

PREPARING ALUMINIUM-SCANDIUM INTER-ALLOYS DURING REDUCTION PROCESS IN KF- AlF_3 - Sc_2O_3 MELTS

Qiaochu Liu, Jilai Xue, Jun Zhu, Chunyang Guan
School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing
Xueyuan Road 30, 100083 Beijing, China

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Abstract

Al-Sc Alloys have attracted much attention in recent years due to their great potential in many advanced applications. In this work, Al-Sc alloys were prepared on liquid Al cathode in KF- AlF_3 - Sc_2O_3 (CR=1.22) melts during reduction process. Scanning electron microscope (SEM) and Inductively coupled plasma atomic emission spectroscopy (ICP-AES) showed that the primary Al_3Sc were highly faceted and Sc contents were 0.44 and 0.73 wt.% in the alloys produced at 750 °C with current density of 0.5 and 1.0 A/cm², respectively. At 1.0 A/cm², Sc content increased to 0.95 wt.% at 800 °C and 1.27 wt.% at 850 °C. But higher mass loss from the melts was found with increased operating temperatures. Cyclic Voltammetry and Linear Sweep Voltammetry studies demonstrate that the reduction of Sc^{3+} occurs at liquid Al cathode and Al_3Sc formation is electrochemically irreversible. In addition, the effect of ultrasound on the Sc distribution was also investigated.

Introduction

In recent years, Al-Sc Alloys have attracted much attention due to their great potential in many advanced applications. Sc is one of the most effective additives to the Al alloys, and a small addition of Sc (0.2 wt.%) lead to excellent performance in strength, weldability, resistance to re-crystallization, and corrosion resistance [1,2]. Up to now, however, Al-Sc alloys main applications are in aerospace, airplane and rapid trains because of the extremely high price of Sc metal, which is due to the difficulties in the reduction process and the small quantities of material produced. Therefore, the development of a new and inexpensive production process for Sc metal or an Al-Sc alloy is needed. The method of preparation Al-Sc alloy by electrolysis in molten salts has been reported to be successful in NaF- AlF_3 or CaCl_2 melts [3-5].

Another important advance in molten salts technology is the application of so called low temperature electrolyte in traditional industries, for instance, aluminum smelting [6, 7], as it can offer many benefits such as higher current efficiency, lower energy consumption, reduced emissions, and so on. Compared with other low temperature electrolyte system, KF- AlF_3 system seems to be a promising candidate owing to its wider range of low temperature (<1023K) liquid compositions and higher oxide (Alumina) solubility. The studies on KF- AlF_3 -based electrolyte system were focused mainly on its physical or chemical properties and corrosion effects on inert anode.

So far, to our best knowledge, little information is available on the aluminum based alloy made by direct electrolysis in potassium cryolite system. This paper will present our recent study on a new

process to prepare Al-based alloy using low temperature molten salt electrolysis.

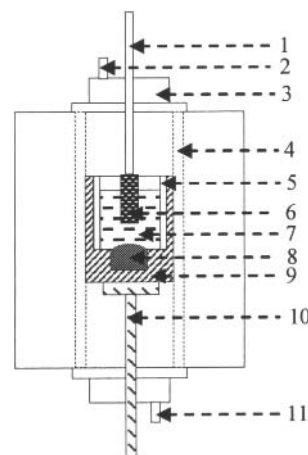
Experiment

Chemicals and Molten Salts

Potassium cryolite (CR=1.22) melts were prepared by a pre-molten method. AlF_3 (analytical grade) and KF (analytical grade) were mixed using a mortar and pestle in stoichiometric amounts. The mixture was then placed in a graphite crucible and heated to 973 K for 4 hours. Following this procedure, metal ion impurities were further removed by pre-electrolysis for 0.5 h at -1.0 V. All operations were performed under an argon atmosphere.

Set-up for Electrolysis

Figure 1 is the experimental set-up used in this investigation, in which a 16-gramme molten aluminum was used as liquid cathode in a bath of K_3AlF_6 (CR=1.22) with 2 wt pct scandium oxide. Anode was made of graphite and its surface area was immersed into melt around 4.2 cm². Approximately, 100 g pre-melted K_3AlF_6 (CR=1.22) was packed into a graphite crucible, and this was placed in a furnace with an isothermal heating zone. A flow of 150 cm³ min⁻¹ of dried argon was used to protect the reaction system. During an experiment, the system was allowed to heat up at 2 K min⁻¹ to 1023 K, and then the anode was lowered into the molten salt. The electrolysis process was carried out at a current density of 0.5 A/cm² and the cell voltage was recorded against the time elapsed.



