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Journal of Nuclear Materials 344 (2005) 142–145
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Thermochemical properties of the intermetallic compounds in the lanthanum–cadmium system

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Abstract

Thermochemical properties on the intermetallic compounds in the lanthanum–cadmium (La–Cd) system were investigated electrochemically. The redox reactions of the La^{3+}/La couple at the Cd-coated W electrodes, which were prepared by the electrodeposition of Cd at the W electrode, were studied by cyclic voltammetry and chronopotentiometry at 673, 723, 773, 823 and 873 K in the LiCl–KCl eutectic melts containing 1.2 wt% $LaCl_3$. There were several cathodic and anodic peaks corresponding to the formation and the decomposition of the intermetallic compounds, $LaCd_x$, respectively, in the cyclic voltammograms. Since the amount of Cd adsorbed on the W electrode could be evaluated during the electrochemical measurement, the compositions of all $LaCd_x$ could be analyzed exactly from the accumulated coulomb numbers of every anodic peak, which was attributed to the decomposition of each $LaCd_x$. The formation energy of each $LaCd_x$ could be also estimated by chronopotentiometry.

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1. Introduction

Pyrochemical reprocessing of nuclear fuels using molten salts has been developed for recovering actinides from spent metallic and nitride fuels [1–5]. In the electrorefining step of the pyrochemical reprocessing, spent metallic or nitride fuels are dissolved at the anode in LiCl–KCl eutectic melts, and the actinides (An) are recovered as metals at the cathode. It has been proposed that U is selectively recovered at the solid cathode, since the formation energy of UCl_3 is lower than those of the chlorides of other An. Pu and the minor An are then obtained at the liquid metal cathode with the fission product elements such as lanthanides (Ln), due to their low activity coefficients in the liquid metals such as Cd, Bi, etc. [2,3]. Since Cd has a low melting point and the activities of An and Ln in the liquid Cd phase are very low [6], Cd is useful as a typical liquid solvent for the reductive extraction method and a liquid cathode for the electrorefining method. Therefore, several studies have been conducted on the distribution behaviors of An and Ln between the molten salt and the liquid Cd and on the electrochemical behaviors of these elements at the liquid Cd electrode [7–10]. The authors have reported the redox reactions of the Np^{3+}/Np and Pu^{3+}/Pu couples at the liquid Cd electrodes in LiCl–KCl melts by considering the formation of various intermetallic compounds [11–13]. Further thermochemical elucidation on the intermetallic compounds between An or Ln and Cd is necessary for the technological and industrial application.

In the present paper, the redox reaction of the Ln^{3+}/Ln couple at the Cd-coated W electrode in LiCl–KCl

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doi:10.1016/j.jnucmat.2005.04.032

molten salts is investigated by the use of La as a typical Ln. The formation energies of various La–Cd alloys and their compositions can be readily interpreted from the results of electrochemical measurements.

2. Experimental

The electrochemical cell used for the studies on the redox reaction of the La^{3+}/La couple at the W or Cd-coated W electrode was previously shown [11]. A W wire of 1.0 mm diameter also served as a working electrode. The W wire was encased in a high-purity alumina tube in such a way that the apparent surface area of $0.165\ cm^2$ was exposed to the molten salt. The Cd-coated W electrode was prepared by the electrodeposition of Cd metal on the surface of the W electrode in the LiCl–KCl melts containing not only $LaCl_3$ but also $CdCl_2$. A silver–silver chloride (Ag^+/Ag) electrode served as a reference electrode. The reference electrode consisted of a closed-end Pyrex glass tube, in which the LiCl–KCl eutectic salt containing 1.00 wt% AgCl was placed (0.00390 mole fraction), and an Ag wire of 1.0 mm diameter was immersed in the salt. A carbon rod (99.998%; Tokai Carbon Co., Ltd.) of 3.0 mm diameter sheathed with a Pyrex glass tube of 3.0 mm inner diameter and 5.0 mm outer diameter was used as a counter electrode. The surface area of the carbon counter electrode in contact with the salt phase was about $3\ cm^2$.

