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ARTICLE

Direct Electrochemical Formation of Different Phases Al-Y Alloys by Codeposition in LiCl-KCl Melts

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Abstract: Electrochemical preparation of different phases Al-Y alloys were investigated in LiCl-KCl-$AlCl_3$-Y_2O_3 melts at 773 K by cyclic voltammetry, square wave voltammetry, open circuit chronopotentiometry and polarization curve. The electrochemical measurements show that the underpotential deposition (UPD) of Y on pre-deposited Al forms two Al-Y intermetallic compounds. The results of X-ray diffraction (XRD) indicate that the two different Al-Y intermetallic compounds are Al_2Y and α-Al_3Y. The microstructure and the micro-zone chemical composition of Al-Y alloys were characterized by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS), respectively. The results illustrate that element Y is mainly distributed on nubby precipitates. Different phases Al-Y alloys can be obtained by adjusting the concentration of $AlCl_3$.

Key words: molten salt; eletrodeposition; Al-Y alloys; Y_2O_3

Aluminium alloys are widely used as light alloys for structural components. With the rapid development of aerospace and military industries, mechanical properties of Al alloys are required to be further improved to satisfy the wide applications. Aluminium alloys possess hugely industrial significance because of their outstanding combination of mechanical, physical and tribological properties over the base alloys. These properties include high specific strength, high wear resistance, high stiffness, better high temperature strength, controlled thermal expansion coefficient and improved damping capacity[1,2]. These properties can be obtained through addition of alloy elements, cold working and heat treatment. Alloying elements are selected based on their effects and suitability.

It is well accepted that the additions of rare earth elements are of great importance to improve the microstructure and the mechanical properties of aluminum alloys[3-5]. The addition of Y is of great significance to further improve the mechanical properties. Agnew et al.[6] suggested that addition of Y could accommodate the *c*-axis deformation through accelerating the *c*+*a*-axis glide, which weakened the deformation anisotropy to improve plasticity. Sun and co-workers[7] found that the addition of Y in Mg-3Al-1Zn alloy formed uniformly distributed finer and harder Al_2Y precipitates which increased the hardness and wear resistance of the Mg-Al alloy. The Y addition to Mg-3Al-1Zn alloy also improved the corrosion resistance. Wu et al.[8] investigated the effects of Y addition on the microstructure and the mechanical properties of Mg-8Li-(1,3)Al alloys. Results showed that, the Y in LA81 and LA83 alloys could refine and spheroidize the microstructure of alloys. The mechanical properties of LA81 and LA83 alloys were improved because of the Y addition. The improvement of elongation percentage was

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much more obvious than that of strength. Li and co-workers[9] found that Y had a distinct grain refining effect on the Al-5 wt% Cu based alloy. Introduction of Y decreased the liquidus and shortened the crystallization range of Al-5 wt% Cu based alloy. Y additions decreased the hot-tearing susceptibility of the Al-5 wt% Cu based alloy significantly.

The conventional method for the preparation Al-RE or Al-Li-RE alloys is directly mixing the metallic elements. This method has some drawbacks, such as a complicated production process, serious oxidation problem and high energy cost. Molten salts especially molten chlorides have been extensively used as reaction media for performing selective solubilization or precipitation in chemical reactions [10].

Electrochemical preparation of Al-Li-Y alloys from molten salt has been reported by Li et al.[11]. However, they detected only one intermetallic compound signal, and ignored another intermetallic signal. In the present paper, different phases Al-Y alloys were investigated by cyclic voltammetry, square wave voltammetry, open circuit chronopotentiometry and polarization curve. Direct electrochemical preparation of different phases Al-Y alloys can be achieved by adjusting the concentration of $AlCl_3$.

1 Experiment

The LiCl-KCl mixture (LiCl:KCl=50:50, wt%, analytical grade) was dried under vacuum for more than 72 h at 473 K to remove excess water, and then melted in an alumina crucible which was placed in a quartz cell inside in an electric furnace. The temperature of the melts was measured with a nickel-chromium thermocouple protected by an alumina tube. The molten salts were purified by pre-electrolysis at −2.0 V (vs. Ag/AgCl) for 4 h. All experiments were performed under Ar atmosphere.

