ELECTROPRODUCTION OF CERIUM AND Ce-Co ALLOY

SOHAN SINGH, A. L. PAPPACHAN and H. S. GADIYAR

Metallurgy Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085 (India) (Received September 4, 1985; in final form December 30, 1985)

Summary

Preparation of batches of 1 - 2 kg of cerium metal by electrowinning from a fused chloride bath is described. The metal is obtained in the molten state by electrolysis at temperatures above its melting point. Under optimum conditions arrived at in this work (temperature, 900 °C; concentration of CeCl₃ in the melt, 30 - 50 wt.%; cathode current density 18 A cm⁻²) a metal of purity 99% or more is obtained at a high current efficiency of 86%. An alloy of cerium and cobalt (56 wt.% Ce) was obtained by deposition of the metal on a cobalt cathode.

1. Introduction

Cerium is the most abundant of the 15 rare earth elements, constituting about one-fourth by weight of all the rare earth elements. Its abundance in the earth's crust is greater than some of the common elements, such as cobalt, mercury, cadmium, tin, vanadium, molybdenum, silver, gold and platinum group metals. Monazite, an orthophosphate of lighter rare earth elements and thorium, contains about 60% rare earth oxide, half of which is cerium oxide [1]. Among the countries of the free world, India ranks second only to the U.S.A. in rare earth resources [2, 3].

Cerium, like the other rare earth elements, forms very stable compounds and a large amount of energy is necessary to decompose these compounds to extract the metal. For example, the free energy of formation of Ce_2O_3 is $-110.8 \text{ kcal } (\text{g atom O})^{-1}$ compared with $-100.5 \text{ kcal for Al}_2O_3$ and -109.5 kcal for MgO at 1300 K [4]. Methods for the preparation of cerium metal are, therefore, limited to either the metallothermic reduction of its salts or oxides with energy expensive reductants like calcium, or electrowinning from fused salt baths. Fluoride or chloride is usually used as the bath material. Though purer metal has been obtained [5] by the metallothermic reduction of cerium fluoride with calcium, the electrowinning method has its advantages. Electrolytic methods are much cheaper than any metallothermic process. It is estimated that the cerium metal prepared by metallothermic reduction is about ten times more expensive than that prepared by the electrolytic process [5]. Electrowinning from the chloride bath has the added advantages of (a) low operating temperature, usually 100 °C above the melting point of the metal, (b) good solubility of the chlorides in water and (c) availability of comparatively cheap raw material. Because of its relatively low melting point (798 °C) cerium is electrowon in the molten state. Winning the metal in the molten form minimizes the formation of products of high surface area and facilitates metal-slag separation. Moreover, as the metal is obtained in ingot form no further consolidation is required. Molten cerium metal reacts or forms alloys with all other elements except inert gases and the metals of the titanium, vanadium and chromium groups of the periodic table [6, 7], so problems arise with the experimental environment and containment of the pure metal. Cerium metal has been electrowon with varying degrees of purity from molten halide baths [8 - 11].

In the present paper electrowinning of batches of the order of 1 - 2 kg of cerium metal is described, using either ceric oxide or hydrated cerium chloride as the starting material. Conditions have been optimized to obtain a metal of high purity at a high current efficiency.

2. Experimental details

2.1. Preparation of electrolyte

The starting material was either ceric oxide or hydrated cerium chloride obtained from Indian Rare Earths. The oxide was converted to chloride by refluxing it with concentrated hydrochloric acid under pressure. Approximately 98% of the oxide could be converted to chloride. The chlorination reaction proceeds with the liberation of chlorine:

 $2CeO_2 + 8HCl \longrightarrow 2CeCl_3 + 4H_2O + Cl_2$

The decanted solution was heated at reduced pressure to remove most of the free water, leaving a thick slurry. This was then vacuum dehydrated using liquid-nitrogen traps. The temperature was slowly increased to about 250 °C over about 24 h. The pressure was maintained at less than 100 μ mHg during the dehydration process to avoid the formation of oxychloride or oxide, which adversely affect the current efficiency and the metal purity during the electrolysis step.

