

Electrochemical behavior of praseodymium and Pr-Al intermetallics in LiCl-KCl-AlCl₃-PrCl₃ melts

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Abstract: The electrochemical behavior of Pr(III) and formation process of Pr-Al intermetallics were investigated by different electrochemical methods. The reduction of Pr(III) ion to metallic Pr is an one-step three-electrons reaction. The reversibility of Pr(III)/Pr(0) system was evaluated by cyclic voltammograms with different scan rates. The co-reduction of Pr(III) and Al(III) ions formed three different Pr-Al intermetallics at electrode potentials around -1.40 , -1.80 , and -1.95 V vs. Ag/AgCl at 723 K, respectively. Open-circuit chronopotentiometry and electromotive force (emf) measurements were carried out to estimate the relative molar Gibbs energies of Pr for the formation of different Pr-Al intermetallics in the temperature range of 723–843 K. The activities of Pr in the Pr-Al intermetallic compounds were calculated.

Keywords: molten chlorides; Pr-Al intermetallics; electrochemical behavior; thermodynamic properties; activity; rare earths

Molten salts, possessing excellent properties such as high radiation and thermal resistance, low neutron cross-section and high solubility of fuel components, have been involved in most pyro-processing of spent fuel^[1,2]. During reprocessing spent fuel, a desirable separation of minor actinides (MAs: Np, Am and Cm) from rare earths (REs) is the most difficult to achieve, because the chemical behavior of REs is very similar to that of the MAs^[3]. To improve the MAs/REs separation efficiency and recycle the molten salts, REs should be regenerated when their concentrations exceed 10 wt.% in the molten salts system^[4].

Massot and co-workers^[5–7] have investigated the extraction of cerium, neodymium, samarium and europium via the joint deposition of Al and REs ions in molten fluorides and found that the extraction efficiency was greater than 95%. Castrillejo and co-workers^[8–10] have studied the reduction behavior of Yb, Sm and Sc ions assisted by Al ions in LiCl-KCl eutectic melts to form Al-Yb, Al-Sm and Al-Sc alloys, respectively. Hao and co-workers^[11–13] have proved that the extraction of Pr, Er and Eu from their oxides in LiCl-KCl eutectic salts is possible with the assistance of AlCl₃, which has strong chlorination ability in molten salts system. Liu and co-workers^[14–16] have employed the similar method to extract La, Ce, and Gd in molten salts system. To further develop this kind of extraction methods, a deep under-

standing of thermodynamic properties of REs and Al in molten salts systems is important to design an effective extraction and separation processes.

However, literature is still sparse with regard to the systemic thermodynamic data of RE-Al systems^[17,18]. In recent years, emf (electromotive force) method has been widely used to calculate the experimental thermodynamic data^[19]. Castrillejo et al.^[20] have employed emf measurements to determine the activities of praseodymium and standard Gibbs energy as well as enthalpies and entropies of formation for Pr-Cd and Pr-Bi intermetallic compounds. The activities and relative partial molar Gibbs free energies of dysprosium for various Ho-Ni intermetallic compounds were evaluated in the KCl-HoCl₃^[21] melts on a Ni electrode by emf measurements. Nourry et al.^[22] have also adopted emf measurements to determine the standard Gibbs energy of different intermetallic compounds of Ni/Nd, Cu/Nd, Ni/Gd and Cu/Gd systems.

In this work, we studied the electrochemical behavior of different Pr-Al intermetallics formed by co-reduction of aluminum and praseodymium ions on tungsten electrodes at temperatures between 723 and 843 K in the LiCl-KCl eutectic. Three different Pr-Al intermetallics have been detected by cyclic voltammetry and confirmed by different electrochemical techniques^[11]. At temperatures between 723 and 843 K, open-circuit chronopotentiometry was carried out to estimate the activities of Pr in

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the Pr-Al intermetallic compounds and the relative molar Gibbs energies of Pr for the formation of different Pr-Al intermetallics.

1 Experimental

First, all operations of the salts were performed in a glove box under a pure argon atmosphere (less than 5 ppm O₂). The mixture of eutectic LiCl-KCl (58.8:41.2 in mol.%), prepared from anhydrous LiCl and KCl (Aladdin, 99.9%) salts, was first dried under vacuum for more than 72 h at 473 K to remove excess water, and then introduced to an alumina crucible placed in a cylindrical quartz cell located in an electric furnace. Then the electrolyte was melted under a pure argon atmosphere and temperatures of the melts were monitored with a nickel-chromium thermocouple sheathed with an alumina tube. Metal ion impurities in the melts were removed by pre-electrolysis at -2.00 V (vs. Ag/AgCl) for 4 h with an Al plate (99.99% purity) cathode at 723 K. Aluminum and praseodymium elements were introduced into the bath in the form of anhydrous AlCl₃ and PrCl₃ (99.9%, Aladdin) powder. The total concentrations of dissolved aluminum and praseodymium elements were calculated by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Elemental, IRIS Intrepid II XSP) with frequent samples analysis. It should be pointed out that the concentration of aluminum chloride is approximate because of its volatility.

