

PREPARING Al-Sc-Zr ALLOYS IN ALUMINUM ELECTROLYSIS PROCESS

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Abstract

Al-RE Alloys have attracted much attention in recent years due to their great potential in many advanced applications. In this work, Al-Sc-Zr alloys were prepared in a laboratory electrolysis cell. Effects of Sc_2O_3 and ZrO_2 additions and the electrolysis time on Sc-Zr contents and their ratio in the alloys were investigated in Na_3AlF_6 based melt at 960 °C. SEM and ICP-AES show that Sc and Zr contents in the alloy produced were 0.25-0.32 wt% and 0.26-1.24 wt%. SEM-EDS analysis reveals that $\text{Al}_3(\text{Sc,Zr})$ particles form in Al alloy prepared by electrolysis. Cyclic voltammetry results demonstrate that Zr^{4+} proceeds a two-step process electrolysis at -0.7V and -1.05V, respectively, while no single peak appears for Sc deposition.

Introduction

It is known that a small addition of Sc in aluminum can significantly improve its properties [1-3], and a combined addition of Sc with other transition metals, for instance, Zr can offer even better properties and lower production costs. The addition of minor zirconium to aluminum alloys with scandium enhance positive effect on their operational properties, due to the formation of extremely fine, coherent $\text{Al}_3(\text{Sc,Zr})$ particles with L_1_2 structure, which can substantially inhibit recrystallization and dislocations [4-5]. These alloys have good welding performance, superior corrosion resistance and strong toughness, etc [6-8], which can be used in transportation, construction, aerospace, and other engineering fields.

There are a number of publications on preparing Al-Sc alloy in molten salt [9-11], while few in open literature are dealt with electrochemical preparing Al-Sc-Zr alloys. Generally, Al-Sc-Zr alloys are prepared by melting Al-Sc and Al-Zr alloys together in a furnace [12-13]. The preparation of these alloys with master alloys is expensive due to high price of Sc and Zr raw materials and smelting costs. Therefore, it is low costs to prepare Al-Sc-Zr alloys directly using their metallic oxides in aluminum electrolysis process.

In this work, we are intend to directly prepare Al-Sc-Zr alloys in aluminum electrolysis cell by adding Sc_2O_3 and ZrO_2 into cryolite based electrolyte. Variation of Sc and Zr contents in aluminum alloys were investigated by changing the electrolysis time parameter and the oxide addition in electrolyte. SEM-EDS and voltammetry techniques were applied to characterizing the microstructure of the alloy and electrochemical behaviors.

Experimental

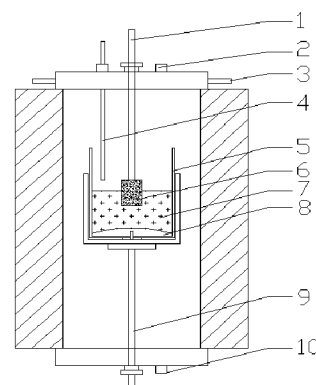
Chemicals and Electrolyte

Sodium cryolite (CR=2.4, industrial grade), MgF_2 (analytical grade) and CaF_2 (analytical grade) were mixed and melted at 960 °C to form molten electrolyte similar to that used in

conventional industrial Hall-Heroult cells. Scandium oxide (>99.99 wt%) and zirconium oxide (>99.99 wt%) were also added into this cryolitic melt. All these chemicals before mixing were subject to dry treatment in a muffle furnace. The electrolyte composition was of Na_3AlF_6 - 4 wt% MgF_2 - 2 wt% CaF_2 - 2 wt% Sc_2O_3 - (0.05 wt%-1 wt%) ZrO_2 , in which there was no Al_2O_3 addition involved at this stage of investigation.

Set-up for Aluminum Electrolysis

Figure 1 is the schematic drawing of the experimental setup used as a laboratory cell. A inner diameter $\Phi 50$ mm \times 80 mm graphite crucible embedded with an inner diameter $\Phi 45$ mm \times 108 mm corundum crucible served as cell lining. A small hole of diameter $\Phi 5$ mm was drilled at the bottom of the corundum crucible that was crossed with a small graphite plug to carry the electrical current from the cell bottom to the liquid aluminum (99.99 wt%). The corundum crucible containing 160 g electrolyte and 15 g Al metal was placed in a vertical tube furnace with temperature controller.



