ELSEVIER

Preparation of lanthanum and cerium metals by hydrometallurgy

K. Hasegawa[a], Y. Sano[b], A. Aoshima[b], Y. Shiokawa[a],*

[a]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[b]*Tokai Works, Japan Nuclear Cycle Development Institute, Tokai-mura 319-1194, Japan*

Abstract

Lanthanum and cerium metals were prepared by electrolytic synthesis of amalgams in aqueous solutions followed by the thermal decomposition. The amalgamation yields were almost quantitative. The preparation yield of lanthanide metals, however, deteriorated during thermal decomposition due to a density difference between lanthanide and mercury. The gaseous impurities in the prepared metals were found to be comparable with those in commercially available ones.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metal preparation; Lanthanum metal; Cerium metal; Amalgam; Hydrometallurgy

1. Introduction

Metal ions belonging to groups 6–16 are amalgamated in aqueous solutions [1], whereas electropositive metals such as lanthanide and actinide have usually been deposited in molten salts [2,3] because the deposition potentials are more negative than the cathodic limit of the aqueous potential window. It has been shown, however, that uranium and neptunium metals have been quantitatively prepared by the controlled current electrolysis in aqueous solutions using a mercury electrode followed by thermal decomposition of the amalgam. Moreover, the purity of uranium metals was found to be more than 99.99% and the contents of oxygen and nitrogen were below 10 and 5 ppm, respectively [4,5]. The result shows actinide ions are amalgamated outside aqueous potential window and the quality of electropositive metals prepared by hydrometallurgy seems to be comparable with that by the conventional pyrometallurgy.

The standard potentials $E_o(M^{3+}/M)$ of La, Ce, U and Np are -2.37, -2.34, -1.66 and -1.79 V, respectively. Therefore, it is interesting whether more electropositive lanthanide ions can be reduced to metallic states in aqueous solutions. In the present work, preparation of lanthanum and cerium metals is attempted by the elec-

trolytic amalgamation in aqueous solutions followed by the thermal decomposition.

2. Experimental details

The amalgamation cell of 300 ml capacity consisted of cathode and anode compartments divided by a cation-exchange membrane of the H^+ type. The surface area and volume of the mercury cathode were 32 cm^{-2} and 15 ml, respectively, and a platinum anode was immersed in 1 M sulfuric acid solution.

The stock solutions of La(III), Ce(III) and U(VI) were prepared by dissolving the oxides in hydrochloric acid solutions. Prior to the amalgamation, the hexavalent uranium was electrochemically reduced to the trivalent state, which was confirmed by the spectrophotometry. The amalgamations of La(III), Ce(III) and U(III) were carried out at the mercury cathode in acetate buffer solutions of pH 3.4–3.7 containing 1.0 M acetic acid and 0.4 M sodium acetate by the controlled current electrolysis at the density of 220 mA cm^{-2}. The pH of the catholyte was kept almost constant during the electrolysis by supplying hydrogen ions through an ion-exchange membrane from the anode compartment, although the vigorous evolution of hydrogen gas took place.

The resulting amalgam was rinsed by water and ethyl alcohol and then transferred to a magnesia crucible,

---

*Corresponding author.

E-mail address: shiokawa@imr.tohoku.ac.jp (Y. Shiokawa).

degassed at 1000 °C in a vacuum. The amalgam was heated in a vacuum below 10^{-7} Torr at temperatures above the melting points of lanthanide metals after most of the mercury was evaporated below 250 °C.

The mercury, nitrogen, oxygen and carbon in the prepared metals were analyzed, because these four elements were apt to contaminate the products except the impurities in lanthanide oxides used as the source materials.

3. Results and discussion

It is necessary to mention the potential applied to the working mercury electrode. The amalgamation is accompanied by reduction of hydrogen ions and the current–voltage characteristics depends on the pH as illustrated in Fig. 1. At the controlled current electrolysis of 150 mA cm^{-2}, for example, the potentials are controlled at −1.32 V in the solution of pH 1.0 and at −1.66 V for pH 3.0, respectively. Then, some electropositive ions are amalgamated even in the aqueous solution by adjusting of the pH and current density.

Fig. 2 shows the typical reduction behavior of La(III), Ce(III) and U(III) at pH 3.6 by the controlled current electrolysis at 220 mA cm^{-2}. The amalgamation of La(III) and Ce(III) is found to be more sluggish than that of U(III) and the reduction of La(III) seems to be more rapid than that of Ce(III).

