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Electrochemical preparation of Al–Sm intermetallic compound whisker in LiCl–KCl Eutectic Melts

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ABSTRACT

This work presents the electrochemical study of Sm(III) on an aluminum electrode in LiCl–KCl melts at 773 K by different electrochemical methods. Three electrochemical signals in cyclic voltammetry, square wave voltammetry, open circuit chronopotentiometry, and cathode polarization curve are attributed to different kinds of Al–Sm intermetallic compounds, Al_2Sm, Al_3Sm, and Al_4Sm, respectively. Al–Sm alloy with different phase structure (Al_2Sm and Al_3Sm) could be obtained by the potentiostatic electrolysis with the change of electrolytic potentials and time. Al–Sm alloy containing whiskers (Al_4Sm) was obtained by potentiostatic electrolysis (−2.10 V) on an aluminum electrode for 7 hours with the change of electrolytic temperature and cooling rate in LiCl–KCl–$SmCl_3$ (16.5 wt. %) melts. The XRD and SEM&EDS were employed to investigate the phase composition and microstructure of Al–Sm alloy. SEM analysis shows that lots of needle–like precipitates formed in Al–Sm alloy, and their ratios of length to diameter are found to be greater than 10 to 1. The TEM and electron diffraction pattern were performed to investigate the crystal structure of the needle–like precipitates. The results show that the needle–like precipitates are intermetallic compound whiskers. The micro–hardness test and potentiodynamic polarization test illustrate that the micro–hardness and corrosion property of Al–Sm alloy containing whiskers are remarkably improved in comparison with the Al–Sm alloy without whiskers, respectively.

1. Introduction

At present, high–performance metal materials still are the most important structural materials in aerospace industry. Aluminum–lithium and magnesium–lithium alloys with low density, high specific modulus and high specific strength are widely used as superlight structural materials [1–3]. However, the aluminum–lithium and magnesium–lithium alloys have the weaknesses of the poor corrosion resistance, poor toughness and fracture toughness, low strength, low Young's modulus and mechanical properties, which limit their wide–ranging application in aerospace industry [3–5].

To improve the mechanical properties of aluminum–lithium and magnesium–lithium alloys, the addition of other metallic elements has been widely studied. Zhang et al. [6] and Liu et al. [7] investigated behavior of the third metallic element Ce in Al–Li based alloy, and found element Ce can effectively refine grain and improve the mechanical properties of the Al–Li based alloy. The similar theory was also reported in the process of preparation of Mg–Li based alloy in the reference [8–11]. With the addition of the third metallic elements (Gd and Y), the mechanical properties of Mg–Li based alloy were also improved. Birbilis et al. [12] studied the corrosion resistance of the magnesium alloy with the addition of the third metallic element As in magnesium alloy. They found the kinetics of the hydrogen evolution reaction and the corrosion resistance of magnesium alloy were strongly influenced by the presence of element As. Moreover, the element As has ability to significant reduce the corrosion rate of magnesium alloy. Zhang et al. studied the electromeical behavior of Gd (III) [13] and Sb (III) [14] ions in LiCl–KCl–$MgCl_2$ melts and prepared the Mg–Li–RE (rare earth) alloy by the method of molten salt electrolysis. The result shows that Gd (III) element can obviously refine the grain size of Mg–Li–Gd alloy.

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The reports about molten salt electrolysis have attracted more and more attention in recent years in the field of preparation alloys and spent fuel reprocessing. The electrochemical behavior of Sm [15,16] and Tm [17,18] ions were investigated on W and Al electrodes. The Al–Sm and Al–Tm alloys were also successfully synthesized in LiCl–KCl melts, respectively. Tsuda et al. [19,20] investigated the electro–deposition of Al–Mo–Mn and Al–Mo–Ti ternary alloys in $AlCl_3$–EtMeImCl molten salts. Martínez et al. [21] investigated the electro–deposition of magnesium in LiCl–KCl melts containing different $MgCl_2$ concentrations on a tungsten electrode. Pesic et al. [22] investigated the electrochemical behavior of $CeCl_3$ in LiCl–KCl melts. Our group investigated the electrochemical behavior of Nd (III) [23], Yb (III) [24], Tm (III) [25] and Al (III) [26] and successfully synthesized the Al–Li based and Mg–Li based alloys with these metallic elements, respectively. During the process of the co–reduction of Al (III) and Eu (III) ions in chloride melts, Yan et al. [27] found that there are many needle–like precipatates formed on the surface of the Al–Li–Eu alloys. The results from the XRD and SEM show that the needle–like precipatates are Al–Eu intermetallic compound. But further investigation has not been carried out to verify whether the needle–like precipatates are intermetallic compound whiskers.

Whiskers with highly oriented structure, high strength and high elongation, have great potential in improving the mechanical properties of aluminum–based alloys [28]. Recently, researchers [29–32] have done some investigation on promoting the mechanical properties of magnesium–lithium alloys by adopting the whiskers of SiC, B_4N, Saffil Al_2O_3 (δ–Al_2O_3 containing 5% SiO_2), and fiber. Nevertheless, the alloy matrix interfacial adhesion strength is limited because the whiskers and fibers are the external. The mechanical properties of the magnesium lithium alloys only get a little improvement. However, the direct growth of intermetallic whiskers internal aluminum lithium alloys by the method of electrolysis in the molten salts has never been reported up till the present moment.

