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ASPECTS OF THE LIQUID CERIUM ELECTRODEPOSITION IN MOLTEN HALIDE MEDIA

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ABSTRACT

Metallic cerium at liquid state has been prepared by fused salt electrolysis of 30-50% $CeCl_3$+NaCl-KCl (equimolar) mixture, in the temperature ranged 800-850°C. The coalesced metal nodules of 97.3% purity were recovery from the solidified bath at room temperature.

1 - INTRODUCTION

Rare earth metals have been obtained by molten halide electrolysis since 1875 [1]. Applaying a similar procedure some publications [2-5] were done dealing in preparing both pure metals and alloys.

Laboratory scale is the major way of rare earth metal production and from the industrial point of view only misch metal have been usually done.

The metal and alloys use are wide [6] and more recently emphasis has been given to their employing as raw material [7] to permanent magnets manufacture.

Some results related with liquid metallic cerium electrodeposition are shown from a mixture of fused chloride salts - $CeCl_3$+NaCl-KCl, varying $CeCl_3$ from 30 to 50 weight pct in the temperature range of 800 to 850°C in an argon atmosphere.

2 - EXPERIMENTAL

ELECTROLYTIC SOLUTION

The electrolytic solution was prepared with reagent grade compounds. The anidrous chloride used, with total impurities of 20% was produced following a previous procedure [8] with care with moisture removal. Each salt batch was carefully mixed and then transfered to the electrolytic cell. The electrolytic system was maintained under 10^{-1} torr vacuum and continuously fluxed with an oxigen free argon, inside a chamber.

CONTROLED ATMOSPHERE ELECTROLYTIC CHAMBER (CAEC)

The CAEC was built entirely in stainless steel, being water-cooled and with the following parts:

- graphite electrolytic cell
- electrodes: graphite anodes and tungsten cathode
- electrolytic cell cooling system
- electric feed system - AC/DC currents

The figure 1 shows schematically the arrangement inside the CAEC.

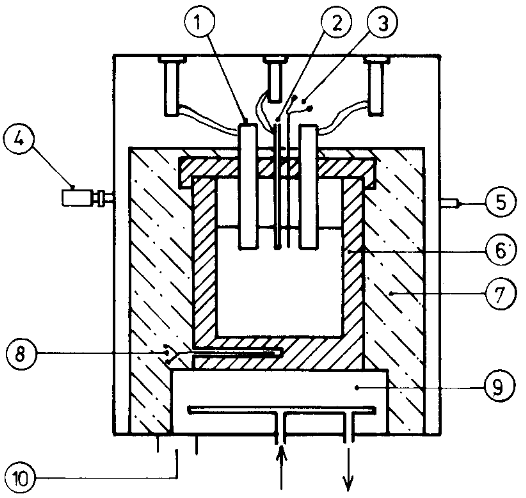

FIGURE 1-CELL DESIGN

① - GRAPHITE ELECTRODE
② - TUNGSTEN CATHODE
③ - TOP THERMOCOUPLE
④ - PIRANI GAUGE
⑤ - ARGON INLET
⑥ - GRAPHITE CRUCIBLE
⑦ - INSULATION
⑧ - BOTTON THERMOCOUPLE
⑨ - HEAT EXCHANGER
⑩ - TO VACUUM PUMP

ELECTROLYTIC CELL OPERATION

Prior to the electrolysis is necessary to have a molten salt pool. This was done striking an electric arc between two electrodes placed nearly above salt surface. To maintain the temperature of this bath region, was applied AC current between the same electrodes.

As the required temperature was reached DC current between the graphite anode and the tungsten cathode was applied. A temperature gradient was maintained between the deposition region and the cell botton. The deposition region temperature was maintained above the metal melting point and, in the cell botton, below in 550^{o}C.

The metal was deposited at liquid state on the cathode and had coalesced on the cell botton, shielded by a solid electrolyte skull, who prevent the contact between solid metal and cell botton.

The table 1 shows the main electrolytic process parameters.

TABLE 1 - PROCESS PARAMETERS OF ELECTROLYSIS

RUN	CEC-06	CEC-08	CEC-10
Average Voltage DC (V)	7.3	7.2	5.4
Average Current DC (A)	40	40	30
Average Cathodic Current Density (A/cm^2)	4.26	17.1	2.48
Average Anodic Current Density	0.79	4.3	0.47
Current efficiency (%)	25.5	36.7	54.4
Temperature range (^{o}C)			
. deposition zone	798	820	834
. botton zone	447	766	380
Electrolysis duration (min)	90	120	120
Metal recovery (g)	26.6	51.5	56.8

3 - RESULTS AND DISCUSSION

Table 2 shows the values obtained by spectrographic flame analysis of metallic cerium nodules. The main impurities Fe, W, C, Mg, Al and other rare earths and come from the start material used to prepare $CeCl_3$ and probably during the arc striking between the W and C electrodes spaced 2,5cm each other wich contaminate the metallic cerium electrodeposited.

The relative low metal yield, table 1, is mainly due a temperature fluctuations inside the fused electrolyte bath, during electrolysis operations. Here as the temperature rises, the metal solubility in its salt increases and otherwise the coalescence of the metal is incomplete [5].

TABLE 2 - METALLIC CERIUM ANALYSIS

RUN	Ce (%)	Fe (%)	W (%)	C (%)	TR (%)	Na (ppm)	Al (%)	Mg (%)
CEC-00	97.3	0.30	0.18	0.27	0.87	384	0.01	0.03
CEC-06	99.8	0.30	0.05	-	-	-	0.01	0.1
CEC-08	97.7	0.15	-	0.02	-	-	-	0.16
CEC-10	98.9	0.09	-	0.01	-	-	0.01	0.05

We haven't electrolyte feed during the electrolysis, so the current efficiency is directly proportional to the $CeCl_3$ content at the bath, table 3 shows some figures.

TABLE 3 - $CeCl_3$ CONTENT AND CURRENT EFFICIENCY

RUN	$CeCl_3$ (%)	Current Efficiency (%)
CEC-06	30	25.5
CEC-09	40	42.8
CEC-11	50	60.7

Metallographic analysis, figure 2 reveals a microstructure from a coalesced metal with a grain boundary second phase precipitate and a few interior grain inclusions.

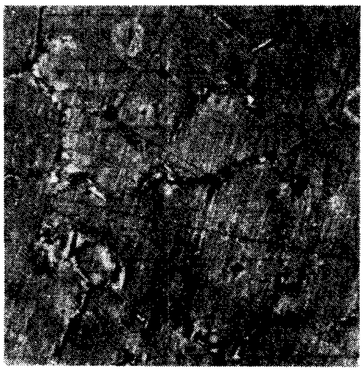

FIGURE 2

Optical micrography of metallic cerium 100x.

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