THE PRODUCTION OF ZIRCONIUM BY FUSED SALT ELECTROLYSIS

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THE PRODUCTION OF ZIRCONIUM BY FUSED SALT ELECTROLYSIS

A. INTRODUCTION

The basic purpose of this investigation has been development of an electrolytic process for the production of metallic zirconium. Some degree of success has been obtained and disclosed in previous reports. The principal difficulty with these previously developed methods has been centered in the small amount of plated zirconium produced, the great majority of the metal coming out either as an alloy with the cathode metal or as a metal powder-salt mixture on the cathode. Considerable investigation has been undertaken with respect to variations in bath composition, temperature of electrolysis, current density, and cathode material, all yielding little improvement or change in the type of deposit obtained. Investigations with bath agitation seemed to show improvement in the plating, but further work of this type has shown the deposit obtained not to be pure zirconium.

The present phase of the work has been in the direction of improving the character of the deposit. Efforts have been made to remove impurities both by purification of the materials involved and by exclusion of the atmosphere from the electrolysis. It is quite conceivable that metal and atmospheric impurities could hinder the obtaining of a good metal plate.

Under these improved conditions, some study has been made of

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crystal growth at the cathode. Efforts have also been made to ascertain the nature of the codeposited salt. Considerable improvement in character of the zirconium crystals produced has been noted.

Recently work has been initiated utilizing ZrO₂ as the source of zirconium. Somewhat higher temperatures of electrolysis will of necessity be concurrent with this phase of the investigation. The principal reason for use of such a bath is to eliminate the codeposition of an alkali or alkaline earth metal. This seems to be a major source of difficulty in the previous work. Such a bath offers some promise since a stable ZrO or Zr₂O₃ does not exist even at standard conditions, so a complete breakdown of ZrO₂ and deposition of Zr should be feasible.

B. EXPERIMENTAL WORK

1. Agitation in Fused Salt Baths

As was described in the previous report, the use of bath agitation in the fused salt electrolysis for the production of zirconium indicated that significant increases in plate thickness could be obtained with this innovation in the electrolytic bath.

As a consequence, a large number of electrolyses have been attempted employing various types of agitation in the salt bath. Initially results were quite encouraging yielding substantial metallic deposits on the cathode. The deposit was inert to acids and alkali except aqua regia and the early metallographic evidence indicated phase regions representative of a high zirconium content plate.

On further investigation, however, it was found that such
plating could only be obtained on nickel. Reliable information is unavailable for the Ni-Zr system and temperatures of eutectic formation given are inconsistent.

Allibone and Sykes\(^{(1)}\) and Sykes\(^{(2)}\) have studied the alloys of zirconium with nickel, iron and copper. In the Zr-Ni system, they have correlated some of the microstructures and phases obtained with composition of the alloy. Some of the microstructures obtained by fused salt electrolysis have been compared and related to those given by Allibone and Sykes\(^{(1)}\).

A eutectic is formed at 16 wt. % Zr. Beyond this 16% eutectic alloy, a second constituent appearing in well defined angular crystals which is \(\text{Ni}_4\text{Zr}\) at about 25% Zr. At 34% Zr, a third constituent, another intermetallic compound, appears. Above 60% Zr, another complete eutectic will exist. The melting points of the two compounds \(\text{Ni}_4\text{Zr}\) and \(\text{Ni}_3\text{Zr}\) are very high, over 2900°F. No exact temperature of eutectic formation is given. From the information at hand, it seemed that such formation should not take place at 1600-1700°F. However, on raising the temperature to 1900°F, the eutectic formation was clearly evident with the formation of a metallic pellet on the crucible bottom. This pellet was of the same structure as the previous metallic deposits and was also acid-alkali inert. Apparently the Zr content is quite high in this material.

