# Preparation of Zirconium and Hafnium Metal Powders Using Fused Salt Electrolysis

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## ABSTRACT

The paper describes the preparation of zirconium and hafnium metal powders from their respective secondary resources, such as zircaloy-2 scrap and calcium reduced off-grade hafnium powder by a fused salt electrorefining process. The effect of the various experimental variables, such as temperature of electrolysis, current density and concentration of soluble metal in the bath, has been optimised to recover these metals in a state of right purity and with good yield. The metal powders so prepared meet the specification for fabrication. The paper also incorporates the results on electrolytic processing of zircaloy scrap on a 10-kg batch scale to optimise the cell design, with respect to space time yield and specific energy consumption.

**Key Words:**
zirconium, hafnium, electrodeposits, powders

## 1. INTRODUCTION

Zirconium and hafnium, the chemical homologues, belong to the group IVB elements of the periodic table. These metals are chemically similar on account of $4d^25s^2$ and $5d^26s^2$ valence electrons. In fact, this similarity is so great that there is no ore where hafnium has not substituted itself to the lattice of zirconium. On account of this similarity, separation of hafnium from zirconium is one of the most difficult operations. These metals, however, are very different in many of their physical properties, especially with respect to their neutron absorption cross-section. This specific property has led to their different uses in nuclear programmes. Zirconium, on account of its very low neutron absorption cross section ($1.8 \times 10^{-29}$ $m^2$), is a very useful material for cladding of nuclear fuel and pressure tubings. Hafnium, because of its high neutron absorption cross-section ($1.05 \times 10^{-26}$ $m^2$) is an ideal control rod material for light water reactors. Another use of zirconium is as a construction material in chemical industries because of its resistance to corrosive attack by organic and mineral acids. Hafnium is used as an alloying additive to niobium and tantalum metals for achieving increased resistance to oxidation at elevated temperatures and to nickel-based superalloys, for improving transverse creep ductility and rupture life time by strengthening the grain boundary.

The Kroll process is practiced worldwide for the production of these metals. Zirconium so produced meets the required specifications for fabrication, whereas hafnium made by this process calls for adequate purification. Fabrication of zirconium to finished components generates a lot of scrap, part of which gets contaminated owing to reactivity of the metal with atmospheric contaminants. Reclamation of this type of scrap needs chemical processing as zirconium forms stable combinations with the interstitials. In the case of hafnium, as Kroll hafnium is not suitable for fabrication, it was felt that a suitable feed should be produced which could be purified to the required specifications for fabrication. Of the numerous processes available for reclaiming these metals, only iodide and fused salt electrolytic processes are suitable for removing interstitials from them. Though the iodide process is an elegant one for purification of these metals, it is unsuitable on account of poor reactivity of iodine towards the melted stock, low throughput and the special type of reactor geometry required for placing feed for process optimisation. So this process is discounted for large scale adoption. Thus, there is a strong case for adopting the electrorefining process for extraction of these metals from their secondary resources. The electrolytic process offers many advantages such as (i) the release of metals in a state of high purity as electricity is a clean reductant, (ii) the elimination of contamination from the reductants and from their associated impurities, (iii) the possibility of carrying out the process on a continuous and semicontinuous basis by maintaining close control over process variables, and (iv) the use of large current densities.

## 2. DESIGN AND OPERATION OF THE CELL

### a. Cell Design

The electrolytic cell employed in these studies was a conventional electrochemical reactor in which the anode feed was placed in close contact with the container material and the cathode was hung from the top /1/. Additional requirements to be considered in the design of the cell are the reactivity of these metals with atmospheric gases and the high temperatures involved in the cell operations. These considerations require the cell to be operated in an inert atmosphere and hot metal deposits to be cooled to room temperature before exposing them to the atmosphere. High temperature operations require the cell to be fabricated from oxidation resistant materials. The cell so designed and fabricated is shown in Fig. 1. The cell has two chambers, the bottom "electrolytic chamber" being fabricated from Inconel 600. A nickel crucible was employed to contain electrolytes and anode feeds. The upper "cathode receiving" chamber was made of AISI 310 stainless steel and provided with a vacuum seal for cathode insertion, two ports, one for evacuation and the other for backfilling with argon. A slide valve assembly was provided between the cathode receiving chamber and the electrolytic chamber, which in its closed position prevented the entry of air into the electrolytic chamber when opening the latter for removal of the cathode deposit. The cathode assembly was a molybdenum strip attached to a stainless steel rod. In addition, successful operation requires electrolytes to be as pure as possible and free from moisture. Moisture is the most deleterious impurity for conveying oxygen to the metal deposits.