1-Stainless steel anode rod; 2-Gas outlet; 3-Cooling coil;
4-Thermocouple; 5-Corundum crucible; 6-Graphite anode;
7-Molten electrolyte; 8-Aluminum cathode; 9-Stainless steel
cathode rod; 10-Gas inlet

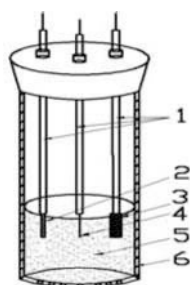
Figure 1. Schematic drawing of experimental setup for electrolysis

During the whole experiment process, a flow of 30 ml/min of argon was kept through the reaction tube in the furnace to provide a protective atmosphere. The laboratory electrolysis process was carried out at a constant current with the cathode current density of 1 A/cm² and duration of 2 h at 960 °C. The testing temperature was measured by a thermocouple and the cell voltage was monitored by a voltmeter, both continuously logged into the data system in a PC.

Apparatus for Voltammetry Measurement

Figure 2 illustrates a brief schematic drawing of the experimental apparatus for electrochemical study. Various electrochemical measurements were carried out using an Im6eX electrochemical workstation (Zahner Co., Ltd.).

The electrolyte used in voltammetry study in was the cryolitic melt similar to that mentioned above with addition of scandium oxide and zirconium oxide. A platinum wire was used as a reference electrode, a molybdenum wire as the working electrode, and a graphite rod ($\Phi 6$ mm) as the counter electrode. Before the test, the Mo wire was polished with SiC paper and cleaned in dilute hydrochloric acid and then in ethanol by ultrasonic to a shine finish. The graphite electrode was pre-cleaned by boiling it in 5 wt% dilute hydrochloric acid for 1 h, and then washing with deionized water. All electrodes had been dried before test in oven to eliminate possible influence from the moisture.



1-Corundum tube; 2-Mo wire; 3-graphite electrode; 4-Pt wire; 5-Molten salt; 6-Reaction chamber
Figure 2. Schematic illustration of the experimental apparatus for electrochemical study in cryolitic melt

Characterization of Al Alloys

Figure 3 is the photograph showing a typical alloy product obtained by electrolysis for 2 h at 960 °C in the sodium cryolitic melt. At the end of the electrolysis process, the crucible containing the alloy product was moved down to the bottom of the furnace for a fast cooling. After that, the aluminum alloy was removed from the crucible, and the solid electrolyte on the surface of the alloy was cleaned carefully.

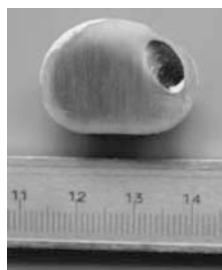


Figure 3. Photograph showing aluminum alloy obtained by electrolysis (in sodium cryolite (CR=2.4) mixed with 4 wt%MgF₄-2 wt%CaF₂-2 wt%Sc₂O₃-0.05 wt% ZrO₂)

In order to know more information about the characteristics of the alloy, the alloy sample was cut into half. A number of specimens were taken from one of the half parts, and was dissolved to determine Sc and Zr contents using ICP-AES technique. Another half was sanded with SiC paper, polished, etched in Dix-Keller solution for SEM observation.

Results and Discussion

Relation Between Electrolysis Time and Cell Voltage

Figure 4 displays the relation between cell voltage and electrolysis time. At the beginning of electrolysis process in the first few minutes, the cell voltage reduced from 3.64 V to 3.42 V without

current density changing. This may be caused by uneven temperature distribution in the cell when graphite anode inserted into the electrolyte melt. After that, the voltage was fluctuated around 3.35 V. The course of dissolving and electrolysis of scandium oxide and zirconium oxide in the molten salts may lead to small change in cell voltage.

The recording of cell voltage against time demonstrates a relative stable operation and good control state during laboratory electrolysis, which is considered important in a possible large scale testing in future.

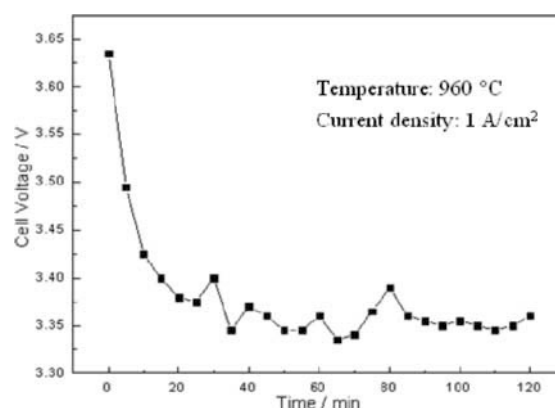


Figure 4. Variation of cell voltage vs. electrolysis time (2 wt% Sc₂O₃ addition, 0.1 wt% ZrO₂ addition)

Contents of Zr and Sc in Al Alloys Produced

Table I shows the effect of electrolysis time on Sc and Zr content in Al alloys produced by electrolysis in the sodium cryolitic melt at 960 °C. All electrolysis tests were performed at the current density of 1 A/cm², while the additions of Sc₂O₃ and ZrO₂ were different from test to test.

