ZIRCONIUM ELECTROPLATING ON URANIUM
FROM MOLTEN ALKALI FLUORIDE SALTS

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JUNE 1, 1968

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FROM MOLTEN ALKALI FLUORIDE SALTS

By

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ABSTRACT

Conditions were established under which zirconium could be electroplated onto uranium from molten alkali fluoride melts. Although good electroplates were made from several such solvents over a fairly wide range of conditions, the best results were obtained using the KF-LiF eutectic under the following conditions: current density from 20 to 40 mA/cm², temperatures from 625 to 675°C, and ZrF₄ concentration from 2 to 10 wt.%.

The zirconium plates were fine grained and non-porous up to a thickness of about 5 mils, after which isolated crystallites began to grow. It was proposed that the change in plate structure was related to chemical changes in the electrolyte. A method to prevent melt degradation was proposed, and an attempt to test the method was made.

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INTRODUCTION

Interest in increasing the power density of nuclear reactors has focused attention on the ability of the fuel element cladding to withstand the more rigorous demands thus put upon it. For this reason, metals from groups IV-B, V-B, or VI-B have promise as a fuel element cladding material. Of these, zirconium is perhaps the most desirable; not only because of its low neutron cross section, but also because of its corrosion resistance.⁽¹⁾

Zirconium is already being used as a fuel element cladding material in the form of Zircaloy-2 (1.5% Sn, 0.15% Fe, 0.1% Cr, and 0.05% Ni). Much of the benefit derived from the use of zirconium is offset by fabrication costs in cladding the uranium fuel. If some way were found to decrease this expense, use of zirconium would be more attractive. The most obvious way is to apply the zirconium directly on the fuel element as an electroplate. Because of the chemically active nature of zirconium metal, attempts to electrodeposit the metal from aqueous solutions have been fruitless. Nor has electrodeposition from organic solutions proven successful.

Since zirconium could not be deposited from aqueous or organic solutions, attention was turned to the use of molten salt solutions. Successful production of zirconium by electrodeposition from a mixed fluoride-chloride melt has been reported.^(4,5) However, this work was primarily concerned with electrowinning the metal; and conditions were sought for which the metal deposit was in the form of powder or large crystals which could easily be removed from the cathode, and would be suitable for reworking. In electroplating metals, on the other hand, the desired deposit is adherent to the substrate, composed of fine crystals, smooth, and non-porous. Until the publication of a series of

papers by Mellors and Senderoff there had been no successful procedures reported for the deposition of thick coherent plates of the group IV-B, V-B, and VI-B metals.^(6a-d) This work of Mellors and Senderoff is particularly important in that previous work on the electrodeposition of metals from molten salts has always resulted in the production of loose dendrites, powder or sponge;⁽⁷⁾ with the exception of diffusion plating for some metals.⁽⁸⁾ It should be noted that the earlier work was done for the most part with chloride or mixed chloride-fluoride systems; and, as Mellors and Senderoff point out, a pure fluoride salt electrolyte is essential for the production of plates.^(6a) For electroplating zirconium, a LiF-KF or LiF-NaF-KF solvent was found satisfactory.^(6c) The addition of chloride to a zirconium electroplating solution caused serious deterioration of the plate. Attempts in this laboratory to electroplate zirconium from molten alkali chloride salt resulted in the production of slimes.⁽⁹⁾

As pointed out by Ibl, the structure of the deposit, in simple terms, depends strongly on the rate of formation of new nuclei and the rate of growth of the crystals already present.⁽⁷⁾ Grain size is a strong function of the ratio of these two rates. That is, if the rate of nucleation is small compared to the rate of crystal growth, a deposit with coarse grains results. In the reverse case, a fine grained deposit results. Powder formation is a limiting case in which the nucleation rate is large and the crystal growth, particularly intergrowth, is small.