1-Stainless steel rod, 2-Exhaust gas out, 3-Cooling coil, 4-Furnace tube, 5-Corundum tube, 6-Graphite anode, 7-Electrolyte, 8-Aluminum pad, 9-Graphite crucible, 10-Graphite rod, 11-Gas-inlet

Figure 1. Schematic drawing of the electrolysis set-up.

Apparatus for Electrochemical Study

All electrochemical studies were performed using an Im6eX electrochemical workstation (Zahner Co., Ltd., Kansas City, MO) with the THALES 3.08 software package.

Tungsten wire was used as a reference electrode. All potentials were referred to the tungsten couple. The working electrodes were molten aluminum ($d = 28\text{mm}$, 99.999 pct purity) pad. As a counter electrode, a spectral pure graphite rod ($d = 6\text{ mm}$) was used. The aluminum working electrode was polished thoroughly using SiC paper and then cleaned in ethanol using ultrasonic cleaning. The active electrode surface was determined after each experiment by measuring the immersion depth of the electrode in the molten salts.

Characterization of Al-Sc Alloys

Figure 2 shows the samples of Al-Sc alloys prepared by electrolysis. After electrolysis, all samples were washed with ethanol (99.8 pct purity) in an ultrasonic bath to remove salts and stored inside the vacuum drying dish for analysis. Each sample was dissolved and diluted in aqua regia ($\text{HNO}_3:\text{HCl}:\text{H}_2\text{O} = 1:3:8$, v/v), and the Al and Sc contents of the samples were determined by an Inductively Coupled Plasma (ICP-AES) Atomic Emission Spectrometer (OPTIMA 7000DV; PerkinElmer Co. Ltd., MA) analysis. The alloy samples were mechanical treated, grinded, polished, then etched. The etching reagents used mixture of $\text{HNO}_3:\text{HF}:\text{HCl}:\text{H}_2\text{O}=5:2:3:190$ (Dix-Keller regia). Scanning electron microscopy (SEM) (JSM-6480A; JEOL Co., Ltd.) was used to observe the morphology of the alloys.

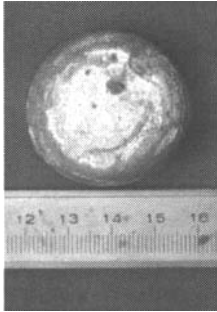


Figure 2. Photograph showing the aluminum metal sample obtained by electrolysis.

Ultrasonic Electrolysis

In order to investigate the effect of ultrasonic treatment on the process of Al-Sc alloys electrolysis, the electrolysis system was modified. It was almost the same as a normal laboratory electrolysis cell, but the only difference was that the crucible was connected with an acoustic radiator by thread. The ultrasonic system used for this research consisted of a 1.5 kW acoustic generator, an air-cooled 20 kHz transducer made of piezoelectric lead zirconate titanate crystals (PZT), and an acoustic radiator made of Stainless steel (304).

In the experiments, the melts were heated up to $750\text{ }^\circ\text{C}$ and ultrasonic process loaded after the power was supplied. The ultrasonic system was on for 2 seconds and off for another 2 seconds, alternatively, during the electrolysis. The specimens thus treated were cooled in the furnace till room temperature. The microstructure of the specimens was analyzed.

Results and Discussion

The Relation Between Electrolytic Time and Cell Voltage

Figure 3 shows the relation between cell voltage and time, when electrolysis was carried out at current density of 0.50 A/cm^2 and temperature of $750\text{ }^\circ\text{C}$. The cell voltage was nearly constant during the entire electrolysis process. The slightly waved voltage in the middle stage of the deposition is caused by the content of Sc_2O_3 solved in the melts, which density is lower than at the beginning, inducing a decrease of conductivity and leading to the wave of cell voltage. The rest of Sc_2O_3 added in the electrolyte dissolved gradually in 15-20 minutes, the conductivity was improved and the cell voltage stabilized in the range 3.6-4.0V.

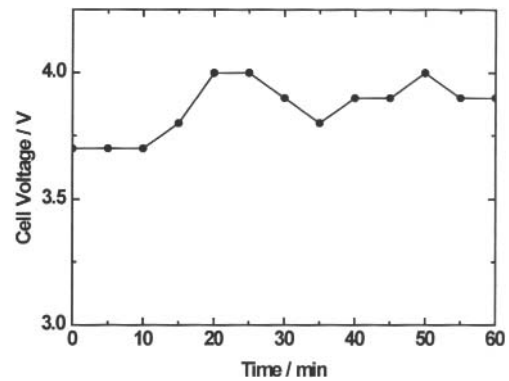


Figure 3. Relation between cell voltage and electrolysis time.