The electrochemical measurements were performed using an Im6eX electrochemical workstation (Zahner Co., Ltd.). The reference electrode (RE) was a silver wire (d =1 mm) which dipped into 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. A spectral pure graphite rod (d = 6 mm) served as the counter electrode (CE). The working electrode (WE) was molybdenum wire (d =1 mm, 99.99 %), which was polished thoroughly using SiC paper, and then cleaned ultrasonically with ethanol prior to use. The specimens for SEM/EDS were mounted in thermosetting resins using a metallographic mounting press and then mechanically polished, and finally etched with a solution of 2 vol% HNO_3 in alcohol. The active electrode surface area was calculated after each experiment by measuring the immersion depth of the electrode in the molten salts.

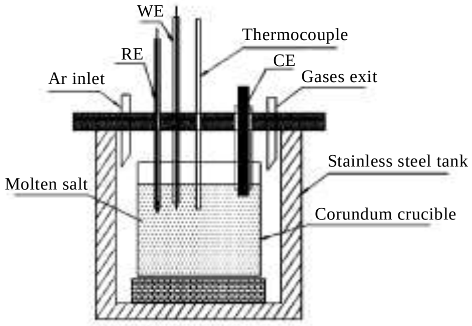

Fig.1 Apparatus of electrolysis cell

The Al-Y alloys were prepared by galvanostatic electrolysis with various $AlCl_3$ concentrations. These specimens were analyzed by XRD (X'Pert Pro; Philips Co., Ltd.) using Cu-Kα radiation at 40 kV and 40 mA. Scanning electron microscopies (SEM) (JSM-6480A; JEOL Co., Ltd.) was used to observe the morphologies of the alloys.

2 Results and Discussion

2.1 Cyclic voltammetry

Cyclic voltammetry was performed at 773 K on a molybdenum electrode in LiCl-KCl-$AlCl_3$ (2wt%)-Y_2O_3 (2wt%) melts (Fig.2). The cathodic/anodic peaks B/B' at about −1.03/−0.95 V correspond to the deposition and the subsequent reoxidation of aluminum. In the positive scanning, cathodic peak D occurs at approximately −2.14 V, which is associated with the formation of a Li-Al alloy by underpotential deposition of lithium on the solid aluminium already coated on the molybdenum electrode[12,13]. Anodic signal D' is caused by the oxidation of Li-Al alloy. In terms of the Al-Y phase diagram, Al and Y can form several inter-

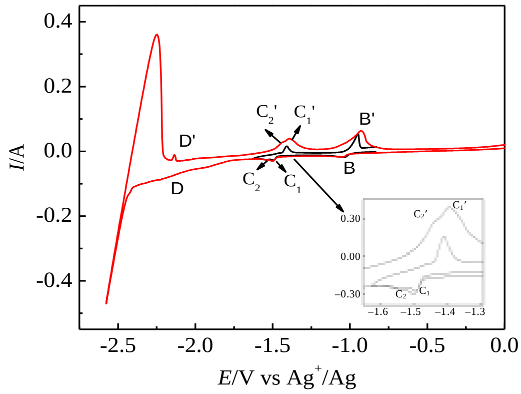

Fig.2 Typical cyclic voltammograms obtained at a molybdenum electrode (S= 0.322 cm^2) in LiCl-KCl-Y_2O_3 (2wt%)-$AlCl_3$ (2wt%) melts with different potential windows at 773 K (scan rate: 0.1 V s^{-1})

metallic compounds. When Y content is not high, Al and Y mainly form α-Al_3Y and Al_2Y intermetallics at lower temperature[14]. In the cathode-going scan, there are two close peaks C_1 and C_2 at around –1.49 V and –1.54 V. We speculate that peaks C_1 and C_2 are attributed to the formation of α-Al_3Y and Al_2Y intermetallic compounds, respectively. The corresponding anodic current peaks are C_1' and C_2' at around –1.41 and –1.46 V, respectively. From the inset graph in Fig.2, the peaks C_1 and C_2, C_1' and C_2' can be clearly observed.