Since the formation of new crystals requires more energy than the growth of already existing ones, nucleation is enhanced by a high activation polarization; that is, that part of the polarization due to the presence of an energy barrier for charge transfer at the electrode solution interface.⁽¹⁰⁾ As pointed out by Winand in his studies of the discharge of zirconium(IV) from molten salts, while zirconium(IV) discharges in a single step to the metal without passing through lower oxidation states, there does exist an activation overpotential attributable to the decomposition of complex ions.⁽¹¹⁾ As a matter of fact, it has long been known that zirconium forms complex fluozirconates with the uni- and divalent fluoride salts.⁽¹²⁾ In addition, it has been shown from infrared spectrophotometric studies of the $\text{KF-LiF-K}_2\text{TaF}_7$ system that tantalum(V) forms a stable complex ion in the fluoride melt.⁽¹³⁾ These

results also showed that by changing the composition of the solvent it was possible to change the nature of the complex ion that was formed.

On the basis of the preceding discussion, the zirconium electroplating studies reported herein were confined solely to fluoride solvents with the added restriction that the melting point of the solvent be as low as possible. Three different solvent systems were studied: 1) LiF-NaF-KF (46.5 mole%-11.5 mole%-42.0 mole%) - m.p. 454°C; 2) LiF-CsF (37 mole%-63 mole%) - m.p. 475 $\pm$ 5°C; 3) LiF-KF (45 mole%-55 mole%) - m.p. 575°C. (14)

EXPERIMENTAL

Cell

The schematic for the cell used for the melt purification and electroplating is shown in Figure 1. The cell, as shown, is set up for plating. For melt purification the zirconium anode and the cathode were removed and a graphite liner was inserted into the cell body. The nickel top was fastened to the flange on the cell body with stainless steel bolts, and a copper gasket provided the gas tight seal. Monel Swagelok fittings were used to make gas tight fittings on all inlets and exit ports.

Electrodes

The cathodes were made from copper rod and machined from uranium fuel elements, and were 1-1/2 inches long by 1/4 inches diameter. One end was drilled and tapped to accept a threaded 1/8 inch Inconel rod. The rod was insulated from the cell by a 1/4 inch outside diameter, 1/8 inch inside diameter alumina sleeve. The internal sleeve diameter was such that the Inconel rod made a snug slip fit, which allowed pulling the plated specimen up to the argon atmosphere in the cooling chamber of the lid. The copper and uranium cathodes were cleaned in hot 8-10 M HNO₃, and quickly rinsed and dried just before they were placed in the cell.

The zirconium anode was formed by rolling sheet metal into a cylinder to give a snug fit in the cell. The electrical contact to the anode was made through the nickel cell.

Melt Purification

Regardless of the care taken in making up the mixture of salts, some

FIGURE 1
Electrolysis Cell

water was always present. As the charge was heated, reactions could occur yielding such products as oxide, hydroxide, and peroxide ions.^(15,16) The presence of these hydrolytic reaction products in the melt has been shown to cause poor quality, non-adherent electroplates.⁽⁶⁾ To remove these products a technique has been reported involving an HF-H₂ sparge of the melt, and was used in this work.⁽¹⁷⁾ It has been shown that in using this technique the oxygen content can be decreased to less than 100 ppm.⁽¹⁸⁾ In some of the early experiments NH₄•HF was used to provide HF through thermal decomposition. However, the HF evolution was too rapid for the technique to be successful.

In general the procedure was as follows. First, the dry chemicals which composed the electrolyte were weighed and mixed (a normal charge was usually about 400 gm). The mixture was put into the graphite liner which was placed into the nickel cell. The copper gasket was put in place, the lid bolted on, and all the fittings put in place to insure a gas tight cell. An argon atmosphere (deoxygenated with an 850°C zirconium column) was introduced into the cell and the temperature slowly raised until the charge melted. A copper sparge tube was introduced and a 1:1 HF-H₂ mixture was bubbled through the melt at about 650°C for 24 hours. The HF-H₂ was purged from the melt with argon and the charge allowed to freeze. The cooled charge was removed from the graphite liner (a well purified charge slipped easily from the liner) and either stored in a desiccator or placed in the electrolysis cell.

When ready for electrolysis, the purified charge was placed in the gas tight electrolysis cell and heated under an argon atmosphere until molten. To remove impurity metals, the melt was held at 650°C and pre-electrolyzed twelve hours at 200 mA/cm² using an 1/8 inch diameter Inconel rod cathode.

Melt Repurification Apparatus.

