

Electrodeposition of hafnium from the aqueous bath

ARVIND T RANE

Tata Institute of Fundamental Research, Bombay 400 005, India

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Abstract. A method is described for electrodepositing ^{181}Hf from urea-oxalate aqueous bath. The optimum conditions were determined by studying the effects of current density, time of deposition and the cathode metals. More than 80% of ^{181}Hf is deposited on a nickel cathode in one hour.

Keywords. Electrodeposition ; hafnium ; urea-oxalate ; current density.

1. Introduction

Electrodeposition of refractory metals is very difficult and they are usually deposited from molten salt baths with the exception of chromium which could be deposited from the aqueous bath. These methods are not suitable for the deposition at tracer level. Hence a search was made to electrodeposit hafnium from the aqueous bath.

Some refractory metals like zirconium (Joshi and Bhatki 1968), niobium (Joshi and Bhatki 1970) and tantalum (Joshi and Bhatki 1972) were reported to have been electrodeposited from the aqueous bath using saturated urea-oxalate solution. For the deposition of zirconium, carrier-free $^{95}\text{Zr}_{(t_{1/2}=65\text{d})}$ was used. The deposition yield was found to be > 80% only after 40 hr but no deposition was observed in the first 20 hr. This was attributed (proved in a later study by Rane and Joshi, unpublished) to the codeposition with the traces of niobium $-95\text{m}_{(t_{1/2}=90\text{hr})}$ formed by the beta decay of ^{95}Zr . The traces of ^{95}Nb formed and deposited on the cathode in the first 20 hr were just enough to enable the codeposition of ^{95}Zr which gradually increased with the simultaneous growth and deposition of ^{95}Nb and was maximum in 40 hr when it reached saturation. The deposition time for zirconium was brought down to 1 hr when traces of inactive niobium carrier ($\sim 1\ \mu\text{g}$) were added to the pure zirconium-95 activity. Thus, it is possible to electrodeposit radiochemically pure ^{95}Zr , free from any ^{95}Nb contamination in a reasonably short time. The fact that the deposition of zirconium is possible because of codeposition with niobium was confirmed by the deposition of $^{97}\text{Zr}_{(t_{1/2}=17\text{h})}$ which decays to $^{97}\text{Nb}_{(t_{1/2}=72\text{m})}$. Few traces of ^{97}Nb formed in the first one hour were just sufficient for the quantitative deposition of ^{97}Zr in

the next hour. Urea-oxalate was also used for the electrodeposition of manganese-54, technetium-99 and actinium-228 (Rane and Bhatki 1972, 1973), all in the carrier-free form. The present investigation is an attempt to study systematically the electrodeposition of hafnium, at tracer level, by varying several parameters such as time, current density and cathode to achieve the maximum yield of deposition.

2. Experimental

All the reagents used were of AnalaR grade. They were used without further purification. The urea-oxalate was prepared as follows: 120 g of urea (≈ 2 mol) were dissolved in a minimum amount of distilled water. 126 g of oxalic acid (≈ 1 mol) were dissolved separately in the similar way. The urea solution was then added slowly to the oxalic acid solution with constant stirring when crystalline urea-oxalate separated out. The temperature of the mixture was slowly raised to dissolve the precipitated urea-oxalate. The solution was allowed to cool slowly when fine needle-shaped crystals of urea-oxalate separated out. The product was filtered and recrystallised from distilled water. A saturated solution of urea-oxalate in water was prepared and used as electrolyte in the present study.

Hafnium-181 was obtained by irradiating ordinary hafnium metal (1-2 mg) in CIRUS reactor, Bhabha Atomic Research Centre, Bombay. It was dissolved in few drops of conc. hydrofluoric acid and the excess of acid was evaporated to dryness. The dried mass was taken in distilled water and a stock solution was prepared.

Electrolytic nickel foils of 1 mil thickness were used as cathode and platinum wire as anode. Electrolytic pure iron, tin, copper and aluminium foils of the similar thickness were also used as cathode. A conventional glass chimney with hooks at corresponding positions to those on the stainless steel base served as electrolytic cell. The height of the cell was 5 cm and its diameter was 1.12 cm.