Results of the bath agitation work are shown in Table I.
### TABLE I

**Electrolysis of Agitated Fused Salt Baths**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>2235-C-1</td>
<td>50 ZrCl$_4$ 25 NaCl 25 KCl</td>
<td>Ni Plate</td>
<td>Bath</td>
<td>800</td>
<td>35</td>
<td>1200</td>
<td>2.5</td>
<td>8</td>
<td>+.004</td>
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<tr>
<td>2235-C-2</td>
<td>65 K$_2$ZrF$_6$ 35 NaCl</td>
<td>Ni Plate</td>
<td>Bath</td>
<td>400</td>
<td>30</td>
<td>1400</td>
<td>10</td>
<td>9</td>
<td>+.009</td>
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<td>2235-C-3</td>
<td>65 K$_2$ZrF$_6$ 35 NaCl</td>
<td>Ni Plate</td>
<td>Bath</td>
<td>600</td>
<td>30</td>
<td>1400</td>
<td>5.6</td>
<td>6.5</td>
<td>+.008</td>
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<td>2235-C-4</td>
<td>50 ZrCl$_4$ 25 NaCl 25 KCl</td>
<td>Ni Plate</td>
<td>Bath</td>
<td>400</td>
<td>30</td>
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<td>3.6</td>
<td>11</td>
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<td>2235-C-5</td>
<td>100 K$_2$ZrF$_6$</td>
<td>Ni Plate</td>
<td>Bath</td>
<td>600</td>
<td>18</td>
<td>1200</td>
<td>9.5</td>
<td>6.5</td>
<td>No plate</td>
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<tr>
<td>2236-C-1</td>
<td>65 K$_2$ZrF$_6$ 35 NaCl</td>
<td>1/2&quot; Ni rod</td>
<td>Cathode</td>
<td>400</td>
<td>30</td>
<td>1400</td>
<td>4.5</td>
<td>6</td>
<td>+.000</td>
</tr>
<tr>
<td>2236-C-2</td>
<td>65 K$_2$ZrF$_6$ 35 NaCl</td>
<td>1/2&quot; Ni rod</td>
<td>Cathode</td>
<td>800</td>
<td>60</td>
<td>1500</td>
<td>3.1</td>
<td>3.8</td>
<td>+.005</td>
</tr>
<tr>
<td>2237-C-1</td>
<td>65 K$_2$ZrF$_6$ 35 NaCl</td>
<td>Ni ring</td>
<td>Bath</td>
<td>600</td>
<td>57</td>
<td>1500</td>
<td>5.3</td>
<td>6.2</td>
<td>Black powder</td>
</tr>
<tr>
<td>2237-C-3</td>
<td>65 K$_2$ZrF$_6$ 35 NaCl</td>
<td>Ni plate</td>
<td>Bath</td>
<td>800</td>
<td>60</td>
<td>1640</td>
<td>4.1</td>
<td>6.5</td>
<td>+.002</td>
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<td>2237-A-1</td>
<td>65 K$_2$ZrF$_6$ 35 NaCl</td>
<td>Cu ring</td>
<td>Bath</td>
<td>800</td>
<td>60</td>
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<td>3.8</td>
<td>6.5</td>
<td>-.001</td>
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<td>2237-E-1</td>
<td>65 K$_2$ZrF$_6$ 35 NaCl</td>
<td>Zr plate</td>
<td>Bath</td>
<td>800</td>
<td>60</td>
<td>1640</td>
<td>4.2</td>
<td>6</td>
<td>Cathode Dissolution</td>
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<td>Ni ring</td>
<td>Bath</td>
<td>400</td>
<td>20</td>
<td>1640</td>
<td>3.5</td>
<td>5.5</td>
<td>- - - - -</td>
</tr>
<tr>
<td>2241-C-1</td>
<td>65 K$_2$ZrF$_6$ 35 NaCl</td>
<td>Ni plate</td>
<td>Bath Max.</td>
<td>120</td>
<td>1640</td>
<td>5.0</td>
<td>6.5</td>
<td>+.015</td>
<td>powder</td>
</tr>
<tr>
<td>2241-C-2</td>
<td>65 K$_2$ZrF$_6$ 35 NaCl</td>
<td>Ni plate</td>
<td>Bath Max.</td>
<td>60</td>
<td>1640</td>
<td>6.0</td>
<td>24</td>
<td>powder</td>
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TABLE I (cont'd.)

<table>
<thead>
<tr>
<th>Bath Compn.</th>
<th>Place of Agitation</th>
<th>Est. Speed</th>
<th>Time</th>
<th>Temp. Av</th>
<th>E</th>
<th>Δd</th>
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<tbody>
<tr>
<td>Run No.</td>
<td>Cathode</td>
<td>R.P.M.</td>
<td>Mins.</td>
<td>°F.</td>
<td>V</td>
<td>Cathode</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------</td>
<td>------------</td>
<td>------</td>
<td>----------</td>
<td>---</td>
<td>-------</td>
</tr>
<tr>
<td>2241-C-2</td>
<td>Ni</td>
<td>Bath</td>
<td>60</td>
<td>1700</td>
<td>4.8</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>ring</td>
<td>Max.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2241-C-3</td>
<td>Ni</td>
<td>Bath</td>
<td>30</td>
<td>1700</td>
<td>5.1</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>plate</td>
<td>Max.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The effects of agitation are clearly demonstrated in this series of runs. Current density seemed to have little effect on results. Likewise the bath compositions did not seem to alter the character of deposit appreciably; for this reason, most of the work was done with the K$_2$ZrF$_6$-NaCl bath. Stirring speed did have some effect. In general, the best results were obtained with maximum degree of agitation, both in respect to production of the Ni-Zr eutectic and in the deposition of the black powder. In 2241-C-2 and C-3, a very dense adherent powder was deposited that contained approximately 75% metal. The physical setup of the bath also seems to have appreciable effect. These conditions have not been decisively determined, but it appears that the agitating medium must be in close proximity to the cathode in order to achieve maximum effectiveness.