Figure 2 is a schematic of the system designed to recirculate the melt as a means of continuously repurifying it during electrolysis. This procedure is discussed in more detail in a later section, but it essentially involved pumping the melt to the HF sparge cell from where it overflowed to the argon sparge cell, then overflowed back to the electrolysis cell. Each sparge cell was a 6 inch by 1 inch inside

diameter nickel can with a melt retention capacity of about 50 ml. The cells had flanged tops to which the nickel lids could be bolted and sealed with copper gaskets in a fashion similar to the electrolysis cell. Alumina insulators for conductivity probes were attached to the lids through monel Swagelok fittings. The 1/4 inch monel gas and melt inlet and exit lines were welded to the cells; all other connections were made with monel Swagelok fittings. The gas inlet on the gas lift for pumping the melt to the HF sparge cell was 1/8 inch monel tubing, and was welded into the 1/4 inch melt lift tube 1/2 inch from the bottom, as shown in Figure 2. The submergence was about 5 inches and the lift about 19 inches. The chromel-alumel thermocouple TC-1 monitored the electrolysis cell temperatures, TC-2 monitored the melt transfer line temperature, and TC-3 was the control thermocouple for the sparge cells tube furnace.

Electrolysis

After the initial purification steps, the melt was ready for the planned electrolysis experiments. The cathode was inserted into the cell, allowed to heat and finish drying in the argon atmosphere, and then immersed into the melt. The electrolysis was immediately started.

The electrolyses were run at constant current using a Harrison Laboratories Model 814A or Electro Product Laboratories Model N dc supply. A Mosely 7100, 2-pen recorder was used to record the cell voltage and current (iR drop across a known resistance).

Furnace and Controller

A crucible type furnace controlled by either a Wheelco or a Barber-Coleman Model 193C controller was used in this work. The electrolysis melt temperature was recorded with a Minneapolis-Honeywell potentiometric recorder from the output of a chromel-alumel thermocouple encased in a copper well immersed in the melt.

DISCUSSION

In order to develop experimental techniques as well as judge the feasibility of zirconium plating from molten fluorides, the first work was done using copper cathodes. Copper was used initially rather than uranium because it was feared that the active nature of the uranium metal surface might induce problems of adherence of the zirconium plate,

FIGURE 2
Continuous Purification System

thereby making it difficult to determine proper conditions for plating.

After a number of experiments, techniques and conditions were developed which resulted in adherent and non-porous zirconium electroplates on copper from a LiF-NaF-KF-ZrF_4 melt. The range of conditions of temperature, cathode current density, and zirconium(IV) concentration for which this was possible was also determined as an aid to the studies using the uranium cathode. The cross-section of zirconium plated copper is shown in Figure 3.

General Results

Using uranium cathodes a large number of experiments were conducted to determine optimum plating conditions, and also to determine the effect of solvent composition on the plate. As stated earlier, three different fluoride solvent systems were studied. While it was possible to produce uniform, adherent electroplates of good quality from all three, the LiF-KF system seemed to yield the best results. In this particular solvent, the optimum cathode current density range was from 20-40 mA/cm^2 , and the optimum temperature range was from 625 to 675°C. The quality of the plate did not seem to be particularly affected by the zirconium(IV) concentration, at least in the range studied which ran from 2 to 10 wt%. It was necessary in all cases to keep a purified argon atmosphere over the melt. This served, among other things, to keep the surface of the uranium cathode from oxidizing as it was being lowered into the melt. Should an oxide coat form on the uranium, it could keep the zirconium plate from adhering. Figures 4 through 8 show examples of the external surfaces of some electroplates and also the region of the interface between the uranium and zirconium. These figures show the following: The exterior of the plate exhibits a good deal of crystallinity, the adherence of the zirconium electroplate to the uranium appears to be very good, and there is an apparent third phase which exists between the uranium and zirconium phases. Whether a definite uranium-zirconium compound is formed is not known. However, the zirconium-uranium phase diagram shows a solid solution phase with a fairly broad composition range in the region of 70% zirconium at about 650°C. The observed third phase may be the result of that solid solution. Electron microprobe examinations of the interfacial region showed