Dehydration of the highly hygroscopic cerium chloride in the presence of hydrogen chloride [12] was found to be slow and tedious. Dehydration in the presence of ammonium chloride [10, 13] gave a chloride free of oxide and oxychloride. However, it was found that the metal won from the cerium chloride prepared by the latter process was always contaminated with nitrogen, despite repeated vacuum distillation to remove the ammonium chloride. The vacuum dehydration method was therefore found to be more suitable. The chloride obtained readily dissolved in absolute alcohol and gave a completely clear solution, showing that no oxide or oxychloride was present [14]. Mixtures of sodium chloride and potassium chloride and of lithium chloride and potassium chloride at their eutectic compositions were selected as the solvent salts because of their thermal and electrolytic stability, low melting point, high specific conductivity and many other favourable physico-chemical properties. The LiCl-KCl eutectic (42 mol.% KCl) was prepared as follows. The salt mixture was dried in a dry HCl atmosphere at 100 - 200 $^{\circ}$ C and was subsequently melted. Dry HCl gas was bubbled through the melt which was then purged with argon to remove any dissolved HCl [15]. The melt was found to be clear and colourless. This was cooled, crushed and mixed with the required amount of cerium chloride. In the case of the NaCl-KCl eutectic (50 mol.% each), the mixture was vacuum dried for long periods and then was mixed with cerium chloride.

2.2. The electrolytic cell

The essential features of the electrolytic cell were (i) a graphite crucible to contain the molten salt, which also served as the anode and (ii) a molybdenum metal cathode, since molybdenum, tungsten and tantalum are the only metals which are not significantly attacked by molten cerium [5]. The cathode was sheathed in an alumina tube to protect it from the interface boundary and chlorine attack, and to limit the area of exposure. The surface area of the anode was many times that of the cathode to avoid the troublesome anodic effect. Since graphite, though inert to chlorine, is attacked by molten cerium [16] to form cerium carbide, the metal was collected in a recrystallized alumina crucible. The crucible material should essentially be chemically inert, shock resistant and able to withstand the temperature. Tantalum and zirconia crucibles were also used to collect the molten metal. It has been reported that the most stable ceramics are BN and Y_2O_3 [17]. Alumina was favoured in this study because it is readily available and is relatively inexpensive. A protective argon atmosphere was used during the experiments and pre-electrolysis at a low voltage was carried out using a graphite cathode to eliminate any moisture that might have been introduced during the loading and transfer operations.

In the simplest form of the electrolytic cell, with graphite as the container and anode, a partially sheathed molybdenum rod as the cathode and an alumina crucible to collect the molten metal, there was no provision for metal-slag separation. After the electrolysis, the contents of the cell were treated with water to dissolve the electrolyte and to isolate the metal. In the modified form of the cell (Fig. 1), the electrolyte was tapped through the opening at the bottom of the cell, while the metal remained in the alumina crucible inside the cell. The opening remained plugged due to the presence of solid electrolyte, which was heated just after the electrolysis to drain out the melt. This cell was used to handle 6 - 7 kg of charge. Both cells were equipped with a device to feed the charge during electrolysis. A screw feeder with a low-amplitude vibrator attachment was found useful for the purpose. Before charging, the cell was heated to the working temperature and was later cooled in flowing argon.



Fig. 1. Electrolytic cell: 1, Hastelloy casing; 2, graphite cell; 3, molten electrolyte; 4, molybdenum cathode with refractory sheath; 5, argon inlet; 6, thermocouple with sheath; 7, screw feeder; 8, refractory crucible to collect metal.