Agitation of the cathode itself only seems to result in dissolution of the cathode metal in the bath. In this respect, a number of runs were made using rotating Ni and Mo discs as cathodes. Baths were invariably badly discolored after these runs and the discs decreased appreciably in weight. Some eutectic formation was evident as a heavy metallic rim was always noted on the edge of the disc indicating a metallic flow outward.
In attempting plating of Cu with agitation (Run 2237-A-1), there was no formation of the previously described thin plates, and the baths were badly discolored from solution of the copper. Similar results were obtained using zirconium cathodes (Run 2237-E-1).

Figures Nos. 1 through 4 show some typical microsections of nickel cathodes with deposits obtained by agitating the bath during the course of electrolysis.

All of these microsections show eutectic mixtures of the Ni-Zr system with large particles of the intermetallic, Ni₄Zr present in several of the microsections.

2. Electrolysis in an Inert Atmosphere

It is well known that in aqueous electrolysis, the presence of significant amounts of impurities can cause poor plating characteristics. Particularly in the case of zirconium, it was thought that the presence of oxygen from the atmosphere might be a deterrent toward obtaining a successful electrolytic deposition at the cathode. It was also found that the K₂ZrF₆ used contained a significant amount of iron and some titanium, alumina, and silicon, as well as appreciable ZrO₂.

A carbon resistance furnace was constructed which operates in an argon atmosphere. The heat source is a multi-slotted carbon tube giving in effect a carbon length of about 2 meters with 1/4 in² cross section. This is inserted in a carbon can which in turn is set in a steel can insulated with lampblack. A lampblack-transite-normolith cement head is used. The head and furnace leads are water cooled. An opening is provided for an electrode, and another for sighting an optical pyrometer. The furnace is
grounded so the carbon crucible itself is used as the other electrode. An argon inlet is fitted in the bottom of the furnace. The argon gas is passed through a hot copper drying train, CaCl₂, P₂O₅, and glass wool, prior to entrance into the furnace. The furnace is capable of running to 2000°C at full power, and performance has been satisfactory in all respects. Figure No. 5 shows the cross-section of this resistance furnace.

Steps were also taken to purify the K₂ZrF₆ employed. The iron and most of the silicon was removed by washing with HCl. Addition of NH₄HF₂ and KF removed the excess ZrO₂ according to the reaction given:

\[ 2\text{NH}_4\text{HF}_2 + 2\text{KF} + \text{ZrO}_2 \rightarrow \text{K}_2\text{ZrF}_6 + 2\text{NH}_3 + 2\text{H}_2\text{O} \]

Carbon crucibles were also used in all subsequent runs, as it was felt that significant impurities might have been leached from the previously used zircon crucibles.

The first few runs in the carbon resistance furnace were made using the original materials and conditions in order to ascertain any atmospheric effects on type of plating obtained. Ni, Mo, and Zr cathodes were tried. The temperature was raised to 1900°F, in order to promote further crystal growth and/or eutectic formation at the cathode. Runs were generally stopped after 30 minutes in order to afford a uniform comparison and to make a maximum number of runs. Representative results of this work are shown in Table II, Page No. 8.
### TABLE II