Figure 3

Cross-section of a Zirconium-plated Copper Cylinder

Conditions: $T = 700^{\circ}\text{C}$, $i = 10 \text{ mA/cm}^2$

Electrolyte: $\text{LiF-NaF-KF} + 10 \text{ wt\% ZrF}_4$

8X

Figure 4

View of the Exterior and Cross-section
Of a Zirconium-plated Uranium Cylinder

Conditions: $T = 650^{\circ}\text{C}$, $i = 10 \text{ mA/cm}^2$

Electrolyte: $\text{LiF-KF} + 5 \text{ wt\% ZrF}_4$

8X

Figure 5

Photomicrograph of the Cross-section
Of a Zirconium-plated Uranium Cylinder

Conditions: $T = 650^{\circ}\text{C}$, $i = 10 \text{ mA/cm}^2$
Electrolyte: $\text{LiF-KF} + 5 \text{ wt\% ZrF}_4$

A-100X
B-500X

Figure 6

Photomicrographs of the Cross-section
Of a Zirconium-plated Uranium Cylinder

Conditions: $T = 625^{\circ}\text{C}$, $i = 10 \text{ A/cm}^2$

Electrolyte: LiF-KF 5 wt% ZrO_2

Figure 7

View of the Exterior and Cross-section
Of a Zirconium-plated Uranium Cylinder

Conditions: $T = 625^{\circ}\text{C}$, $i = 40 \text{ mA/cm}^2$

Electrolyte: $\text{LiF-CsF} + 10 \text{ wt\% ZrF}_4$

8X

Figure 8

Photomicrograph of the Cross-section
Of a Zirconium-plated Uranium Cylinder

Conditions: $T = 625^{\circ}\text{C}$, $i = 40 \text{ mA/cm}^2$
Electrolyte: $\text{LiF-CsF} + 10 \text{ wt\% ZrF}_4$

A-100X
B-500X

only that there was interdiffusion of the two metals. On a macroscopic scale the plate appears to be non-porous, at least on the basis of immersion of the sample in concentrated HCl with which unprotected uranium reacts vigorously. However, the photomicrographs show that the body of the plate contains voids. Apparently, the reason no porosity is indicated when the plated uranium cylinder is treated with the acid is that there is a thin layer of sound metal lying directly above the uranium, perhaps the apparent third phase.

Careful examination of the zirconium electroplate shows that the structure of the deposit changes as a function of distance normal to the substrate. The initial portion of the plate, up to a maximum of about 5 mils, exhibits the very fine-grained, non-porous structure as shown in Figure 9. After this initial portion of the plate has been formed, a transformation in the structure of the deposit takes place and isolated crystallites begin to grow (see Figure 10). In the most favorable case, the result of this type of growth is a plate with a rough surface which contains voids in the region where the crystallites began to grow independently and where there was no chance for intergrowth, cf. Figure 11. In the least favorable situation, the isolated crystallites continue to grow in a direction normal to the uranium-zirconium interface and show no intergrowth at all, cf. Figure 13. This results in most of the zirconium being deposited in the form of large needles or very coarse crystals. These growths show little mechanical strength at the point where they join the more compact portion of the plate, and when removed they leave a depressed area in the plate. Attempts which were made to stop the selective growth of isolated zirconium crystallites by variation of melt temperature, zirconium(IV) concentration, cathode current density, or pretreatment of the uranium cathodes, were of no avail. Agitation of the melt by a stream of purified argon did seem to remedy the situation, but not reproducibly.

It should be mentioned that increasing the temperature of the electrolyte tended to promote the growth of large crystals as did increasing the initial cathode current density. The effect of increasing the temperature was expected since an increase will generally lower the activation polarization allowing nucleation at the smaller

Figure 9

Photomicrographs of the Cross-section
Of a Zirconium-plated Uranium Cylinder

Conditions: $T = 800^{\circ}\text{C}$, $i = 10 \text{ mA/cm}^2$

Electrolyte: $\text{LiF-NaF-KF} + 10 \text{ wt\% ZrF}_4$

500X

Figure 10

View of External Surface
Of a Zirconium Electroplate

Conditions: $T = 625^{\circ}\text{C}$, $i = 20 \text{ mA/cm}^2$
Electrolyte: $\text{LiF-KF} + 5 \text{ wt\% ZrF}_4$

15X

number of sites with a low energy barrier and consequently decreasing the nucleation rate.⁽⁷⁾ On the other hand, increasing the current density usually tends to increase the nucleation rate producing more and smaller crystals.⁽⁷⁾ Unfortunately, attempts to improve the plate by reducing the values of the two variables, current density and temperature, to their lowest practical limits were not successful.