### b. Cell Operation

In the cell operations, cleaned and dried anode feeds were placed in the annular space between the nickel crucible and the distributor. The nickel crucible was filled with the desired amount of electrolyte. If any component of the electrolyte was volatile, a suitable way of adding this component to the electrolyte was devised. After placing the nickel crucible in the bottom chamber, the upper chamber along with the slide valve was bolted to the electrolyte chamber. The whole system was tested for vacuum integrity and then backfilled with purified argon prior to melting the electrolytes by use of an external resistance furnace. After melting the electrolytes, pre-electrolysis was carried out at 1.5V to 2.0V and completion of pre-electrolysis was observed by a sharp rise in voltage. After pre-electrolysis, actual metal deposition runs were carried out by placing the molybdenum cathodes. After a stipulated period of electrolysis, cathodes carrying

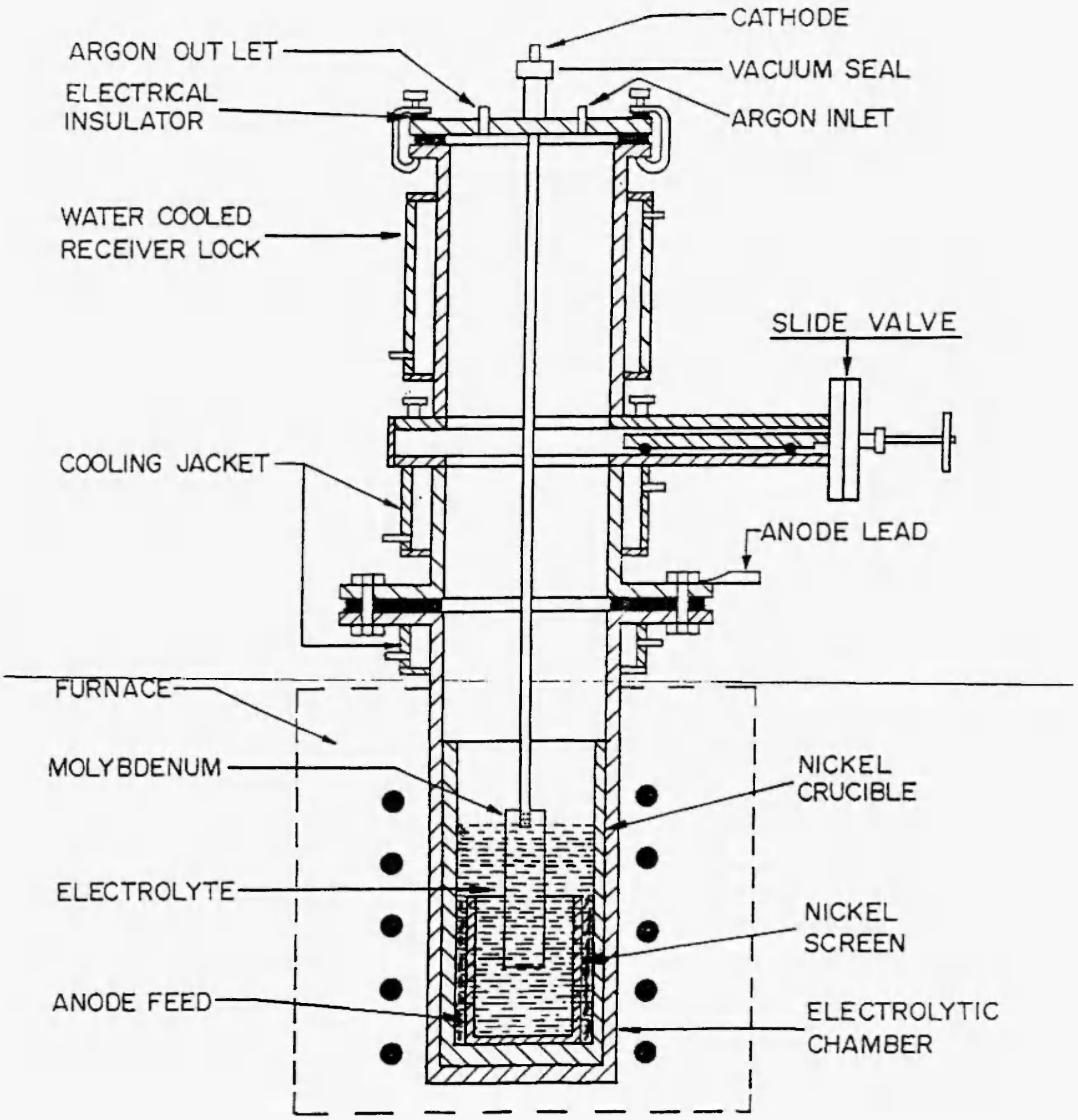