**Electrolysis in an Inert Atmosphere**

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (mins)</th>
<th>Temp. °F.</th>
<th>Cathode</th>
<th>E Av. V</th>
<th>I Amps.</th>
<th>C.D. A/dm²</th>
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</thead>
<tbody>
<tr>
<td>2247-C-1</td>
<td>30</td>
<td>1900</td>
<td>Ni plate</td>
<td>3.5-4.0</td>
<td>5.4</td>
<td>50</td>
</tr>
<tr>
<td>2247-C-2</td>
<td>30</td>
<td>1900</td>
<td>Ni plate</td>
<td>3.5-4.0</td>
<td>5.4</td>
<td>50</td>
</tr>
<tr>
<td>2247-B-1</td>
<td>25</td>
<td>1900</td>
<td>Mo plate</td>
<td>4.0</td>
<td>5.4</td>
<td>50</td>
</tr>
<tr>
<td>2247-B-2</td>
<td>120</td>
<td>1900</td>
<td>Mo plate</td>
<td>2.0-2.5</td>
<td>1.3</td>
<td>12</td>
</tr>
<tr>
<td>2247-E-1</td>
<td>30</td>
<td>1900</td>
<td>Zr plate</td>
<td>3.5</td>
<td>5.4</td>
<td>50</td>
</tr>
<tr>
<td>2248-B-1</td>
<td>120</td>
<td>1920-30</td>
<td>Mo plate</td>
<td>1.5</td>
<td>0.6</td>
<td>5.6</td>
</tr>
<tr>
<td>2248-B-2</td>
<td>30</td>
<td>1900</td>
<td>Mo plate</td>
<td>3.2-3.7</td>
<td>5.4</td>
<td>50</td>
</tr>
<tr>
<td>2248-B-3</td>
<td>30</td>
<td>1900</td>
<td>Mo plate</td>
<td>3.3-3.8</td>
<td>5.4</td>
<td>178</td>
</tr>
<tr>
<td>2248-B-4</td>
<td>30</td>
<td>1900</td>
<td>Mo plate</td>
<td>3.5-4.0</td>
<td>5.4</td>
<td>178</td>
</tr>
<tr>
<td>2248-E-1</td>
<td>30</td>
<td>1900</td>
<td>Zr plate</td>
<td>3.0-3.5</td>
<td>5.4</td>
<td>50</td>
</tr>
<tr>
<td>2249-B-2</td>
<td>20</td>
<td>2200</td>
<td>Mo plate</td>
<td>5</td>
<td>12</td>
<td>350</td>
</tr>
<tr>
<td>2249-B-3</td>
<td>15</td>
<td>23-2400</td>
<td>Mo plate</td>
<td>7</td>
<td>20-30</td>
<td>5-600</td>
</tr>
</tbody>
</table>

Bath in all cases 35% K₂ZrF₆, 65% NaCl

In the first 2 runs, the Ni-Zr eutectic formation was definitely ascertained. In 2247-C-2, a small pellet weighing 2.0-2.5 g. was found in the bottom of the crucible. This pellet was of high apparent Zr content since little Ni was lost from the cathode. The pellet was very hard and sparks on grinding. The photomicrographs of this specimen are shown in Figures No. 7 and 8. In all runs of this type, there was no evidence of black Zr powder in the bath.

The runs in which Mo cathodes were used produced a varying range of results. In general, only metal powders were produced and these
were of the best quality thus far observed. No black material was observed in the bath itself in any of these runs. In 2247-B-2, interesting crystal formations resulted. There appeared to be a distorted cubic formation presumably representing the tendency of the BCC zirconium to revert to an HCP form. In all of this series of runs, dendrites were observed in varying sizes and shapes to a degree not heretofore observed when the air atmosphere was present. Despite the improvement in crystal growth of the Zr, there was still present an appreciable quantity of salt intermingled with the zirconium crystals. The deposits wash out readily, however, leaving a reasonably pure grade of Zr crystals. These are very pyrophoric. Roughly, half of each deposit was found to be salt.

Photographs of the zirconium powder obtained are shown in Figure Nos. 8 through 10. Spectrographic and X-ray analysis have shown this powder to be pure zirconium.

A sufficient quantity of this powder has been obtained to carry out some fusion runs for densification of the Zr produced. A high vacuum system and induction furnace set-up good to $10^{-5}$ microns of Hg pressure are being completed for this purpose. Results obtained with the characteristics of the melted zirconium will be reported on in a subsequent report.

Zirconium was unsatisfactory as a cathode material as in previous runs. The 0.010" sheet material (Foote Mineral) has numerous fractures throughout and readily goes into the fused salt baths.

Following the work in an argon atmosphere, a number of runs were made using purified K$_2$ZrF$_6$. The material was washed with HCl to remove Fe and Si, and then recrystallized from water. It was then treated
with NH₄HF₂ and KF to remove any ZrO₂ present. Examples of such runs are reported in Table III.