It was obvious that the content of Zr in alloy increased with the prolonged electrolysis time and the maximum value could reach 3.27 wt%, while at the same time Sc content appeared to be almost unchanged. To understand further such phenomenon, another set of experiments were arranged with varied addition of ZrO₂ into the cryolitic melt.

Table I. Sc and Zr Content in Al Alloys Produced with Varying Period of Time in Electrolysis

Sample No.	Sc ₂ O ₃ (wt%)	ZrO ₂ (wt%)	Current Density (A/cm ²)	Time (h)	Sc (wt%)	Zr (wt%)
ASZ-1	2	1	1	0.5	0.25	0.75
ASZ-2	2	1	1	1	0.28	3.27
ASZ-3	2	1	1	2	0.26	1.24

In Table II, the contents of Sc and Zr in the Al alloys produced are listed with varying ZrO₂ additions while a constant addition of 2 wt% Sc₂O₃. Two electrolysis experiments were performed at 960 °C for 2 h and a thermal reduction experiment (ZW-1) was done for comparison under identical testing conditions without electrical current. It is noticed that Sc content in the thermal reduction is similar to the values in Table I, suggesting Sc in this

case may not come from the electrolysis process. This may explain the fact that Sc content is almost unchanged with variation in electrolysis time.

Table II. Sc and Zr Content in Al Alloys Produced with Various ZrO₂ Additions in Electrolyte

Sample No.	Sc ₂ O ₃ (wt%)	ZrO ₂ (wt%)	Current Density (A/cm ²)	Sc (wt%)	Zr (wt%)	Ratio
ZW-1	2	0.1	0	0.25	0.30	1:1.2
ZW-2	2	0.1	1	0.32	0.45	1:1.4
ZW-3	2	0.05	1	0.27	0.26	1:1

From thermodynamic calculation, the decomposition voltage of ZrO₂ (2.40V) is lower than that of Sc₂O₃ (2.70V) at 960 °C. This gives Zr an advantage in electrochemical deposition, leading to its increase with increasing electrolysis time and ZrO₂ concentration in cryolitic melt (see Table I and Table II). Zr content can vary with changing ZrO₂ concentration in cryolitic melt and electrolysis time as well. This may provide a technical possibility in controlling the alloys composition.

It is an interesting phenomenon, however, that the change in the ratio of Sc₂O₃ to ZrO₂ has almost no effect on the ratio of Sc to Zr in Al alloys produced. This may also imply that it has to look for other ways to control Sc content and the related composition of Al alloys prepared using electrolysis method. The obtained results, so far, suggest that the investigation has still long way to go towards this direction.

Characterization of Al Alloys Produced

Figure 5 shows SEM-EDS micrographs of Al alloy sample prepared by electrolysis. There are precipitate particles with regular shape in Figure 5(a) and is the enlargement of a square precipitated particle in Figure 5(b). The precipitated particles of square with protruding lobes and the triangular shape are all Al-Sc-Zr phase, which are quite similar to those observed in literature [14, 15].

The chemical composition of the precipitated particle can be further confirmed by the SEM-EDS results, as shown in Figure 5(c), in which the particle only has Al, Sc, Zr elements and the proportion of the sum of (Sc, Zr) atoms to Al atoms is 1:3, i.e., the same as Al₃(Sc,Zr).

In Figure 6, the SEM photographs illustrate the element mapping of Al₃(Sc,Zr) particle presented in Figure 5(c). It is obvious that the amount of Al within the particle is lower than that in the alloy matrix (see Figure 6(a), Al mapping).

It is known that Al₃Zr with L1₂ space lattice structure would have priority to generate in the molten aluminum alloys containing Sc and Zr [16]. And then Sc atom may diffuse to the particle of Al₃Zr and replace part of Zr atom, forming Al₃(Sc,Zr) with the L1₂ space lattice structure. This is why the mapping of Sc and Zr element displays complementarity within the area of the precipitated particle (see Figure 6(b) and Figure 6(c)).