**Fig. 1:** Electrorefining cell.

deposits were withdrawn to a cathode receiver for cooling to room temperature under argon cover, prior to removing from the cell. The cooled mass was leached in dil. HCl for the removal of entrapped electrolytes. The metals were washed free of halides, acetone-rinsed and vacuum-dried prior to computing current efficiency. The metal-powders were evaluated for purity, hardness and particle size.

## 3. DEVELOPMENT OF PROCESSES FOR PREPARATION OF ZIRCONIUM AND HAFNIUM POWDERS

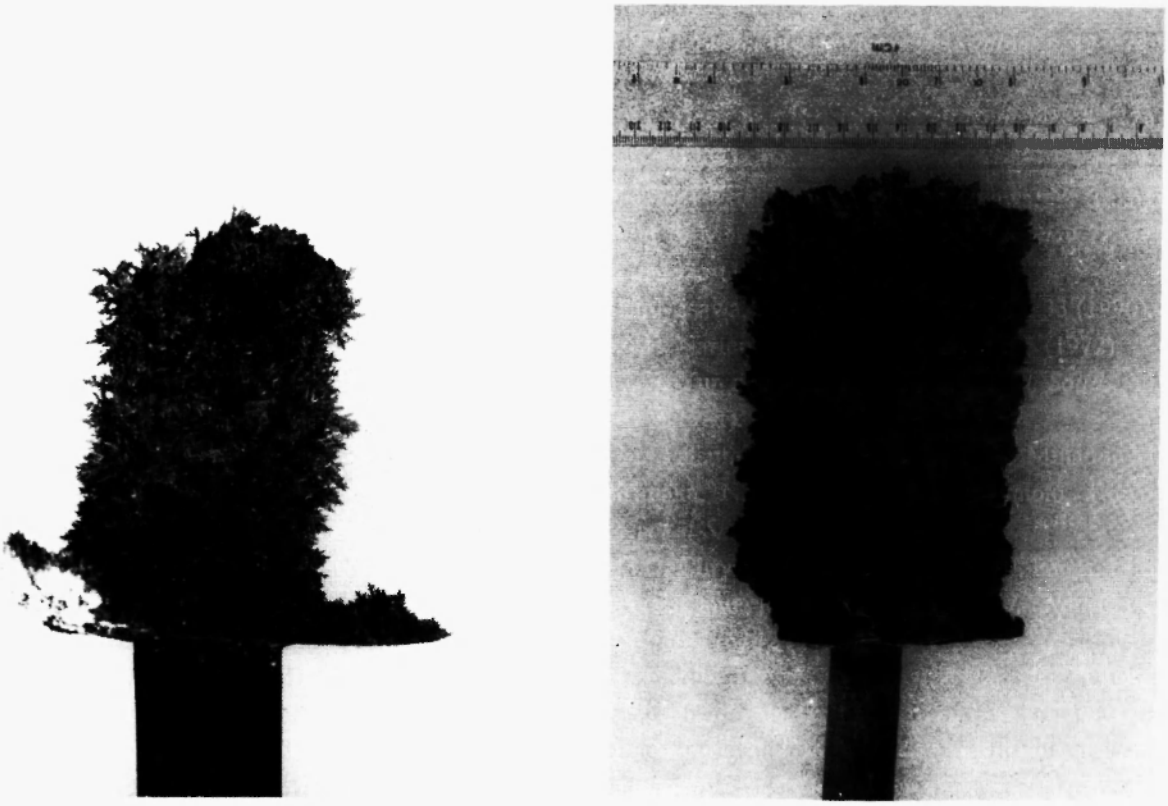
Processes have been developed for preparation of zirconium and hafnium metal powders from their secondary resources. For the preparation of zirconium, the anode feed was zircaloy-2 scrap and for hafnium, it was hafnium metal powder, prepared from calciothermic reduction of $HfO_2$. The experimental variables optimised were (i) temperature of electrolysis, (ii) current density, and (iii) percentage of soluble metal in the bath.