All electrochemical measurements were performed using PARSTAT2273 electrochemical workstation (Princeton Applied Research) with the PowerSuite software package. A silver wire ($d=1$ mm, 99.99% purity) dipped into a solution of AgCl (1.0 wt.%) in LiCl-KCl eutectic contained in an alumina tube was used as the reference electrode. All potentials were referred to this Ag/AgCl couple unless otherwise specified. A spectral pure graphite rod ($d=6$ mm) served as the counter electrode. Working electrodes were tungsten wires ($d=1$ mm, 99.99% purity), which were polished thoroughly using SiC paper, and then cleaned ultrasonically with ethanol prior to use. Between each measurement the W working electrode was cleaned by applying an anodic polarization. The active electrode surface area was determined after each experiment by measuring the immersion depth of the electrode in the molten salts.

2 Results and discussion

2.1 Electrochemical behavior of LiCl-KCl-PrCl₃ on a tungsten electrode

The cyclic voltammogram, presented in Fig. 1, is plotted in LiCl-KCl eutectic melts containing PrCl₃ at 723 K on a tungsten electrode. The sharp increase of cathodic

current at about -2.4 V and the corresponding anodic

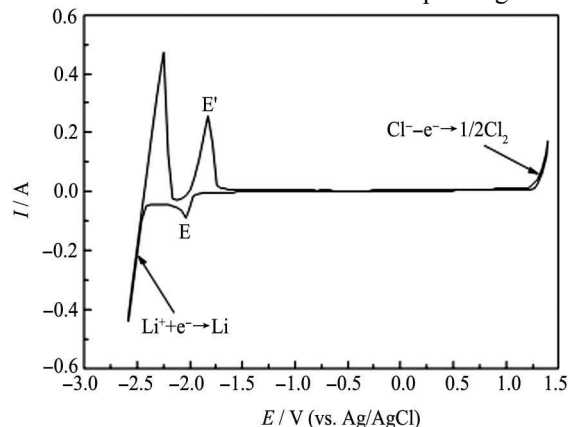


Fig. 1 Cyclic voltammogram of LiCl-KCl-PrCl₃ (1.548×10^{-4} mol/cm³) melts on a tungsten electrode at 723 K, $S=0.342$ cm², Scan rate: 0.2 V/s

current are considered to be the reduction of lithium metal and the reverse reaction, respectively. In the positive potential region, a sharp increase of anodic current at about 1.2 V is observed, which is attributed to the oxidation of chloride ions to chlorine gas. The reduction peak (E), at approximately -2.04 V, shows a steep rise and gradual decay associated with Pr(III) reduction, characteristic of deposition of a new insoluble phase on the inert electrode limited by diffusion^[23]. The reverse anodic scan shows an oxidation peak (E') of the depletion of the deposited metal.

Figs. 2 shows the voltammograms of the redox reaction

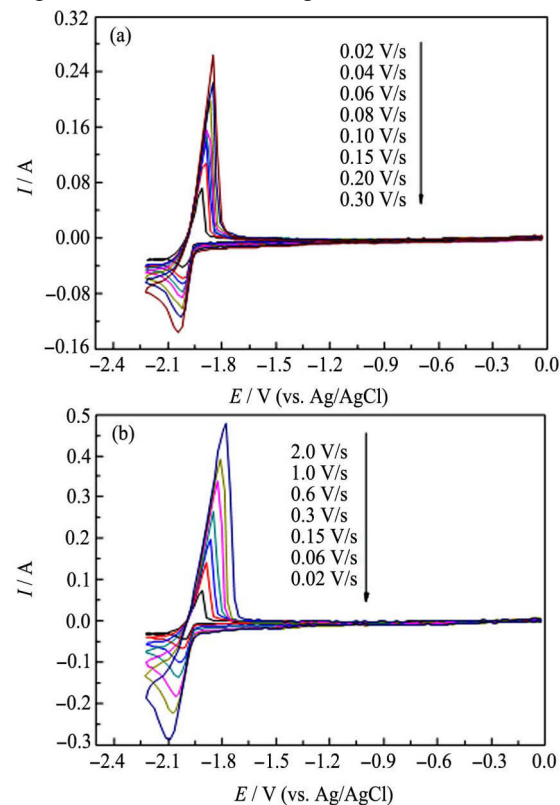


Fig. 2 A series of voltammograms related to the reduction of Pr(III) (1.528×10^{-4} mol/cm³) on a tungsten electrode at 723 K, $S=0.385$ cm², Scan rates: from 0.02 to 0.30 V/s (a), from 0.02 to 2.0 V/s (b)

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