To date the reason for the drastic change in crystal structure during the course of an electroplating experiment is not clearly understood. Nor is it understood why the crystal size should be larger for plates at higher current densities. These results may be related, and evidence will be presented further on to show the relationship between at least the change in plate structure and the chemical changes which take place in the melt.

Melt Composition

As mentioned earlier, the presence of an activation polarization enhances the formation of new nuclei, and one way of increasing the activation polarization is by complexing the electroactive ion. On the basis of the spectrophotometric studies mentioned earlier it seemed reasonable to assume that zirconium(IV) existed in molten fluorides as a complex ion; and since it was shown that the tantalum(V) complex could be changed by changing the composition of the solvent,⁽¹³⁾ it seemed reasonable to assume that the same thing could be done with zirconium(IV). It was hoped that if the proper choice of a solvent could be made, the nucleation rate of the zirconium crystals could be enhanced and the resulting electroplate would be more uniform and free of voids.

The choice of solvents was made on the basis of the anticipated higher fluoride activity (fluoride "donating" ability) of LiF-CsF and LiF-KF melts. That is, as the difference between the radius of the cation and anion becomes larger, the extent of polarization of the anion by the cation becomes larger and the bond between the two becomes more covalent in nature. Therefore, as a first approximation, the fluoride activity of a particular molecule increases as the size of the cation increases for the same anion. On this basis, the most likely solvent to choose, if the parameter of interest is the fluoride

activity, is one containing CsF.

Attempts to interpret the results of these electroplating experiments are complicated by the existence of an unexpected chemical reaction. This reaction whose existence has been corroborated by the work of Mellors and Senderoff,⁽⁶⁾ can best be formulated as

where M represents an alkali metal. The existence of this reaction was unexpected since reference to theoretical emf tables for the various solid and molten fluorides shows that for the two reactions of interest there is a difference in emf of about -0.7 volts.⁽¹⁹⁾

That reaction 1 does in fact take place indicates that almost all the zirconium is in the form of an extremely stable complex ion. As a result, the LiF-CsF solvent could not be used because of its corrosion action toward the zirconium plate as is shown by reaction 1. This is supported by the observation that in order to produce a zirconium deposit it was necessary to use a cathode current density of 40 mA/cm² or greater; and as the melt temperature was increased, this lower current density limit had to be increased. Furthermore, in some instances a film of corrosion product had formed underneath the zirconium plate which prevented adherence of the plate. The corrosion product is, as yet unidentified; however, it is believed that it results from the reaction:

which can occur because of the enhanced fluoride activity in this solvent, and the consequent stability of the $UF_{(4+y)}^{-y}$ complex ion.

Melt Degradation

Throughout the numerous experiments that compose this electroplating study, the feeling was prevalent that the reasons for the structural changes which took place in the zirconium deposit were

chemical in nature. Additional weight was lent to this viewpoint by: 1) within reason, changes in the cathode current density seemed to have no real effect on the structural changes which took place in the plate; 2) the longer a particular melt was used, the coarser crystals in the plate became; and 3) the color of a frozen melt sample changed from white to a brown-black during the course of the electrolyses. Attempts to identify the cause of the color change by x-ray analysis of melt samples indicated that it was due neither to an increase in the zirconium salt concentration nor to the introduction of impurities into the melt. It was discovered, however, that the color change which took place could be reversed by passing HF through the melt.

In order to determine definitely whether or not the structural changes in the zirconium electroplate were the result of changes taking place in the melt over a period of time, an experiment was conducted in which the temperature of the melt, cathode current density, and zirconium(IV) concentration were held constant while a definite number of coulombs were passed. The uranium cathode was removed from the melt, a new one inserted, and the process repeated. In each case, the uranium cathode was pretreated exactly the same way to insure that its surface was as reproducible as possible. In this way, it was hoped that should there be any substrate effects, they would be the same for each cathode. The results of these experiments are shown in Figures 11 through 13.