### a. Electrodeposition of Zirconium Powder

Zirconium powder was prepared from zircaloy scrap using NaCl-$K_2ZrF_6$ and NaCl-NaF-$ZrCl_4$ baths /2/. NaCl-$K_2ZrF_6$ and NaCl-NaF were taken in the desired weight ratios. $ZrCl_4$ was added to the NaCl-NaF bath which complexed with NaF. The optimum conditions established for electrorefining zircaloy scrap are given in Table 1. Chemical analysis of the feed and the products and particle size analysis of the products are given in Tables 2 and 3, respectively. Fig. 2 (a) and (b) represents the unleached zirconium deposits from these baths.

### b. Electrodeposition of Hafnium Powder

The electrodeposition of hafnium powder was carried out from off-grade calcium-reduced hafnium. This metal had out-gassing characteristics and presented handling problems on account of its pyrophoric nature /3/. The metal powder was compacted into pellets of 0.015 m dia at 0.25 $Nm^{-2}$ pressure and sintered at 1373 K for an hour under dynamic vacuum better than 6.66 x $10^{-3}$ Pa. This material was used as a feed for preparation of pure hafnium. The electrolytic bath employed in these studies was NaCl-NaF-$HfCl_4$ /4/, in which $HfCl_4$ was added in molten NaCl-NaF by *in situ* chlorination of hafnium metal by chlorine. The best conditions optimised for electrodeposition of hafnium are given in Table 1 and analysis of feed and product are given in Table 2. Fig. 3 displays the unleached electrodeposit of hafnium.



(a) (b)

**Fig. 2:** Unleached zirconium deposits (a) from NaCl-$K_2ZrF_6$ bath, (b) from NaCl-NaF-$ZrCl_4$ bath.

**Table 1**

Optimum conditions on electrorefining of zirconium and hafnium

| Metal | Zirconium | | Hafnium |
|---|---|---|---|
| Wt. of anode feed (kg) | 1.0 | 1.0 | 0.2 |
| Bath | $NaCl-K_2ZrF_6$ | $NaCl-NaF-ZrCl_4$ | $NaCl-NaF-HfCl_4$ |
| Soluble metal in bath (%) | 10 | 3 | 4.5 |
| Wt. of electrolyte (kg) | 3 | 3 | 2 |
| Cathode current density ($a/m^2$) | 2583 | 3229 | 800 |
| Recovery of metal (%) | 60 | 75 | 63.5 |
| Cathode current efficiency (%) | 70 | 79.8 | 60 |