The polarographic-grade LiCl–KCl eutectic salt, $LaCl_3$ (99.99%) and $CdCl_2$ (>99.99%) were purchased from the Anderson Physics Laboratory. Temperatures of the salt phases were measured by a calibrated Chromel–Alumel thermocouple. Cyclic voltammograms and chronopotentiograms were obtained using a voltammetric analyzer, Model HZ-3000 (Hokuto Denko Co.).

The sample preparation and electrochemical measurements were carried out in a glovebox with high-purity argon gas atmosphere (H_2O, $O_2 < 1.0$ ppm).

3. Results and discussion

3.1. The redox reaction of the La^{3+}/La couple at the W electrodes

Fig. 1 shows a typical cyclic voltammograms obtained at the W electrode at 773 K at a potential scanning rate of $0.01\ V\,s^{-1}$ when the mole fraction of $LaCl_3$ in LiCl–KCl eutectic salts was 0.00275. There exists a linear relationship between the cathodic peak current and the square root of the potential scanning rate in the region between 0.01 and $0.1\ V\,s^{-1}$. The peak heights were approximately proportional to the concentrations of the La^{3+} in the molten salts. The cathodic and the anodic peaks correspond to a redox couple given by Eq. (1).

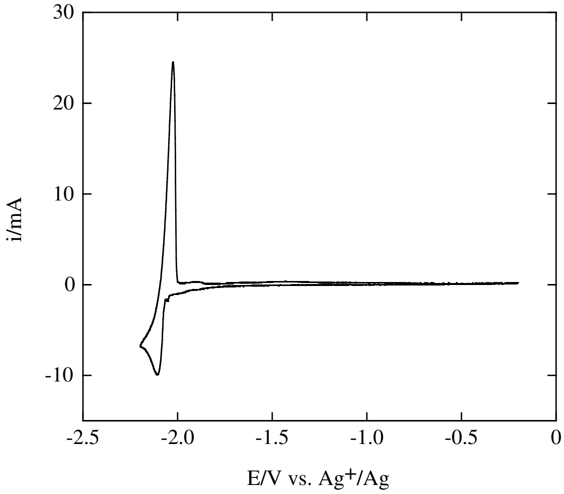

Fig. 1. Cyclic voltammogram for the redox reaction of the La^{3+}/La couple at W electrodes at 773 K. Electrode area: $0.165\ cm^2$. Scan rate: $0.01\ V\,s^{-1}$.

$$\mathrm{La}^{3+} + 3\mathrm{e}^- = \mathrm{La}. \qquad (1)$$

The cathodic peak shifted slightly in the negative direction with the increase of potential scanning rate. These characteristics are attributable to the irreversibility of the redox reaction with the deposit ion of products on the working electrode [14]. Therefore, potentiometric methods were applied in order to obtain accurate values of the redox potentials of the La^{3+}/La couple. The equilibrium potentials of the La^{3+}/La couple, $E_{\mathrm{La}^{3+}/\mathrm{La}}$ in the LiCl–KCl melts obtained by the measurement of electromotive force at 673, 723, 773, 823 and 873 K were −2.126, −2.095, −2.064, −2.033 and −2.002 V, respectively. The formal potentials, $E^{0,}_{\mathrm{La}^{3+}/\mathrm{La}}$, were obtained by considering the concentration of $LaCl_3$. The formal potentials vs. the Ag^+/Ag electrode are expressed by Eq. (2).

$$E^{0,}_{\mathrm{La}^{3+}/\mathrm{La}} = -2.543 + 0.00079 \times T\ (V\ \text{vs. Ag}^+/\text{Ag}), \qquad (2)$$

where T is in K.

By using the data of Yang and Hudson at low-AgCl concentrations in the LiCl–KCl eutectic melt [15], the following equation is obtained for potential of the reference electrode, $E_{\mathrm{Ag}^+/\mathrm{Ag}}$, relative to the Cl_2/Cl^- couple,

$$E_{\mathrm{Ag}^+/\mathrm{Ag}} = -1.0659 - 0.0001805T\ (V\ \text{vs. Cl}_2/\text{Cl}^-). \qquad (3)$$

Therefore, the formal potentials of the La^{3+}/La couple vs. the Cl_2/Cl^- reference electrode, $E^{0,}_{\mathrm{La}^{3+}/\mathrm{La}}$ (Cl_2/Cl^-), can be represented by using Eq. (4).