**TABLE III**

**Electrolysis of Purified K₂ZrF₆ in Argon**

<table>
<thead>
<tr>
<th>Run</th>
<th>Time</th>
<th>Temp.</th>
<th>I</th>
<th>E</th>
<th>C.D.</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>2249-B-5</td>
<td>30</td>
<td>1940</td>
<td>5.4</td>
<td>3.5</td>
<td>50</td>
<td>Mo plate</td>
</tr>
<tr>
<td>2250-B-1</td>
<td>120</td>
<td>1920</td>
<td>5.4</td>
<td>3.0-3.5</td>
<td>50</td>
<td>Mo plate</td>
</tr>
<tr>
<td>2250-B-2</td>
<td>30</td>
<td>1900</td>
<td>5.4</td>
<td>3.3-3.8</td>
<td>100</td>
<td>Rotating Mo paddle</td>
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</tbody>
</table>

Results in 2249-B-5 and 2250-B-1 were the most interesting of this series run in the Argon atmosphere. A tenacious deposit consisting of long needles of Zr metal was obtained. Salt was however still interspersed in the deposit. The salty deposit was found to contain about 48% F, 12% Zr and the balance assumed to be K or Na.

The run with a rotating cathode produced relatively pure black Zr powder, but no crystal formation was observed.

3. **Use of Oxide Baths in Inert Atmosphere**

Oxide baths have previously been employed with the conventional type furnace. It was thought an argon atmosphere might show significant change in the results of such electrolyses. Representative results are given on Page 11.
TABLE IV
Electrolysis of Oxide Baths

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (mins.)</th>
<th>Temp. (°C)</th>
<th>I (Ampa.)</th>
<th>E (Av.V)</th>
<th>C.D. (A/dm²)</th>
<th>Bath Comps. %</th>
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</thead>
<tbody>
<tr>
<td>2255-H-1</td>
<td>30</td>
<td>2750</td>
<td>40</td>
<td>4.5</td>
<td>64</td>
<td>70 CaF₂ 25 ZrO₂ 5 Al₂O₃</td>
</tr>
<tr>
<td>2255-H-2</td>
<td>25</td>
<td>2100</td>
<td>40</td>
<td>4.5</td>
<td>64</td>
<td>80 Na₃AlF₆ 20 ZrO₂</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2100</td>
<td>20</td>
<td>3.25</td>
<td>32</td>
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</tr>
<tr>
<td>2255-H-3</td>
<td>14</td>
<td>1975</td>
<td>35</td>
<td>4.8</td>
<td>40</td>
<td>80 Na₃AlF₆ 13 ZrO₂ 7 Al₂O₃</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2000</td>
<td>15</td>
<td>3.8</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>2255-H-4</td>
<td>30</td>
<td>2000</td>
<td>40</td>
<td>4.5</td>
<td>64</td>
<td>55 Na₃AlF₆ 30 CaF₂ 15 ZrO₂</td>
</tr>
</tbody>
</table>

Results of these experiments were in general all quite similar. The ZrO₂ is sluggishly soluble in most cases and a certain amount always remains on the crucible bottom. The crucible was used as a cathode in all cases. A black deposit resulted in all of the runs. Salt was intermingled with the deposits. There was some evidence of free Al in H-4 and perhaps some Zr₃Al₄ in H-3 and H-4. In H-3 and H-4, the deposits appeared to be at least 80-90% metallic material. Crystal formation was not detected in the oxide bath deposits, however. The metal seemed to have no tendency to form as a plate.

C. Discussion of Results

Several significant developments have been noted in the present phase of the investigation and a number of questions concerning the problem answered.

The value of agitation in fused salt electrolysis of this type has been ascertained. It is obvious from the work described that agitation alone is no solution to the problem of zirconium production. However, in
all cases where an agitated bath was used, results were superior to those under like condition without agitation. The salt content of the deposit is reduced and general quality of the zirconium powder is improved.

Agitation of the bath has made possible the production of an Ni-Zr eutectic at a lower temperature than would be anticipated. This has also been accomplished more readily, however, at higher temperatures in an inert atmosphere. The alloy so produced is of apparent high zirconium content and is highly resistant to corrosive action of acids and bases. Such an alloy might well be of commercial value and its production could be readily accomplished.

The value of an inert atmosphere has been shown by the work done in argon. It is apparent that the presence of air hinders the crystal growth at the cathode. This is probably largely due to the oxygen. Previously air had free access to the bath surface and also undoubtedly diffused through the zircon crucibles, and up through the bath. Reasonably large needle-like zirconium crystals have been successfully grown at the cathode in an inert atmosphere. Agitation was seen to increase the number of nuclei arriving at the cathode and crystal growth no longer appeared.