It is quite obvious from examination of these results that the structure of the deposit changed rather markedly during the series of electrolyses. This supports our hypothesis that changes in the nature and/or composition of the melt were taking place during the course of these experiments, and thus it is the chemistry of the electrolyte which plays a decisive role in determining the structure of the deposit. It is less obvious what chemical changes occur which influence the structural changes in the plate. However, we do know that the changes which take place in the melt must do so over an extended period of time by virtue of the fact that a given electroplate was of better quality than the one immediately succeeding it (Figures 11 through 13). We were also able to make qualitative correlation

Figure 11

External Surface and Cross-section of the First Electroplate (I)

Conditions: $T = 625^{\circ}\text{C}$, $i_1 = 40 \text{ nA/cm}^2$ for $3.2 \cdot 10^3$ Coulombs;
 $i_2 = 20 \text{ nA/cm}^2$ for $1.9 \cdot 10^4$ Coulombs.

Electrolyte: LiF-KF 5 wt% ZrF_4

A-8X

B-500X

Figure 12

External Surface and Cross-section of the Second Electroplate (II)

Conditions: $T = 625^{\circ}\text{C}$, $i_1 = 40 \text{ mA/cm}^2$ for $5.2 \cdot 10^3$ Coulombs;

$i_2 = 20 \text{ mA/cm}^2$ for $1.9 \cdot 10^4$ Coulombs.

Electrolyte: LiF-HF and CF_3

A-SX

B-500X

Figure 13

External Surface and Cross-section of the Third Electroplate (III)

Conditions: $T = 625^{\circ}\text{C}$, $i_1 = 40 \text{ mA/cm}^2$ for $3.2 \cdot 10^3$ Coulombs;
 $i_2 = 20 \text{ mA/cm}^2$ for $1.9 \cdot 10^4$ Coulombs.

Electrolyte: LiF-KF 5 wt% ZrF_4 .

A-8X

B-500X

between the changes in the structure of the electroplate and the changes in the color of the frozen melt samples.

One possible explanation for these results and those shown in Figures 11 through 13 is that the changes in the structure of the electroplate were due to an air leak into the electrolysis cell. It has been shown by Mellors and Senderoff that the presence of oxygenated species in the melt can cause a serious deterioration of the plate.⁽⁶⁾ However, this explanation seems unlikely in view of the precautions taken to purify the argon used as an atmosphere and sparge gas in the cell plus the fact that the cell was at a slightly positive pressure. Our work has shown that the oxygen which is present either in the atmosphere above the melt or in the melt itself will cause a zirconium electroplate to lose its adherence and only upon addition of a rather large amount of oxygen in the gas cover was plate deterioration noted. In this case, a powdery deposit resulted which had very little coherence. Furthermore, the photomicrographs of the zirconium-uranium interface shown in Figures 11 through 13 indicate excellent adherence of the zirconium electroplate in addition to a lack of large concentrations of voids throughout the entire series of experiments. Finally, it is doubtful that the presence of oxygen or any oxygen-containing species would cause the observed color changes in the melt samples.

Ivanovskii and Petenev have shown in an investigation of the cathode deposits obtained by electrodeposition of zirconium from a mixed fluoride-chloride melt that addition compounds of the type $MZrF_4$ ($M = Na$ or K) were formed on the cathode.⁽²⁰⁾ Such a precipitate on the cathode during the zirconium deposition could cause a large decrease in the nucleation rate-growth ratio, which in turn could result in an altered deposit.

On this basis, the following scheme is tentatively proposed to explain the change in the structure of the zirconium plate during deposition. During the course of the electrolysis, a small amount of zirconium(III) may be produced by the reaction:

While zirconium(III) is unstable and tends to disproportionate to zirconium(IV) and zirconium metal,⁽²¹⁾ the complexing properties of

the fluoride solvent may increase the stability of zirconium(III) according to the reaction:

Consequently, after some period of time, the solubility product of the zirconium(III) addition compound could be exceeded and a precipitate formed. It is this precipitate, either suspended in the melt or formed at the cathode (the zirconium(III) concentration would be greatest here), which may be responsible for the drastic changes in the zirconium plate structure. That is, the precipitate may provide low energy nucleation sites with a low energy barrier, thus reducing the number of sites and promoting the growth of large crystals.