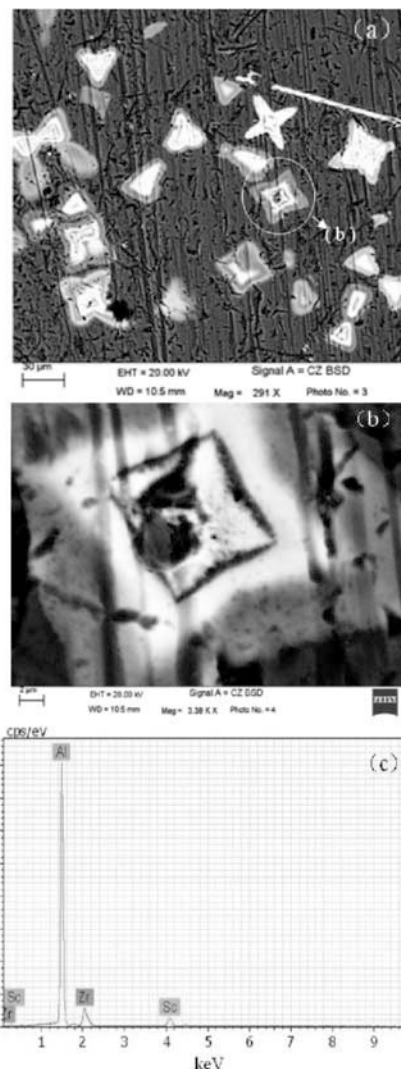


Figure 5. SEM-EDS analysis of Al alloy sample produced in electrolysis: (a) Al-Sc-Zr alloys (sample NO.ZW-2), (b) Al-Sc-Zr particle, (c) EDS analysis on the particle in (b)

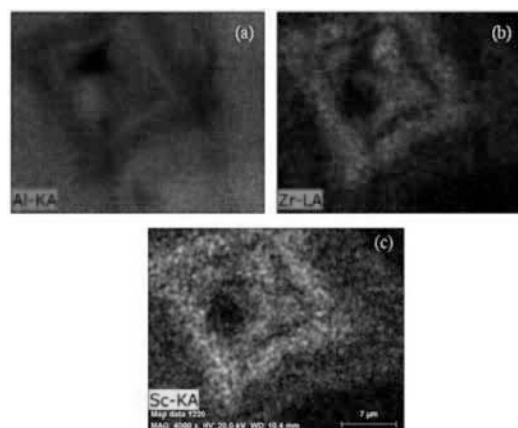


Figure 6. Element mappings of Al₃(Sc,Zr) particle. (a) aluminum, (b) zirconium, (c) scandium

Cyclic Voltammetry

Figure 7 shows the cyclic voltammetry curve of cryolitic melt with 2 wt% Sc₂O₃ and 0.1 wt% ZrO₂ at a molybdenum electrode. It indicates that the electro-reduction of Zr⁴⁺ proceeds a two-step process during electrolysis according to literature [17]. In the cathodic scan, two cathodic current peaks A and B are observed.

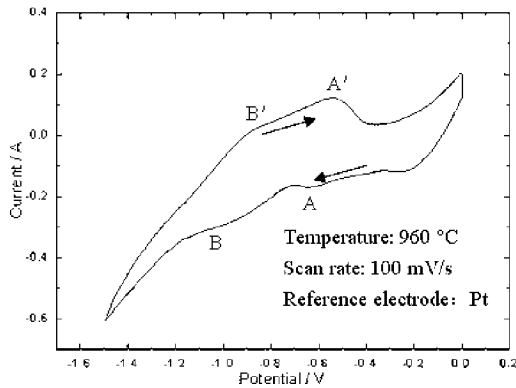


Figure 7. Cyclic voltammetry curve of Sc₂O₃ (2 wt%) and ZrO₂ (0.1 wt%) dissolved in Na₃AlF₆-4 wt%MgF₂-2 wt%CaF₂

Zr⁴⁺ may begin to get two electrons when the scanning potential arrives at -0.7 V (peak A), and the cathodic peak A could be related to the reduction of Zr⁴⁺/Zr²⁺:



And Zr may come out later at -1.05 V. Cathodic peak B could be related to the reduction of Zr²⁺/Zr:



In the reverse scan process, two corresponding oxidation peaks of Zr appeared at A' and B. However, the cathodic peak corresponding to the reduction of Sc is hard to be found in the testing curve above. In the Sc-Zr phase diagram [18], it is showed that scandium and zirconium can be soluble each other arbitrarily. This could decrease the deposition potential of Sc, which would result in a move of peak of Sc³⁺ to near the position of Zr²⁺ peak.

Conclusions

1. Al-Sc-Zr alloy can be electrochemically prepared in sodium cryolite electrolyte at 960 °C with the addition of Sc₂O₃ and ZrO₂; in which Zr content in Al alloys can increase with increased ZrO₂ concentration in electrolyte and prolonged electrolysis time.
2. SEM and EDS analysis show that Al₃(Sc,Zr) particles form in Al alloy prepared by electrolysis.
3. Voltammetry study shows that Zr⁴⁺ proceeds a two-step process in electrolysis, while no single peak appears for Sc deposition.

Acknowledgement

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