Effect of Anodic Current Density on Sc Content

In order to investigate the effect of anodic current density on alloy Sc content, the amount of Scandium was measured by ICP-AES when the electrolysis process was finished at different current density. The effect of anodic current density on Sc content is listed in Table I. It is obvious that the amount of Sc in alloys increased with the raise of anodic current density, which meant the Sc^{3+} ions reduction increased with anodic current density increasing. The Scandium content in the alloy showed a maximum value in the current density around 1.0 A/cm^2 . This was because the Scandium deposition rate on the Aluminum cathode and the alloy forming process were controlled by the current density.

Table I. Effect of Anodic Current Density on Sc Content

Sample Number	Current Density (A/cm^2)	Sc Content (wt.%)
CA-1	0.5	0.44
CA-2	1.0	0.73
CA-3	2.0	0.59

However, under excessive high current density, metallic Sc will deposit at a higher speed. But Sc atoms diffuses slowly in Al liquid, so a part of the deposited Sc atoms on the surface of the cathode cannot diffuse into the internal part of liquid aluminum, and these Sc atoms will dissolve into the molten salt, and result in the decrease of Sc content with the anodic current density of 2.0 A/cm^2 . Another reason may be that with high current density, anode effects occur, a large quantity of anode gas increases the

melt stirring, more Sc metal is taken to the melt, resulting in scandium content decreasing with high current density.

Effect of Electrolytic Temperature on Sc Content

In order to investigate the effect of electrolytic temperature on Scandium content of alloys, the experiment was carried out at temperatures of 750, 800, and 850 °C, respectively, at current density of 1.0 A/cm².

Table II. Effect of Electrolytic Temperature on Sc Content

Sample Number	Temperature (°C)	Current Density (A/cm ²)	Sc Content (wt.%)
DW-1	750	1	0.73
DW-2	800	1	0.95
DW-3	850	1	1.27

Table II shows the effect of electrolytic temperature on Sc content of alloys. The amount of Scandium increases with the raise of electrolytic temperature, which meant the Sc³⁺ ions reduction increased with the increase in electrolytic temperature. Besides, it is obvious that the effect of electrolytic temperature on Sc contents of alloys was more than anodic current density from the results above. In the temperature range of 700-850 °C, the Sc mass content is 0.73 wt.% to 1.27 wt.%. From the Al-Sc binary alloy phase diagram, the liquid-solid phase temperature rapidly increases with composition after the eutectic point (0.56 wt.%). Liquid-solid temperature is 750 °C, when Sc is 0.85 wt.%; and liquid-solid temperature is 850 °C, when Sc is 2.24 wt.%. The results follow the binary alloy phase diagram. But when the temperature is too high, the metal solubility and bath convection is greater, causing a higher metal loss. In addition, the vaporization loss of the electrolyte increases. All of these can cause a decrease in current efficiency.

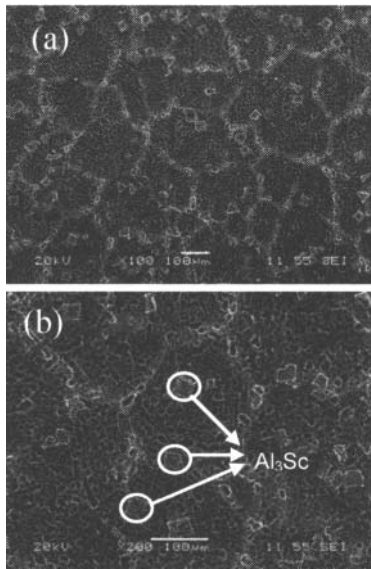


Figure 4. SEM micrographs of Al-Sc alloys (0.73 wt.% Sc)

Electrolysis and Characterization of the Deposits

Figure 4 shows SEM micrographs of Al-Sc alloy sample with Sc mass content of 0.73 wt.%. Figure 4 (a) shows that there are many square shapes of second phase, with most of them highly faceted cubic shape.

In Figure 5, the cubic structure is primary Al₃Sc particles, the rest is α-Al base. Figure 5 (b) and table III confirm that the cubic structure is Al₃Sc particles, the particles only has Al, Sc elements, these two elements are 58.08 wt.% and 35.83 wt.%. After calculation, the conversion of atomic ratio of Al, Sc elements is 3:1. Similar phenomenon is found in other literatures [8, 9]. The reason for primary Al₃Sc particles having highly faceted cubic morphology can be that Al₃Sc particles have L1₂ space lattice structure. When alloy solidification occurs, dendrite arm has a priority growth trend in the <1, 0, 0> and <1, 1, 0> directions.

