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JOURNAL OF RARE EARTHS, Vol. 35, No. 1, Jan. 2017, P. 90
JOURNAL OF RARE EARTHS
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Electrochemical behavior of Y(III) and preparation of Y-Ni intermetallic compounds in molten LiCl-KCl salts

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Received 27 April 2016; revised 21 July 2016

Abstract: The work concerned the electrochemical behaviors of Y(III) on W and Ni electrodes in molten LiCl-KCl salts by a series of electrochemical techniques. The electrochemical reaction of Y(III) to Y(0) proceeded in a one-step reduction process with the exchange of three electrons, $Y(III)+3e^{-}\rightarrow Y(0)$. Compared with the cyclic voltammogram and square wave voltammogram obtained on W electrode, the reduction potential of Y(III) on Ni electrode was observed at less negative potential than the one of Y(III) to give pure Y metal on W electrode, which revealed the occurrence of underpotential deposition of Y(III) on Ni electrode. Electromotive force (emf) measurements were performed to calculate the relative partial molar Gibbs energies and activities of Y in Y-Ni alloys. The standard Gibbs energies of formation for different Y-Ni intermetallic compounds were also estimated. The different Y-Ni alloys were formed by potentiostatic electrolysis at different potentials and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectrometry (EDS). It was found that four intermetallic compounds, YNi_5, Y_2Ni_7, YNi_3 and YNi_2, were selectively produced by controlling applied potential.

Keywords: electrochemical formation; Y-Ni intermetallic compounds; Ni electrode; potentiostatic electrolysis; thermodynamic properties; rare earths

Rare earth metals and their alloys based on a rare earth and a transition metal have many important applications in the field of advanced materials of current interest, such as high-performance magnets, fluorescent materials, chemical sensors, high-temperature superconductors, etc.[1,2]. Owing to these attractive prospects, the demand for RE metals and their alloys is expected to increase in the future[3,4]. Rare earth-nickel intermetallics with interesting physical and thermochemical properties and several of them are of great technological importance as starting materials for hydrogen storage and permanent magnet fabrication[5–7]. At present, these alloys are mainly prepared by smelting at high temperature and by mechanical alloying, which has many disadvantages, such as alloy composition inhomogeneous, complexity of production process and high energy consumption.

Consequently, as a new preparation method, electrochemical formation in molten salts provides a unique chance for the electrowinning and electrorefining of high purity rare earth metals, as well as for the electrochemical synthesis of their alloys[8], because composition and thickness of the alloys can be controlled by electrochemical parameters[9]. Therefore, many researchers explored the electrochemical preparation of RE-Ni intermetallic compounds in different molten salt systems, such as LiF-CaF_2[10–13], NaCl-KCl[10,14–17], LiCl-KCl[18–27] and LiCl-KCl-NaCl[28,29].

The Y-Ni intermetallic compounds have been used as permanent magnet materials[30,31] and hydrogen storage materials[32]. The electrochemical formation of Y-Ni alloys has been studied by Sato and Hara[14] and Ito et al.[28,29]. Sato and Hara[14] produced the Y-Ni alloy in NaCl-KCl melts by potentiostatic electrolysis for 0.5 h at –1.8, –2.0 and –2.2 V (vs Ag/AgCl), respectively. They obtained YNi_3 and YNi_5 intermetallic compounds at –2.0 and –2.2 V for 0.5 h. However, they did not observe the Y-Ni alloy layer at –1.8 V (vs Ag/AgCl). Ito et al.[28] prepared the Y-Ni alloys by galvanostatic electrolysis for 40 h in LiCl-KCl-NaCl melts at current densities of –0.05, –0.1, –0.15 and –0.2 A/cm^2, respectively. They obtained YNi_2, YNi and Y_3Ni_2 intermetallic compounds, respectively. It is obvious that the operation conditions significantly influence the feasibility of pyrometallurgical reprocessing[25].

The electrochemical formation of Y-Ni has only been studied in NaCl-KCl[14] and LiCl-KCl-NaCl systems[28,29],

Foundation item: Project supported by the National Natural Science Foundation of China (21271054, 11575047, 21173060, 11675044), the Major Research Plan of the National Natural Science Foundation of China (91326113, 91226201) and the Fundamental Research Funds for the Central Universities (HEUCF2016012)

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DOI: 10.1016/S1002-0721(16)60178-3

whereas the molten LiCl-KCl salts have not been used for the electrochemical preparation of Y-Ni alloys. Thus, the present work was focused on the study of the electrochemical formation of Y-Ni intermetallic compounds in molten LiCl-KCl-YCl_3 salts. The electrochemical behaviors of Y(III) ions in molten LiCl-KCl salts were investigated on W and Ni electrodes by cyclic voltammetry, square-wave voltammetry and open circuit chronopotentiometry, respectively. The thermodynamic properties, such as the relative partial molar Gibbs energies and activities of Y in Y-Ni alloys as well as the standard Gibbs energies of formation for different Y-Ni intermetallic compounds, were determined by emf measurements. Then the Y-Ni intermetallic compounds were prepared by potentiostatic electrolysis in molten LiCl-KCl-YCl_3 salts on Ni electrode at different potentials, and the samples were characterized by XRD and SEM-EDS.