$$E^{0,}_{\mathrm{La}^{3+}/\mathrm{La}}(\mathrm{Cl}_2/\mathrm{Cl}^-) = -3.609 + 0.00061T\ (V\ \text{vs. Cl}_2/\text{Cl}^-). \qquad (4)$$

The $E^{0,}_{La^{3+}/La}$ values estimated by Eq. (4) (−3.198, −3.183 and −3.168 at 673, 698 and 723 K, respectively) are in fair agreement with the reported values (−3.1804, −3.1637 and −3.1462 at 673, 698 and 723 K, respectively) [16]. The Gibbs free energies, $G^0_{f\ LaCl_3}$, of formation of $LaCl_3$ in the LiCl–KCl melt are calculated from the $E^{0,}_{La^{3+}/La}$ (Cl_2/Cl^-) values by using the following relation:

$$G^0_{f\ LaCl_3} = nFE^{0,}_{La^{3+}/La}\ (Cl_2/Cl^-). \tag{5}$$

The $G^0_{f\ LaCl_3}$ value is expressed by Eq. (6).

$$G^0_{f\ LaCl_3} = 1044.6 + 0.177 \times T\ (kJ\ mol^{-1}). \tag{6}$$

3.2. The redox reaction of the La^{3+}/La couple at the Cd-coated W electrodes

Cyclic voltammogram for the redox reaction of the La^{3+}/La couple at the Cd-coated W electrodes at 773 K is shown in Fig. 2. The anodic and cathodic waves, p_{aCd} and p_{cCd}, were observed around −0.50 V in each voltammogram, which corresponded to the dissolution of Cd ($Cd = Cd^{2+} + 2e^-$). There are several couples of anodic and cathodic peaks. The anodic and the cathodic peaks, p_{aLa} and p_{cLa}, result from the dissolution of La as La^{3+} and the electrodeposition of La in the same manner as the redox reaction of the La^{3+}/La couple at the W electrode. The anodic peaks, p_1, p_2, p_3, p_4 and p_5, are attributed to the dissolution of La as La^{3+} into the LiCl–KCl melts with the decomposition of the La–Cd intermetallic compounds. By comparing the accumulated coulomb number of p_1, p_2, p_3, p_4 and p_5 with that of p_{aCd}, the La/Cd ratios can be estimated. Since Cd metal is always deposited in the potential region more negative than −0.50 V, the La/Cd ratios can be exactly evaluated by the correction of the accumulated amount of Cd metal at each peak The corrected values of La/Cd ratios are 0.510 ± 0.020, 0.275 ± 0.010, 0.110 ± 0.010, 0.030 ± 0.005 and 0.090 ± 0.005. The La–Cd intermetallic compounds, $LaCd_{11}$, La_2Cd_{17}, $La_{13}Cd_{58}$, $LaCd_2$ and LaCd are reported [9]. Therefore, the ratios of La released at peak potentials of p_1, p_2, p_3, p_4 and p_5 to Cd existed on the working electrode are estimated to be 0.500, 0.276, 0.106, 0.0267 and 0.0909, respectively. These values are in fair agreement with the experimental values.

Fig. 3 shows the chronopotentiogram of the La^{3+}/La couple at the Cd-coated W electrode at 773 K after La metal was sufficiently deposited at the Cd-coated W electrode by electrolysis. By analyzing the potentiograms obtained at the temperature region from 673 to 873 K, the potential differences, $\Delta E_{p1\text{-}La}$, $\Delta E_{p2\text{-}La}$, $\Delta E_{p3\text{-}La}$, $\Delta E_{p4\text{-}La}$, and $\Delta E_{p5\text{-}La}$, between the redox potentials of the La^{3+}/La (La–Cd alloys) couple at the Cd-coated W electrode and the $E_{La^{3+}/La}$ value at the W electrode are represented in Table 1. These potential differences are attributable to the chemical reactions noted as the reaction formulas in the table. Here, the stepwise formation constants of these reactions are defined as K_1, K_2, K_3, K_4 and K_5 respectively, and the overall formation constant, β, is expressed by $\beta = K_1K_2K_3K_4K_5$. By considering above relations, the stepwise formation constants can be evaluated in the table. The potential differences are attributable to lowering of La activities in the Cd phase, since several intermetallic compounds are present in the Cd phase. As mentioned above, the analysis of the electrochemical data at the Cd-coated W electrode is readily