In this paper, the electrochemical behavior of Sm (III) was investigated by the different electrochemical methods. Al–Sm alloys containing whiskers and Al–Sm intermetallic compounds with different phases structure were prepared by the potentiostatic electrolysis in LiCl–KCl–$SmCl_3$ melts on a solid aluminum electrode. The phase structure, microstructure and micro–zone chemical analysis and the crystal structure of whisker were characterized by X–ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS) and transmission electron microscopy (TEM) with electron diffraction pattern, respectively. The micro hardness and corrosion potential of Al–Sm alloy with and without whiskers were tested by micro–hardness tester and potentiodynamic polarization curve, respectively.

2. Experimental

2.1. Preparation and purification of the melts

The electrolyte is composed of LiCl and KCl. In order to remove excess water of the electrolyte, the LiCl–KCl mixture (LiCl: KCl = 50:50 (wt.%), analytical grade) were dried under vacuum for more than 48 h at 523 K before it was added into an alumina crucible placed in a quartz cell located in an electric furnace. The temperature of the melts was measured by the nickel–chromium thermocouple which was sheathed by an alumina tube. To remove the impurity of the molten salts, the molten salts were carefully purified by pre–electrolysis at −2.10 V (vs. Ag/AgCl) for 4 h. Samarium elements were introduced into the bath in the form of dehydrated $SmCl_3$ powder.

2.2. Electrochemical apparatus and electrodes

All of the electrochemical measurements were performed by the Autolab electrochemical workstation. The reference electrode was an Ag/AgCl electrode which composed by a Pyrex tube containing a solution of AgCl (1 wt. %) in LiCl–KCl (50:50 wt. %) melts. All of the potentials were referred to this Ag/AgCl couple. The counter electrode was a spectral pure graphite rod (d = 6 mm). Molybdenum wire (99.99%) and aluminum wire (d = 1 mm) were used as working electrode. The working electrodes were polished thoroughly using SiC paper. The surface area of working electrode was determined after each experiment by measuring the immersion depth of the electrode in molten salts. During the potentiodynamic polarization test, a three electrode cell set – up was used for the electrochemical measurement. The working electrodes were the Al–Sm alloy with and without whiskers, respectively. A saturated calomel electrode (SCE) and a 1 cm^2 platinum electrode were used as reference and auxiliary electrode, respectively. The potential was scanned from –0.60 to –0.95 V at a scanning rate of 5 mV/s. When the open–circuit potentials became almost steady the specimens were tested in 3.5 wt. % M NaCl solutions.

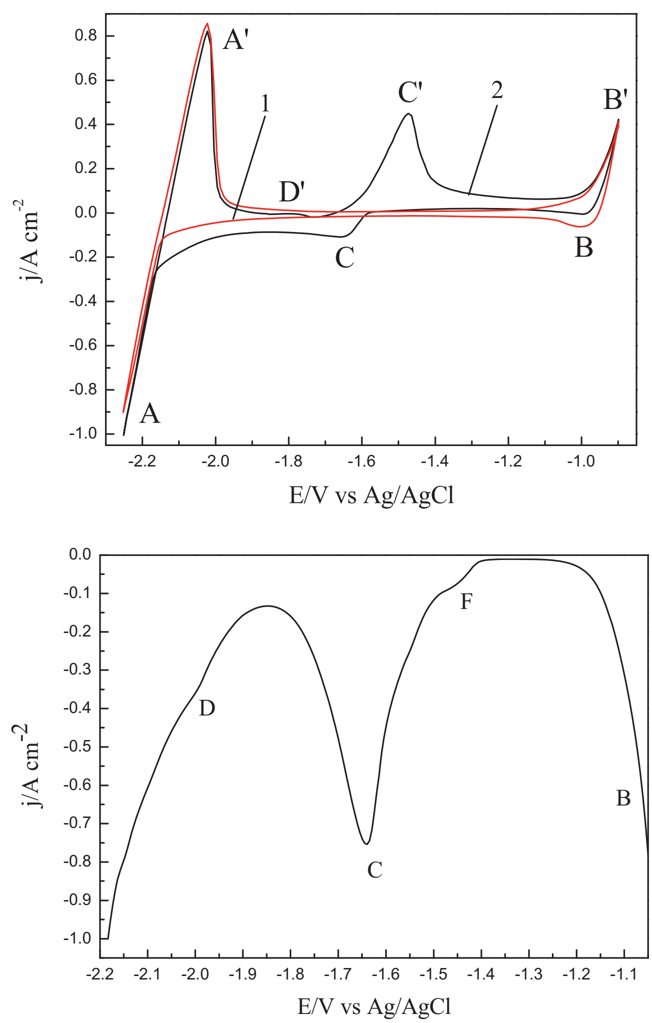

Fig. 1. Voltammograms measured on an aluminum electrode (S = 0.322 cm^2) a: cyclic voltammograms obtained in LiCl–KCl melts before (curve 1) and after (curve 2) addition of 3 wt. % $SmCl_3$ b: square voltammogram obtained in LiCl–KCl melts after addition of 3 wt. % $SmCl_3$, at 773 K.