Another contribution to the growth of these zirconium crystals was the purification of the starting material. A significant amount of iron was found in the K₂ZrF₆ and also in previous cathode deposits as evidenced by magnetic properties. It is also suspected that significant amounts of Si, Ti and other elements may be present. Also a considerable amount of ZrO₂ is known to be present in the K₂ZrF₆. These impurities were removed so far as practicable by readily available methods. Electrolysis of this material produced the best crystals of zirconium so far obtained.
The most distressing problem relative to obtaining a successful zirconium deposition at present is the accern relation of salt with the cathode deposit. Analysis shows the salt to be either a KF-K$_2$ZrF$_6$ mixture or perhaps a reduced form of K$_2$ZrF$_6$. Some runs were made using (NH$_4$)$_2$ZrF$_6$ in place of the potassium salt and the salt content of the cathode deposit did seem to be considerably diminished. This bath is objectionable, however, due to the high degree of fuming and consequent loss of bath material. A bath containing no KF or K$_2$ZrF$_6$ produced a very salty deposit, however, so perhaps the NaCl also enters into the problem.

The present emphasis on the problem is toward producing a salt free cathode deposit. This may be accomplished by further purification of materials, further increase in temperature to 3000-3300°F, or perhaps a development of a procedure for electrolysis at the melting point of zirconium. The principal factor preventing experimentation with the latter at present is lack of a suitable crucible material. In any of these possibilities which show promise, it may be necessary to employ high velocity agitation as a further incentive toward obtaining a successful deposition. It is felt that a successful solution to the problem has been approached from a number of directions through the course of the experimentation and that a careful re-evaluation and correlation of data is needed at present in order to bring the problem to a satisfactory conclusion.
SUMMARY

A further investigation into the problem of obtaining metallic zirconium through the electrolysis of fused salt baths has been made.

An exhaustive study has been undertaken in an effort to determine the effects of agitation on such a process. This has been found helpful toward improving the character and quality of the cathode deposit, although agitation alone does not produce the desired metallic plate. Through such means, however, high Zr content Ni-Zr alloys have been produced and the salt content of the amorphous Zr deposits has been decreased.

Considerable work has been done also toward the elimination of possible interfering impurities. A carbon resistance furnace operating in an argon atmosphere has replaced the open nichrome wound furnaces. This eliminates atmospheric contamination. Carbon crucibles have been employed to eliminate the zircon as an impurity source. As a final precaution, the K₂ZrF₆ has been purified to remove extraneous oxide and halide impurities.

The net result of these various precautions has been the production of the largest and best defined zirconium crystals to date. These are needle-like in shape, easily salt washed, and very pyrophoric.
The principal problem yet blocking an efficient commercial process is that of the simultaneous salt deposition. This represents the present phase of the work, i.e., improving the purity and homogeneity of the cathode deposit.

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HORIZONS INCORPORATED
Cleveland, Ohio
August 4, 1950
Figure No. 1
Specimen No. 2235-C-2
Etchant: Campella's Reagent
Magnification: 175x

Figure No. 2
Specimen No. 2235-C-2
Etchant: Campella's Reagent
Magnification: 400x

Figure No. 3
Specimen No. 2240-C-1
Etchant: 50% HNO₃ - 50% Glacial Acetic Acid
Magnification: 75x

Figure No. 4
Specimen No. 2247-C-2
Etchant: 50% HNO₃ - 50% Acetic Acid
Magnification: 800x
1/2" dia. carbon electrode lead

Copper water cooled joints for resistance element

Carbon support pins for resistance element

Water cooled head

0.3 ohm carbon resistance element (at 20°C.)

NOTE: Shaded areas are carbon, dotted areas are lampblack

Figure No. 5
Ni-Zr Eutectic

Figure No. 6
Specimen No. 2247-C-2
Etchant: 4% HF - 2% HNO₃ - H₂O
Magnification: 40 x

Figure No. 7
Specimen No. 2247-C-2
Etchant: 4% HF - 2% HNO₃ - H₂O
Magnification: 400 x
Figure No. 8
Specimen No. 2248-B-4
Etchant - None
Magnification 35x
Zr crystals

Figure No. 9
Specimen No. 2248-B-4
Etchant - None
Magnification 75x
Zr crystals

Figure No. 10
Specimen No. 2249-B-5
Etchant - None
Magnification 35x
Zr crystals and needles

END OF DOCUMENT