The resultant amalgams were decomposed in the magnesia crucible below 1×10^{-6} Torr at 900–1250 °C. The mercury contents in the decomposed products were analyzed as tabulated in Table 1, where previously reported results [5] are also included. The ratio of mercury in the prepared metal is as high as 30% below the decomposition temperatures of 1000 °C and the contents of mercury are found to be dependent on the temperature. Although the
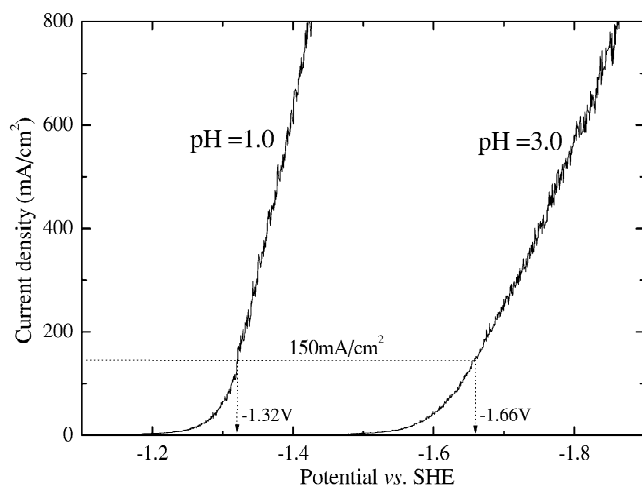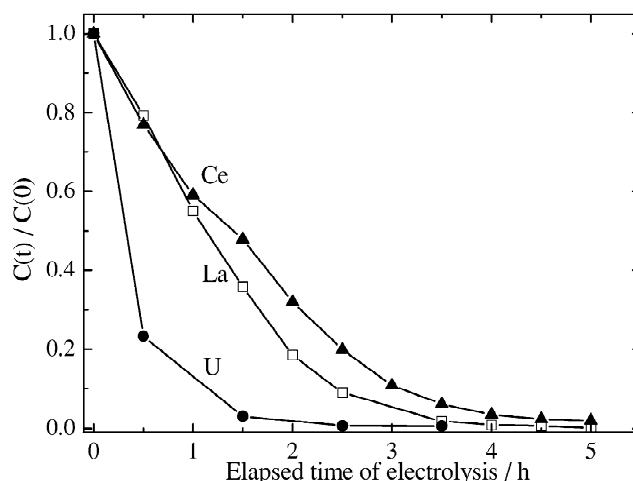

Fig. 2. Amalgamation behaviors of La(III), Ce(III) and U(III) at pH 3.6 by the controlled current electrolysis of 220 mA cm^{-2}.

intermetallic compounds between Ce and Hg decompose into cerium and gaseous mercury up to 555 °C according to the phase diagram [6], cerium metals with less mercury contents can be prepared at the decomposition of 1250 °C. The mercury removal from the amalgams seems to be more effective at the higher temperature than for the longer heating.

The preparation of lanthanide metals is summarized in Table 2 and amalgamations of the lanthanides are almost quantitative except run La-5, which shows that La and Ce ions, more electronegative than actinide ions, can be reduced in the aqueous solution. On the other hand, the preparation yields of lanthanum and cerium metals were usually smaller than 100% as tabulated in the seventh column. Since the amalgamation is almost quantitative, the degradation in the preparation yields results from the thermal decomposition. In this process, the lanthanide amalgam decomposes into lanthanide and mercury [6] and the former with lower density is apt to occupy the upper part in the crucible. During the thermal decomposition, lanthanide metals would be scattered from the crucible

Fig. 1. Current–potential curves for hydrogen evolution in the acetate buffer solutions.

Table 1
The relationship between the thermal decomposition and contents of Hg in the product metals

	Decomposition of the amalgam		Contents of Hg
	Temp (°C)	Time (h)	
La-1	1000	2	17%
La-2	1050	2	8%
La-3	1250	1	27 ppm
La-4	1250	1	17 ppm
Ce-1	900	1	38%
Ce-2	950	3	34%
Ce-3	1000	4	14%
Ce-4	1150	1	8%
Ce-5	1250	1	61 ppm
Ce-6	1250	1	31 ppm