**Table 2**

Analysis of feed and metal powders

| Impurity | Zirconium | | | Hafnium | |
|---|---|---|---|---|---|
| elements % | Feed | Metal from $NaCl-K_2ZrF_6$ bath | Metal from $NaCl-NaF-ZrCl_4$ bath | Feed | Metal from $NaCl-NaF-HfCl_4$ bath |
| Al | 0.01 | 0.01 | 0.0075 | - | - |
| Ca | - | - | - | 0.03 | 0.005 |
| Cu | 0.0145 | 0.003 | 0.0025 | - | - |
| Cr | 0.064 | <0.0015 | <0.0019 | 0.003 | 0.004 |
| Fe | >0.1 | 0.0055 | <0.002 | 0.047 | 0.023 |
| Mg | 0.0055 | <0.001 | 0.001 | 0.002 | 0.001 |
| Mn | 0.001 | 0.003 | 0.002 | 0.001 | 0.001 |
| Mo | - | - | - | 0.003 | 0.001 |
| Ni | >0.1 | <0.0015 | <0.0015 | 0.005 | 0.001 |
| Ti | - | - | - | 0.024 | 0.0195 |
| N | 0.0048 | <0.001 | <0.001 | 0.025 | 0.001 |
| O | 0.199 | 0.108 | 0.09 | 0.69 | 0.0126 |
| C | 0.1 | 0.0049 | 0.02 | - | - |
| Hardness (BHN) | 285 | 135-140 | 165-170 | 430 | 155 |

**Table 3**
Particle size analysis of electrodeposited zirconium

| Bath | Sieve fraction, % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | -20 | -35 | -45 | -60 | -80 | -100 | -120 | |
| | +20 | +35 | +45 | +60 | +80 | +100 | +120 | +20 | -200 |
| NaCl-$K_2ZrF_6$ | 23.30 | 40.18 | 15.17 | 9.94 | 5.71 | 1.62 | 1.54 | 1.89 | 0.65 |
| NaCl-NaF-$ZrCl_4$ | 35.99 | 35.99 | 12.73 | 7.72 | 4.28 | 0.97 | 1.04 | 1.15 | 0.11 |

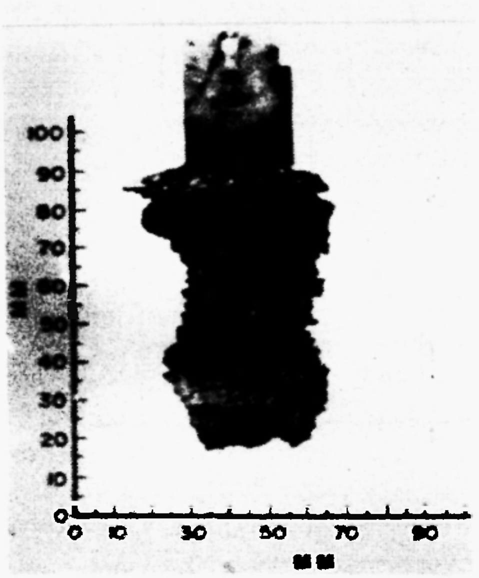


**Fig. 3:** Unleached hafnium deposit

## 4. PREPARATION OF ZIRCONIUM ON EXTENDED SCALE

Preparation of zirconium powder was attempted on an extended scale by treating 10 kg of zircaloy scrap to optimise cell design, using a NaCl-NaF-$ZrCl_4$ bath /1/. This bath offers the advantage that $ZrCl_4$ required for operation is available from the zirconium sponge plant, whereas the use of $K_2ZrF_6$ calls for separate unit operations. The bath also permits high current density to be used. The electrolytic cell was of the same design except that it was provided with an internal heater to supply heat *in situ* for melting of the electrolyte. For cell optimisation, the measure of performance of any electrolytic process is evaluation of space time yield and specific energy consumption. A good cell design means a high space time yield and a low specific energy consumption. Both these parameters determine the economics of the process. Space time yield and specific energy consumption for this cell have been evaluated to be $3.2 \times 10^{-5}$ $h^{-1}$ and 1.76 KWh $kg^{-1}$ of zirconium metal, respectively, while other process parameters were the same as those standardized in the laboratory scale experiments.

## 5. CONCLUSION

The investigations demonstrate the feasibility of preparation of ductile grade zirconium and hafnium metals from their secondary resources.

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