3. Results and discussion

A study of the current efficiency versus temperature was made to arrive at the most suitable temperature for electrolysis. The temperature was varied from 850 °C to 1000 °C in steps of 25 °C. It has been found that the most suitable temperature is 900 °C which is about 100 °C above the melting point of cerium. The current efficiency is at a maximum at this temperature. It decreases at lower temperatures owing to poor coalescence while at higher temperatures it decreases because of the increased solubility of the metal in the melt. 9 mol.% Ce dissolves in CeCl₃ at 900 °C [18].

No metal was deposited when the $CeCl_3$ content in the NaCl-KCl or LiCl-KCl eutectic was 10 wt.% or less. With $CeCl_3$ contents over 50 wt.% difficulties were encountered in obtaining the metal in ingot form at the working temperature owing to an increase in the viscosity of the melt and a decrease in the specific conductivity. With the increase in the CeCl₃ content from 10 wt.% to 30 wt.% the current efficiency improved substantially, but the improvement was marginal above this concentration. As is clear from Table 1, the optimum value of the electrolyte composition is 30 wt.%, which was maintained during electrolysis with the help of the feeding device to replace the cerium ions deposited. Normally, the CeCl₃ content is 45 - 50 wt.% in the initial charge and 80 wt.% in the feed stock. The poor results at lower concentrations may be due to the codeposition of sodium, since the

TABLE 1

Sample number	CeCl ₃ content (wt.%)	Current efficiency (%)	
1	10	0	
2	20	35	
3	30	57.3	
4	40	59.5	
5	50	61.8	

Effect of bath composition on current efficiency

Temperature, 900 °C.

Cathode current density, 9 A cm^{-2} .

Solvent electrolyte, NaCl-KCl (50 mol.% each).

difference between the electrode potential of sodium and that of cerium is only 0.198 V [19]. In an earlier study a similar observation was made in the case of misch metal [20].

The effect of the cathode current density (CCD) on the current efficiency (CE) of metal deposition was studied for CCDs from 5 to 9 A cm⁻² both for KCl-NaCl-CeCl₃ and for LiCl-KCl-CeCl₃. The CeCl₃ content in each case was 50 wt.%. The CE improved with an increase in the CCD. It is clear from Table 2 that for the same CCD and temperature the value of the CE is higher when LiCl-KCl eutectic is used than when NaCl-KCl is used. This is because (i) the fluidity of the former is higher at the working temperature and (ii) the range of stability of LiCl-KCl is higher than that of NaCl-

TABLE 2

Effect of cathode current density on current efficiency

Sample number	Cathode current density (A cm ⁻²)	Current efficiency (%)	
		NaCl–KCl bath	LiCl-KCl bath
1	5	48.6	_
2	6	56.3	61.2
3	7	59.0	—
4	8	61.8	68.3
5	9	62.6	69.1
6	14	83.5	87.5
7	16	84.6	
8	18	86.0	—
9	20	85.0	—
10	22	83.2	-
11	25	82.0	_

Initial bath composition, 50 wt.% CeCl₃ in NaCl-KCl or LiCl-KCl. Temperature, 900 $^{\circ}$ C.

KCl, resulting in less solvent ion codeposition. The CE did not exceed 62.6% in this CCD range. It has been found that in the case of lanthanum under similar CCD conditions the CE is 88% [21, 22]. Kuruda and Matsumoto [10] found that the CE for cerium never exceeded 50% in the CCD range 2 - 6 A cm⁻², but was 90% at 4 A cm⁻² for lanthanum. It is suspected that the low CE for cerium is caused by the partial loss of energy because of the cyclic oxidation-reduction of Ce³⁺ and Ce⁴⁺ at the anode and the cathode respectively.

In the CCD range 14 - 25 A cm⁻², the CE improved considerably for both the melts. At a CCD of 14 A cm⁻², the CE was 83.5% for the NaCl-KCl melt and 87.5% for the LiCl-KCl melts. After consideration of the economic aspects it was felt that the NaCl-KCl bath would be preferable for further studies. The CE reached a peak value of 86% at a CCD of 18 A cm⁻². A further increase in the CCD to 25 A cm⁻² decreased the Ce to 82%. A possible explanation for this improvement in the CE at very high CCDs is that the loss due to cyclic oxidation-reduction is suppressed by the high CCD [8]. Above the optimum value of current density, a decrease in CE occurs owing to the codeposition of solvent ions.

