\text{NC}_2\text{H}_5\text{Br}$ was prepared.

This solution was then electrolyzed using a carbon anode and a cathode of 0.10" copper sheet. A current of 0.5 amps was used and required about 3 volts. This is equivalent to about 5 amps/dm². A temperature of 150-60°C was maintained.

During the first 10 minutes of the electrolysis, the solution appeared to conduct the current well and a metallic plate appeared to form on the cathode. After this time, an organic decomposition seemed to occur. The color of the solution became an opaque brown to black, and the conductivity rapidly decreased. After about a 45 minute run, only tarry materials were found in the bath and no metallic deposit remained on the cathode.

III. CONCLUSION

From observations at the start of the trial run made, it seems that separation of zirconium metal by non-aqueous solution electrolysis is a feasible process. A bright metallic deposit did appear on the cathode surface before the breakdown of the electrolyte came about.

It seems probable that an adjustment of conditions is necessary. It is thought that the ZrCl_4 concentration was too low. The work done with aluminum used a concentration of metal halide considerably greater than 35%. If the breakdown of the electrolyte is organic, a higher ZrCl_4 concentration could conceivably hinder such a decomposition. A lower temperature might be desirable, and this would also tend to prevent a breakdown of the organic material. Possibly an adjustment in current density is also required.

Another possible source of error is contamination of the ZrCl_4 with ZrOCl_2 . Presence of oxygen in the system would give the ZrO^{2+} ion instead of Zr^{4+} hindering formation of a plate and also perhaps aid in breaking down the zirconium-pyridinium complex. It is certainly desirable to make some runs using highly purified ZrCl_4 .

From the results obtained with aluminum and from what has been observed in this work, it seems that further investigation into this process is warranted. There is no readily conceivable reason to prevent successful plating of zirconium from non-aqueous solutions such as the alkyl pyridinium halides.

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