2.2 Square wave voltammogram

Square wave voltammetry is a more sensitive approach than cyclic voltammetry. Fig.3 shows a square wave voltammogram conducted at a step potential of 1 mV and frequency of 10 Hz in the LiCl-KCl-$AlCl_3$ (2 wt%)-Y_2O_3 (2 wt%) melts on a molybdenum electrode at 773 K. It displays four peaks B, C_1, C_2 and D at around –1.01, –1.47, –1.54 and –2.17 V, respectively. These signals correspond to the formation of pure Al metal, two kinds of Al-Y alloys and a Li-Al alloy, respectively. The potentials are consistent with the results obtained from cyclic voltammograms. According to the methodology described in the Ref. [15,16], the number of transferred electrons of peak B at –1.01 V can be calculated. The estimated value of n is 2.97, closed to 3, which is associated with the reaction of Al(III)/ Al.

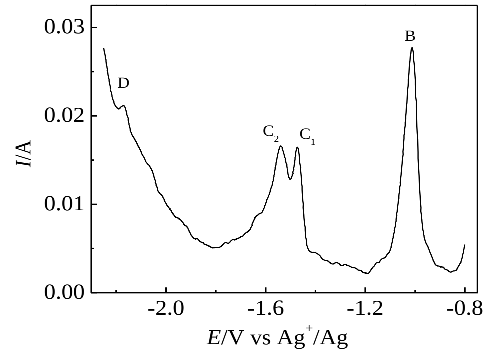

Fig.3 Square wave voltammogram of the LiCl-KCl-$AlCl_3$ (2 wt%)- Y_2O_3 (2 wt%) melts on a molybdenum electrode at 773 K (pulse height, 25 mV; potential step, 1 mV; frequency, 10 Hz)

2.3 Open circuit chronopotentiometry

A thin layer specimen of Al-Y alloy was prepared by cathodic deposition on a molybdenum electrode for a short duration of 10 s at a potential of –2.42 V in the LiCl-KCl-$AlCl_3$ (2 wt%)-Y_2O_3 (2 wt%) melts at 773 K. Then, a transient curve of the open-circuit potential was measured on the electrode, shown as Fig.4. Since deposited Li and Y metals react with Al substrate and diffuse into the Al electrode (already deposited on the molybdenum electrode), the electrode potential gradually shifts to more positive values. During this process, a potential plateau is observed when a composition of the electrode surface is within a region of two-phase coexisting states.

At the beginning, the potential stays at around −2.38 V (plateau E) for a short time, which corresponds to the presence of the deposited Li metal on the electrode. Then, there are four potential plateaus at about: (D) –2.14 V, (C_2) –1.52 V, (C_1) –1.43 V and (B) –1.07 V. Of them, the plateau D is derived from Li-Al alloy and Li coexisting state on the electrode surface. The plateau B is elucidated as the rest potential of the Al electrode (already covering the molybdenum electrode). Apart from these two potential plateaus (B and D), other two plateaus C_2 and C_1 indicating the formation of two Al-Y intermetallic compounds are observed.

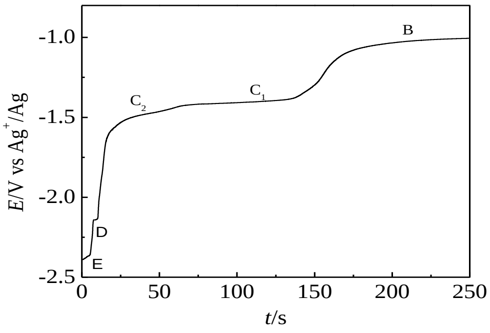

Fig.4 Open circuit potential transient curve for a molybdenum electrode after electrodepositing at –2.42 V (vs. Ag^+/Ag) for 10 s in the LiCl-KCl-$AlCl_3$ (2 wt%)-Y_2O_3 (2 wt%) melts at 773 K

2.4 Polarization curve

The steady state current is only generated by the electrode reaction. Polarization curve measured in steady states can reflect alloy deposition potential, and is an excellent method to investigate electrodeposition of alloys. Fig.5 shows a cathode polarization curve obtained in LiCl-KCl melts containing 2 wt% Y_2O_3 and 2 wt% $AlCl_3$, at a molybdenum electrode at 773 K. A current turning point B is observed at about –0.97 V, which is originated from the deposition of Al. With the potential goes negative, other two current turning points C_1 and C_2 appear at about –1.49 and –1.45 V, respectively. Both turning points C_1 and C_2 are caused by formation of Al-Y intermetallic compounds.