Table 2
The amalgamation and preparation yields of lanthanum and cerium metals

Run	[Metal] (mol dm^{-3})	[Acetate] (mol dm^{-3})	pH	Amalgamation yield (%)	Prepared metal (g)	Yield of metal preparation (%)
La-1	0.109	1.47	3.6–2.9	99.9	1.074	70.9
La-2	0.109	1.49	3.7–3.1	98.3	0.767	50.6
La-3	0.107	1.65	3.6–3.2	99.4	0.728	49.1
La-4	0.109	1.49	3.7–3.1	98.1	0.597	39.4
La-5	0.109	1.45	3.7–3.4	91.8	0.545	36.0
Ce-1	0.100	1.47	3.6–3.0	99.2	1.400	99.5
Ce-2	0.100	1.47	3.7–3.0	99.2	1.216	86.4
Ce-3	0.100	1.40	3.6–3.1	99.7	1.143	81.2
Ce-4	0.107	1.49	3.7–3.6	99.5	1.097	73.2
Ce-5	0.100	1.29	3.6–2.8	99.8	0.892	63.6

accompanied by the intense evaporation of mercury occupied at the bottom. Actually, fine depositions of metals were observed at the inside of the crucible. Such dispersions were never observed in the preparation of uranium metals because of the higher density than Hg [4]. However, the careful control of the temperature in the decomposition process achieves the high preparation yield of 99.5% as is run Ce-1 in Table 2. The prepared cerium metals were shaped into a dull yellowy button of metal, a platy or rod-like metal. The photograph of a 0.876 g sample of cerium metal is shown in Fig. 3.

Since the amount of mercury in the prepared metal can be reduced at high temperatures as shown in Table 1, the impurities of nitrogen, oxygen and carbon in the prepared metals were analyzed as tabulated in Table 3. Nitrogen and oxygen contents in the cerium metals by hydrometallurgy are smaller than or almost equal to those in the commercial ones. It should be emphasized that the gaseous impurities in the lanthanide metals prepared by hydrometallurgy are comparable with those by pyrometallurgy. Gaseous impurities of the cerium metal, however, were 10^1–10^2 times of that in uranium metal. It must be due to a difference in affinity of the metals for nitrogen and oxygen.

Although lanthanum and cerium metal have been tradi-

tionally produced by electrolysis in fused salts or metallothermic reduction [2], it is found that the metals are also prepared electrochemically in the aqueous solution followed by thermal decomposition. Moreover, the procedure would be useful for the small scale preparation and would be especially for the preparation composed of some isotope, such as Sm-154 metal which is required for neutron scattering experiments to elucidate the magnetic properties of the intermetallic compounds. Thus, the metal preparation of not only actinide but also lanthanide is found to be practicable by hydrometallurgy.

Fig. 3. A 0.876-g sample of cerium metal decomposed at 1250 °C.

Table 3
Analysis of gaseous impurities in lanthanum and cerium metals

Sample	N (wt. ppm)	O (wt. ppm)	C (wt. ppm)
La-1	3.0×10^1	1.1×10^3	
La-2	1.1×10^1	1.5×10^3	1.3×10^2
La-3	1.5×10^1	1.6×10^3	1.7×10^2
Ce-1	3.1×10^1	3.6×10^2	1.0×10^2
Ce-2	3.8×10^1	4.8×10^2	1.2×10^2
Ce-3	4.7×10^1	5.4×10^2	8.0×10^1
Ce-4	1.9×10^1	5.5×10^2	2.5×10^2
Ce-5	3.4×10^1	1.8×10^3	1.8×10^2
cm-Ce-1	6.0×10^1	3.6×10^2	
cm-Ce-2	7.8×10^1	4.6×10^2	
cm-Ce-3	3.5×10^1	5.2×10^2	
cm-Ce-4	7.0×10^1	8.9×10^2	
cm-Ce-5	6.9×10^1	9.2×10^2	
cm-Ce-6	7.0×10^1	9.9×10^2	

La-N, Ce-N: prepared by electrolysis of aqueous solutions; cm-Ce-N: commercially available cerium metals of ≈99.9 wt%.

References

[1] A.J. Bard, L.R. Faulker, in: Electrochemical Methods, Wiley, New York, 2001, p. 427.

[2] B.J. Beaudry, K.A. Gshneidner Jr., in: K.A. Gshneidner Jr., L.R. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 1, North-Holland, Amsterdam, 1978, pp. 173–232.

[3] J.C. Spirlet, O. Vogt, in: A.J. Freeman, G.H. Lander (Eds.), Handbook on the Physics and Chemistry of the Actinides, Vol. 1, Elsevier, Amsterdam, 1984, pp. 79–151.

[4] Y. Shiokawa, K. Hasegawa Konas, K. Konashi, M. Takahashi, K. Suzuki, J. Alloys Comp. 255 (1997) 98–101.

[5] K. Hasegawa, Y. Shiokawa, M. Akabori, Y. Suzuki, K. Suzuki, J. Alloys Comp. 271–273 (1998) 680–684.

[6] T.B. Massalski, H. Okamoto, P.R. Subramaian, L. Kacprzak (Eds.), Binary Alloy Phase Diagrams, ASM International, Washington, DC, 1990.