The results shown in Table 3 are for a typical experiment in which 1.356 kg of metal was obtained at a CE of 80%. The initial charge was 3.4 kg with 50 wt.% CeCl₃. 1 h after electrolysis had started an additional charge of 1.6 kg of electrolyte with 80 wt.% CeCl₃ was added at a rate of 400 g h⁻¹. In this way the concentration of CeCl₃ in the bath could be maintained above 30 wt.%. The d.c. power consumption during electrolysis of 1 kg of metal was only 5.7 kW h.

4. Alloy preparation

The intermetallic compound of cerium and cobalt (CeCo₅) is one of the materials used for permanent magnets. The procedure used to prepare the alloy was similar to that used for cerium metal, but in this case, the metal was deposited on a cobalt cathode rather than a molybdenum cathode. At the working temperature the cerium and cobalt form a liquid alloy [17] which drips down the cathode and is collected in an alumina crucible under the cathode. The cathode was pushed down continuously during the electrolysis. The alloy contained 56 wt.% Ce. Additional cobalt metal was added to give the stoichiometric formula CeCo₅. The alloy was homogenized by soaking it above 1204 °C to obtain the CeCo₅ phase.

5. Evaluation of metal

The metal obtained was in ingot form, free of voids and inclusions. The specific gravity of the metal was measured and found to be 6.78, which compares well with the value reported for the pure metal The hardness and

TABLE 3

Typical operating data for electrowinning of cerium from CeCl₃-NaCl-KCl electrolyte

Initial charge	3.4 kg (50 wt.% CeCl ₃)
Additional charge	1.6 kg (80 wt.% CeCl ₃)
Temperature	900 ± 5 °C
Total current	160 A
Cathode current density	17.6 A cm^{-2}
Voltage	8 V
Time of electrolysis	6 h 5 min
Quantity of electricity passed	973 A h
Metal recovered	1.356 kg
Cathode current efficiency	80%
Dc power requirement to win	5.74 kW h
1 kg of metal	

TABLE 4

Evaluation of electrowon metal

Specific gravity	6.78	
Hardness	HV 51	
Tensile strength	14 kg mm^{-2}	
Metallic impurities		
Non-rare earth elements (Fe, Al, Mg, Mo and Si)	0.4 wt.%	
Rare earth elements (La, Pr, Nd and Sm)	0.2 wt.%	
Gaseous impurities		
Hydrogen	0.006 wt.%	
Oxygen	0.106 wt.%	
Nitrogen	0.001 wt.%	
Ce	99.24 wt.%	

tensile strength were determined and the values are reported in Table 4. These values are somewhat higher than the values reported in the literature.

The chemical analysis of a typical sample is reported in the same table. The total non-rare earth impurities constitute 0.4 wt.%, while the total gaseous impurities (oxygen, nitrogen and hydrogen) are 0.113 wt.%. It was found that when the starting material is cerium oxide instead of cerium chloride, the oxygen impurity increases by a factor of five, which may be caused by a small amount of fine cerium oxide mixed with the cerium chloride during conversion and deposited at the cathode along with the metal.

6. Conclusion

Cerium metal of purity 99% or more has been prepared in batches of up to 2 kg. Under optimum conditions of temperature, concentration and CCD,

a high CE of 86% could be obtained. The optimum parameters are (a) temperature, 900 °C; (b) concentration of CeCl₃ in the melt, 30 - 50 wt.%; (c) cathode current density, 18 A cm⁻². An alloy of cerium with cobalt could be prepared directly using a consumable cobalt cathode.

Acknowledgments

The authors are thankful to Dr. C. K. Gupta, Head of the Metallurgy Division, for his encouragement during preparation of this manuscript. Thanks are due to the Heads of the Analytical Chemistry Division, the Spectroscopy Division and the Radiometallurgy Division for analysis of the metal.