It is probable that the zirconium(III) caused the darkening of the melt samples since lower oxidation states of ions are known to do so.⁽²²⁾ However, we were unable to obtain voltammetric evidence (by polarography and chronopotentiometry) for the presence of zirconium(III), and other investigations have indicated that zirconium(IV) is reduced directly to zirconium.^(6,11,23) A possible explanation for this seeming discrepancy would be that the reduction potential for reaction 3 lies close to the reduction potential for the metal deposition, and consequently the voltammetric experiments could not resolve the two reduction processes. In addition, the reducing condition in the melt brought about by the long term uninterrupted electrolysis is conducive to the formation of species of lower oxidation states.

The fact that it is possible to reverse the color change of the melt samples by sparging the melt with HF can be explained by the reaction:

That is, HF oxidizes the zirconium(III). This suggests that the melt could be repurified using an HF sparge. To test this, a melt producing poor quality plates was sparged with HF, and then with argon to remove the HF. The electroplate produced from this melt was considerably improved; the gross crystallinity had been largely replaced

with a smoother surface. However, the influence of reaction 1 on the plate is not known, thus making a straightforward interpretation very difficult at this time.

Melt Repurification

That we could reverse the melt degradation with HF led us to two approaches to maintain good plate quality. The first was to treat the electrolysis solution directly with HF during the plating operation. This was unsuccessful because of severe hydride formation with both the zirconium and uranium. The second was to continuously circulate the melt through purification cells where the HF treatment could be made and the HF removed from the melt before returning the melt to the electrolysis cell. Figure 2 shows the schematic of the apparatus for this system.

The melt was pumped by a gas lift from the electrolysis cell to the HF sparge cell. The overflow from this cell was gravity fed to the argon sparge cell. Finally the melt overflow from the argon sparge cell was returned to the electrolysis cell by a gravity feed. As shown in Figure 2, the portion of the melt transfer lines near TC-2 was outside of the furnaces. In order to prevent the melt from freezing there, it was found necessary to wrap the lines with auxiliary heaters. In addition, the melt flow appeared to be more dependable using helium rather than argon as the gas lift, probably because the helium was easier to preheat. Under these conditions it was easy to maintain melt flow at approximately 30 ml/min with a helium flow of about 200 ml/min. A melt flow of about 60 ml/min could be obtained with little more difficulty.

In order to determine if the melt were flowing properly, the following method was used. A conductivity probe in the HF cell was set so that it detected an overflow. A conductivity probe in the argon cell made contact when the melt was just below the overflow level. In addition, a thermocouple placed at TC-2 indicated melt flow by a rise in temperature. The heaters for this section were regulated at about 500°C, the electrolysis cell melt was 625 to 675°C and the melt in the purification cells about 700°C.

During the first plating run a leak occurred somewhere in the purification section. Because the furnace was plugged at both ends with insulation, most of the fluoride salt vapor remained in the furnace interior. This combination of air, salt vapor, and temperature was very corrosive to the nickel and monel components; and the entire purification system was corroded beyond repair. It was not possible to detect the location of the primary failure.

Although the project was terminated at that time, we feel that, because of the successful initial operation of the recirculating system, the continuous purification system can be made to work. The purification section would be simplified by eliminating the conductivity probes and minimizing the number of Swagelok connections. Thermocouple probes can detect if the melt is flowing, and the basic design of the system is now good enough to eliminate the need for the versatility afforded by the Swagelok connections.

CONCLUSIONS

We have demonstrated that under appropriate conditions it is possible to produce a high quality, non-porous adherent zirconium electroplate directly onto uranium from alkali fluoride melts. However, the chemistry of the electrolyte itself plays a decisive role in determining the structure of the deposit. In order to control the quality of the melt, a continuous purification system was incorporated in the apparatus. Before this scheme could be proven, a leak in the purification system occurred and the subsequent corrosion destroyed the apparatus.

Although we feel that maintaining the purity of the melt will help maintain the quality of the plate, we have not demonstrated this. Nor are we certain that this is the correct approach. Consequently, before further development on zirconium electroplating is continued, a more fundamental program should be carried out toward understanding the chemistry and electrochemistry of zirconium ions in the molten alkali fluoride solvent.

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