2.5 Galvanostatic electrolysis and characterization of the deposits

Galvanostatic electrolysis (2 A) was implemented in LiCl-KCl-Y_2O_3 (2 wt%) melts with different concentrations of $AlCl_3$ on a molybdenum electrode at 773 K for 2 h. Fig.6 shows the XRD patterns of Al-Y alloy samples. As seen from the XRD patterns, Al_2Y, Al_3Y, Al and AlLi phases were detected. When the concentration of $AlCl_3$ is 5 wt% in the melts, Al-Y alloy only contains Al_2Y phase (pattern a).

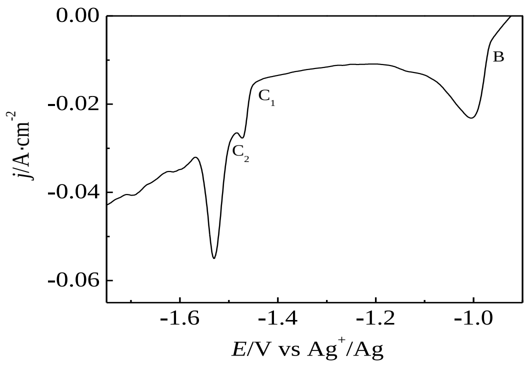

Fig.5 Cathode polarization curve on a molybdenum electrode in the LiCl-KCl-Y_2O_3 (2 wt%)-$AlCl_3$ (2 wt%) melts at 773 K (scan rate: 5 mV s^{-1})

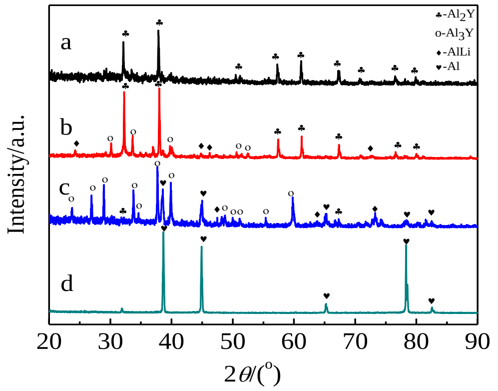

Fig.6 XRD patterns of deposits obtained by galvanostatic electrolysis on a molybdenum electrode (S=0.322 cm^2) in LiCl-KCl-Y_2O_3 (2 wt%) melts with different concentrations of $AlCl_3$ at 2 A for 2 h at 773 K: (a-5 wt%, b-10 wt%, c-15 wt%, d-20 wt%)

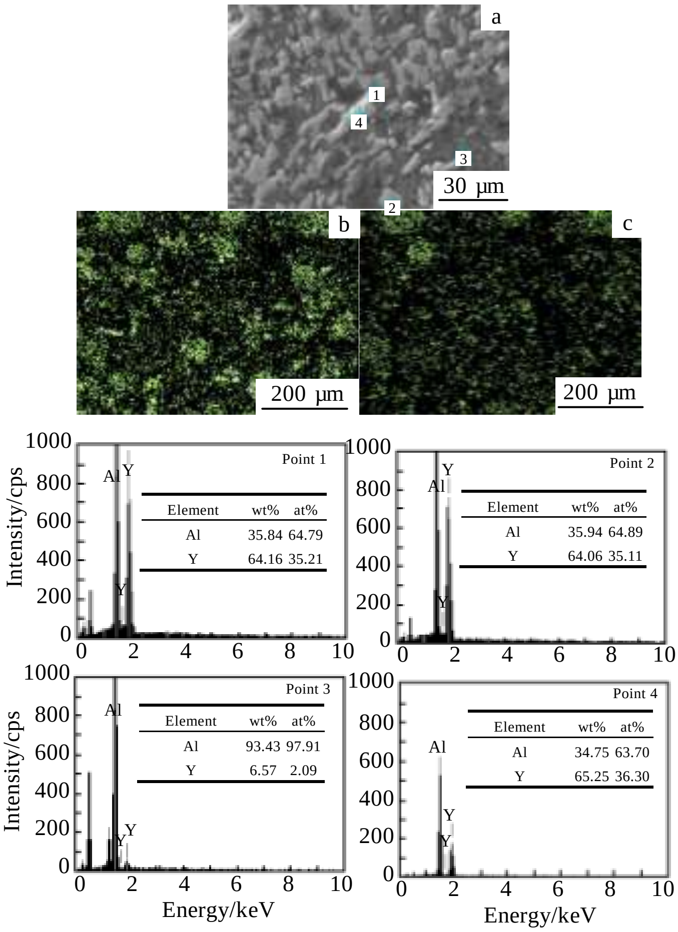

Fig.7 SEM image (a) and EDS analysis of element Al (b), element Y (c) for the Al-Y alloy by co-deposition from LiCl-KCl- $AlCl_3$ (5 wt%)-Y_2O_3 (2 wt%)