References

- 1 B. R. Nijhawan, Symp. on Rare Metals, 1957, Atomic Energy Establishment, Bombay, pp. 83 93.
- 2 J. H. Jolly and R. P. Smith, in C. E. Lundin (ed.), Proc. 12th Rare Earth Research Conf., Vail, CO, July 18 - 22, 1976, University of Denver, Denver Research Institute, Denver, CO, 1976, pp. 809 - 816.
- 3 T. K. S. Murthy and C. K. Gupta, in E. C. Subba Rao and W. E. Wallace (eds.), Science and Technology of Rare Earth Materials, Academic Press, New York, 1980, pp. 3 23.
- 4 C. E. Wicks and F. E. Block, Thermodynamic properties of 65 elements their oxides, halides, carbides and nitrides, U.S. Bureau of Mines Bulletin, 605 (1963).
- 5 B. J. Beaudry and K. A. Gschneidner, in K. A. Gschneidner, Jr, and L. Eyring (eds.), Handbook of Physics and Chemistry of Rare Earths, Vol. I, North-Holland, Amsterdam, 1978, Chapter 2.
- 6 D. A. Hukin and D. W. Jones in C. E. Lundin (ed.), Proc. 12th Rare Earth Research Conf., Vail, CO, July 18 - 22, 1976. University of Denver, Denver Research Institute, Denver, CO, 1976, p. 891.
- 7 K. A. Gschneidner, Jr., in W. D. Corner and B. K. Tanner (eds.), Rare Earths and Actinides, The Institute of Physics, Bristol and London, 1978, pp. 1 - 10.
- 8 J. A. Porter and L. P. Fernandez, U.S. Atomic Energy Commission Rep. DP-802, 1963.
- 9 T. A. Henrie and E. Morrice, J. Met., 16 (1964) 978.
- 10 T. Kuruda and O. Matsumoto, J. Electrochem. Soc. Jpn., 30 (1962) E149 E153.
- 11 E. Morrice, E. S. Shedd and T. A. Henrie, U.S. Bureau of Mines Rep. 7146, 1968.
- 12 J. H. Kleinheksel and H. C. Kremers, J. Am. Chem. Soc., 8 (1928) 959.
- 13 M. D. Taylor, Chem. Rev., 62 (1962) 503.
- 14 R. Didchenko and L. M. Litz, J. Electrochem. Soc., 109 (1962) 247.
- 15 Q. Nguyen and B. J. Welch, J. Electroanal. Chem., 92 (1978) 179.
- 16 A. N. Zelikman, O. E. Krein and G. V. Samsonov, *Metallurgy of Rare Metals*, Israel Program for Scientific Translations, Jerusalem, 1966, p. 294.
- 17 C. Herget and H. G. Domazer, Goldschmidt Informiert, 35 (4) (1975).
- 18 H. Bloom, The Chemistry of Molten Salts, Benjamin, New York, 1967, p. 149; M. Blander, Molten Salt Chemistry, Interscience, New York, Sydney, London, 1964.
- 19 H. B. Herman and J. R. Rairden, in A. L. Bard (ed.), Encyclopedia of Electrochemistry of Elements, Vol. 6, Dekker, New York, 1976, p. 37.

- 20 Sohan Singh and J. Balachandra, J. Electrochem. Soc. India, 22 (1973) 222.
- 21 Sohan Singh and A. L. Pappachan, Proc. Symp. on Chemical Reactions in Nonaqueous Media and Molten Salts, Hyderabad, March 6 - 8, 1978, Department of Atomic Energy, Bombay, 1980, p. 143.
- 22 Sohan Singh and A. L. Pappachan, Proc. Symp. on Advances in Electrometallurgy, Karaikudi, May 3, 1983, Central Electrochemical Research Institute, Karaikudi, 1983, pp. 2 - 55.