A d.c. power supply with a variac was used as a source of e.m.f. A milliammeter with a wire wound potentiometer connected in series was employed to measure and control the current in the electrolytic cell.

Radioactivity was monitored on a NaI(Tl) (2×2 inches) detector connected to a scintillation spectrometer supplied by ECIL (India).

3. Procedure

Throughout the electrodeposition study of hafnium, $10 \mu\text{l}$ of the hafnium-181 activity from the stock solution were taken in a known volume (1 ml) of saturated urea-oxalate solution and transferred into the electrolytic cell. The metallic foil which served as a cathode was sandwiched between the stainless steel base and the glass chimney by rubber bands. The cell was made leakproof by applying grease at its rim. A platinum wire inserted from the top into the solution served as the anode. Direct current was passed after which the cathode was removed from the cell, washed thoroughly with distilled water and then with alcohol and

dried under infrared lamp. The washings and the electrolyte solution were transferred to a small beaker. The gamma-ray activity due to ^{181}Hf deposited on the cathode was counted on the scintillation spectrometer. The washings and the electrolyte solution were also counted in the same geometry. The yield of the hafnium-181 activity deposited on the cathode was thus calculated.

4. Results and discussion

In order to arrive at the optimum conditions of electrodeposition, a systematic study of various parameters such as current density, time of deposition and cathode was undertaken, employing the urea-oxalate solution as electrolyte as described below.

4.1. Variation in current density

The effect of the change in current density on the percentage yield of deposition of hafnium is given in table 1.

4.2. Time of electrolysis

Keeping the current density in urea-oxalate solution constant, the yield of deposition was determined at various time intervals, from 30 min to 2 hr. The results are also given in table 1.

4.3. Change in cathode

Keeping current density and time of deposition constant, the deposition of hafnium was tried on various metals as cathode such as iron, tin, copper, aluminium and nickel. The deposition yields at 80 mA for 1 hr are as follows: iron—63%; tin—42%; copper—57%; aluminium—48% and nickel—65%. Thus it could be seen that maximum yield of deposition was obtained when nickel foil was used

Table 1. Deposition of hafnium-181.

Actual current mA	Current density mA-cm ⁻²	% Yield after 30 min	% Yield after 1 hr	% Yield after 1½ hr	% Yield after 2 hr
10	10.15	3.0	3.5
20	20.30	5.4	23.8
30	30.45	3.7	4.9	31.7	64.5
40	40.60	3.2	11.0	33.4	63.0
50	50.75	3.9	37.8	58.7	71.1
60	60.90	17.4	54.0	63.4	76.1
70	71.05	30.3	53.0	64.0	82.6
80	81.20	30.4	65.1	71.3	83.9
90	91.35	27.3	84.4	78.5	81.5
100	101.50	66.4	83.9	74.1	72.0
110	111.65	69.9	51.4
120	121.80	79.3	69.8

as cathode. The yield of deposition decreased in the following order : nickel > iron > copper > aluminium > tin. Nickel foil was therefore used as cathode throughout in the electrodeposition study of hafnium.

Increase in the current density beyond 80 mA does not increase the yield of deposition. This might be due to the vigorous effervescence taking place at the cathode at high current density, causing lot of fluctuations in the current. Hence the yield is not proportional with reference to time and current in the higher c.d. range. From these results one can conclude that the ideal conditions for the deposition of hafnium would be current density between 80–90 mA/cm² in 1 hr on nickel cathode.

The deposited hafnium activity was found to be strongly adhering to the cathode and could not be removed by washing with water, alcohol, acetone or similar other solvents. The deposited ¹⁸¹Hf activity of the cathode could, however, be removed by keeping it immersed in saturated urea-oxalate solution or treatment with mineral acids. 0.1 N hydrochloric acid removed ~ 13% of the hafnium activity, 3N HCl removed ~ 50%, whereas 9N HCl removed 100% of the activity. It is quite likely that hafnium gets deposited as hydrated oxide. The initial pH of the urea-oxalate solution was 1.5 which changed to > 8 during the course of electrolysis. However, increasing the pH of the electrolyte during the electrolysis, by the addition of ammonium hydroxide did not reduce the time of deposition.

References

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