1 Experimental

1.1 Preparation and purification of the salts

All the electrochemical experiments, storage of all chemicals and salts preparation were handled in a glove box filled with purified argon where the oxygen content and moisture levels were less than 5 ppm. The mixture of eutectic LiCl-KCl (38:45, mass ratio, AR grade) was firstly dried more than 72 h at 473 K under vacuum in order to minimize the amount of residual water before it was added into an alumina crucible placed in a quartz cell inside an electric furnace.

The LiCl-KCl melts may contain trace amounts of Mg(II), Fe(II) and other metal ions. To avoid these impurities disturbing the reduction of Y(III), the pre-electrolysis at –2.1 V (vs Ag/AgCl) for 5 h was performed to remove the impurities in the melts. The Y(III) ions were introduced into the bath in the form of anhydrous YCl_3 (99.9%) powder. A nickel chromium-nickel aluminum thermocouple, sheathed by an alumina tube, was used to determine the working temperature of the melts.

1.2 Electrochemical apparatus and electrodes

Potentiostatic electrolysis and all electrochemical measurements were employed using an Autolab PGSTAT 302N (Metrohm, Ltd.) potentiostat/galvanostat controlled with Nova 1.8 software. The reference electrode was a silver wire (d=1 mm) dipped into a solution of AgCl (1 wt.%) in molten LiCl-KCl salts contained in a Pyrex tube. In this experiment, all potentials were referred to this Ag/AgCl couple. A tungsten wire (d=1 mm, 99.99%) or a nickel wire (d=1 mm, 99.99%) or a Ni plate (20 mm/10 mm; 99.99%) was used as a working electrode. The working electrode was polished thoroughly using SiC paper to remove the impurities on the electrode surface prior to use. The surface of working electrode was obtained by measuring the depth of electrode immersed in the molten salts. Between each measurement, working electrode was cleaned by applying an anodic polarization. The counter electrode was a pure graphite rod (d=6 mm).

1.3 Molten salts electrolysis and characterization of deposits

The samples of Y-Ni alloys were produced by potentiostatic electrolysis on nickel electrode at 873 K. After electrolysis, the deposits were washed with distilled water and then cleaned in hexane (99.8%) to remove solidified salts attached to the surface of the deposits. These samples were analyzed by XRD (X′pert Pro; Philips Co., Ltd.) using Cu Kα radiation at 40 kV and 40 mA. The specimen was mounted in thermosetting resin using a metallographic mounting press and mechanically polished. Then, the surface morphology and micro-zone chemical analysis of these alloys were performed with SEM-EDS (JSM-6480A; JEOL Co., Ltd.).

2 Results and discussion

2.1 Electrochemical behavior of Y(III) on W electrode in molten LiCl-KCl salts

2.1.1 Cyclic voltammetry

Cyclic voltammetry experiments were carried out in molten LiCl-KCl salts before (black curve) and after (red curve) the addition of YCl_3 (2.44×10^{-4} mol/cm^3) on W electrode (shown in Fig. 1). The black curve of purified blank salts has no additional reaction signal within the examined electrochemical window except the current peaks (A/A′). Since the reduction potential of K(I) is more negative than the one of Li(I), the reduction/oxidation

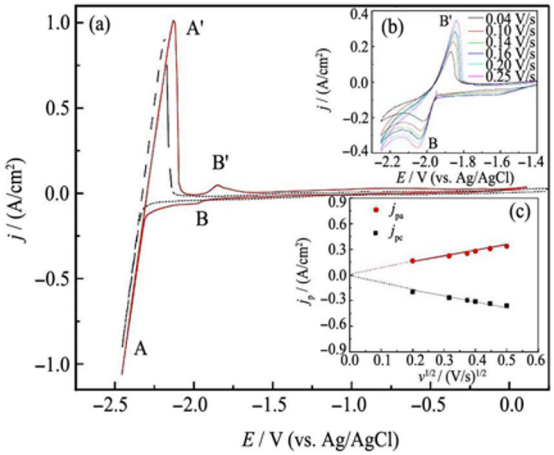

Fig. 1 Cyclic voltammograms obtained in molten LiCl-KCl salts before (dotted line) and after (solid red line) the addition of YCl_3 (2.44×10^{-4} mol/cm^3) on W electrode at 873 K and scan rate of 0.1 V/s (a) and cyclic voltammograms obtained at different scan rates of 0.04, 0.1, 0.14, 0.16, 0.20 and 0.25 V/s (b) and variation of the cathodic and anodic peak currents with the square root of the scan rates (c)