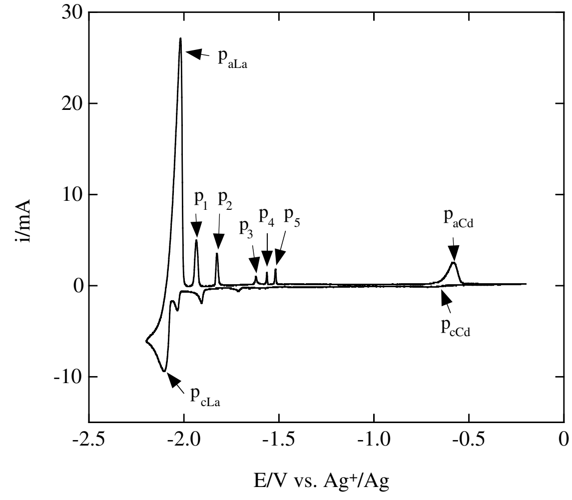

Fig. 2. Cyclic voltammogram for the redox reaction of the La^{3+}/La couple at the Cd coated W electrodes at 773 K. Electrode area: 0.165 cm^2. Scan rate: 0.01 $V s^{-1}$.

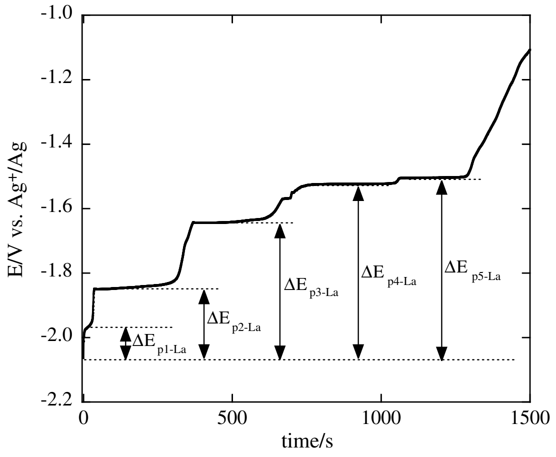

Fig. 3. Chronopotentiogram for the redox reaction of the La^{3+}/La couple at the Cd-coated W electrodes at 773 K. Electrode area: 0.165 cm^2.

Table 1
Potential differences, $\Delta E_{p1\text{-La}}$, $\Delta E_{p2\text{-La}}$, $\Delta E_{p3\text{-La}}$, $\Delta E_{p4\text{-La}}$ and $\Delta E_{p5\text{-La}}$, between the redox potentials of the La^{3+}/La (La–Cd alloys) couple at the Cd-coated W electrode and the $E_{La^{3+}/La}$ value at the W electrode, reaction formulas corresponding to anodic reactions at the peaks and their stepwise formation constants

Potential difference/V	Reaction formula	Stepwise formation constant
$\Delta E_{p1\text{-La}} = 0.1166 - 0.000022T$	$LaCd = La + Cd$	$K_1 = \exp(-0.766 + 4060/T)$
$\Delta E_{p2\text{-La}} = 0.2875 - 0.000086T$	$LaCd_2 = LaCd + Cd$	$K_2 = \exp(-0.766 + 5950/T)$
$\Delta E_{p3\text{-La}} = 0.5461 - 0.000152T$	$LaCd_{58/13} = LaCd_2 + 32/13Cd$ $(La_{13}Cd_{58} = 13LaCd_2 + 32Cd)$	$K_3 = \exp(-2.09 + 9003/T)$
$\Delta E_{p4\text{-La}} = 0.7512 - 0.000326T$	$LaCd_{17/2} = LaCd_{58/13} + 105/26Cd$ $(La_2Cd_{17} = 2/13La_{13}Cd_{58} + 105/13Cd)$	$K_4 = \exp(-6.06 + 7140/T)$
$\Delta E_{p5\text{-La}} = 0.9744 - 0.000560T$	$LaCd_{11} = LaCd_{17/2} + 5/2Cd$	$K_5 = \exp(-8.15 + 7770/T)$

available for the determination of the formation energies and the compositions of the intermetallic compounds.

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