With increasing of $AlCl_3$ content (from 5 wt% to 10 wt%), Al_3Y and AlLi phases appear in the Al-Y alloy (pattern b). This phenomenon indicates that lithium and Y contents in Al-Y alloys can also be affected by changing of $AlCl_3$ concentration. When the concentration of $AlCl_3$ increases from 10 wt% to 15 wt%, another new phase Al appears (pattern c). Moreover, the relatively weak Al_3Y diffraction peaks in pattern b become sharp, while the Al_2Y diffraction peaks become weak, which reveals that Al_2Y phase transforms to Al_3Y phase in the alloy. When the concentration of $AlCl_3$ increases to 20 wt%, the XRD pattern shows only Al phase (pattern d), which indicates the deposit is almost pure Al. These phase transitions of alloys indicate that Al contents increase (the atomic percent of Al in those alloys increase) with the increase of $AlCl_3$ concentration. Therefore, Al-Y alloys with different intermetallic compounds can be prepared by galvanostatic electrolysis via adjusting $AlCl_3$ concentration in LiCl-KCl melts. Moreover, the results of XRD patterns show that the Al-Y alloys contain Al_3Y and Al_2Y phases. It can prove that the two cathodic Al-Y intermetallics signals detected by electrochemical measurement correspond to the deposition of α-Al_3Y and Al_2Y intermetallic compounds, respectively.

The SEM and EDS analyses of the elements were employed to examine the distribution of Al and Y elements in the Al-Y alloys. Fig.7 shows SEM and EDS mapping analysis of the Al-Y alloy, which is obtained via codeposition from LiCl-KCl-Y_2O_3 (2 wt%) melts with 5 wt% $AlCl_3$ at 773 K. From the SEM image, many nubby precipitates are observed on the surface of Al-Y alloy. In Fig.7, the points marked as 1, 2 and 4 were taken from three represented nubby zones, and the point 3 was taken from the black matrix. The results of SEM display that the deposit is composed of Al and Y elements. For the points labeled as 1, 2 and 4, the atom percentage ratios of Al/Y are approximately 2. For the point 3, the deposit basically consists of Al element. Combined with the XRD result, the nubby precipitates are mainly Al_2Y compound.

3 Conclusions

1) Al-Y alloys can be directly prepared via electrodeposition of Al, Li and Y on a molybdenum electrode from Y_2O_3 assisted by $AlCl_3$ in LiCl-KCl melts.

2) The underpotential deposition (UPD) of Y on pre-deposited Al can form two Al-Y intermetallics.

3) Al-Y alloys with different Al_2Y and α-Al_3Y phases can be prepared by galvanostatic electrolysis on a molybdenum electrode at 773 K.

4) The aluminum contents in Al-Y alloys can be adjusted by changing $AlCl_3$ concentration in LiCl-KCl melts.

5) The nubby precipitates are basically Al_2Y compound on the surface of Al-Y alloy obtained from LiCl-KCl-Y_2O_3 (2 wt%) melts containing 5wt% $AlCl_3$.

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LiCl-KCl 熔盐中共沉积直接电化学形成不同相 Al-Y 合金

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摘 要：在 773 K 的 LiCl-KCl-$AlCl_3$-Y_2O_3 熔盐体系中，采用循环伏安、方波伏安、开路计时电位和稳态极化研究了不同相的 Al-Y 合金的电化学制备过程。电化学研究表明钇在预先沉积的铝上欠电位沉积形成了 2 种铝钇金属间化合物。X 射线衍射研究表明：这 2 种 Al-Y 金属间化合物为 Al_2Y 和 α-Al_3Y。通过金相显微镜和电子扫描显微镜对合金样品进行了表征，结果显示钇元素主要分布于块状析出物上。通过调节熔盐中 $AlCl_3$ 的含量可以获得不同相的 Al-Y 合金。

关键词：氯化物熔盐；电沉积；Al-Y 合金；Y_2O_3

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