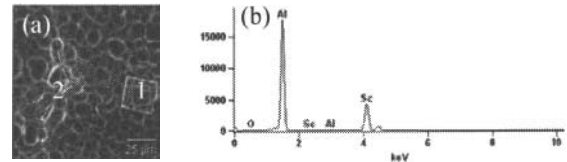


Figure 5. SEM micrograph (a) and EDS image (b) of Al₃Sc primary particle

Table III. The Chemical Constitutions of the Corresponding Areas in Figure 5(a) Obtained by EDS Analysis

Location	O	Al	Si	Ca	Sc	Fe
Area 1	6.09	58.08			35.83	
Area 2	8.46	87.91	1.51	0.77	0.77	0.58

Figure 6 is SEM micrograph and element mapping analysis of a single grain crystal. Al element is mainly distributed in α-Al base, while Sc element is mainly distributed in primary Al₃Sc particles. And from micrograph it can be seen in Figure 6 that part of Al₃Sc particles are nucleation cores of grain, other particles are in the grain boundary. We inferred that the particles in grain boundary were pushed to outside of grain during solidification process, caused by uneven distribution of the solute.

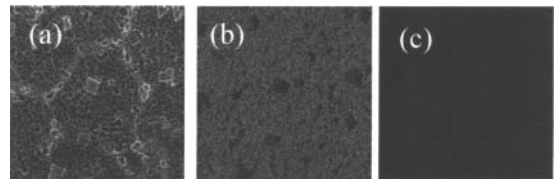
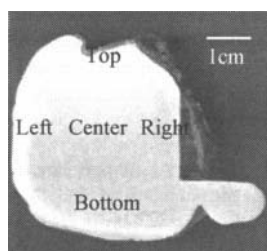


Figure 6. SEM micrographs and element mapping analysis of single grain crystal: (a) magnification×300; (b) Al element; (c) Sc element.

Figure 7 shows ICP analysis of Sc content in different parts of the alloy sample, with the average Sc mass content being 0.73 wt.% in Al-Sc alloys. Sc content of different parts is close, so preparation of Al-Sc alloys electrolysis in melts can not produce macro-segregation alloy.



Location	ICP analysis %
Top	0.75
Bottom	0.74
Left	0.76
Right	0.74
Center	0.77

Figure 7. Sc content at various locations in the metal sample.

Cyclic Voltammetry

Fig. 9 shows typical Cyclic Voltammogram (CV) of the $\text{AlF}_3\text{-KF Sc}_2\text{O}_3$ solution at an Al electrode. A sharp increase in cathodic current from approximately -0.9 V (vs. W wire) is observed. The cathodic signal can be ascribed to the deposition of Sc, since no other ions exist in the molten salt. In the reverse scan, an anodic peak corresponding to the dissolution of Sc is hard to observe. The result is different from literature [10], where, Scandium ions on molybdenum wire electrode reduction potential is $-1.5 \sim -1.6\text{ V}$. For Al electrode, the Sc ions reduction potential is observed from about -0.9 V . Since this potential value is more positive than that of Sc metal deposition, the cathodic current is thought to be caused by the formation of Al-Sc alloys.

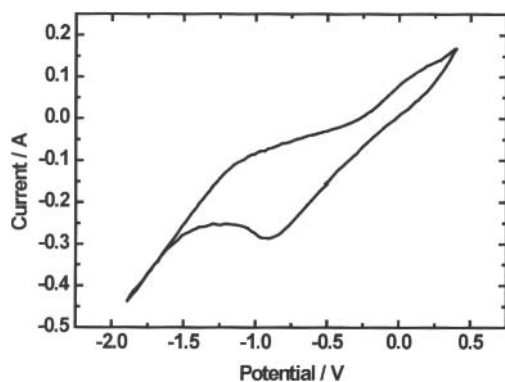


Figure 9. Typical current vs voltage of the KF-AlF_3 melts containing Sc_2O_3 in liquid Al electrodes at 1023 K ($750\text{ }^\circ\text{C}$). Scan rate: 200 mV/s . Tungsten wire as reference electrodes.

From Figure 9, there was no obvious oxidation peak of Sc deposition on Al electrode, but reduction peak was clear. According to electrochemical laws, it could be found that Sc^{3+} reduces on the cathode of liquid aluminum irreversible. The reason maybe the formation of Al-Sc alloy caused electrode surface irreversible.

Linear Sweep Voltammetry

Figure 10 presented Linear Sweep Voltammetry (LSV) measured on Al electrode in KF-AlF_3 containing $2.0\text{ wt pct Sc}_2\text{O}_3$ at 1023 K ($750\text{ }^\circ\text{C}$) with scan rate 20 mV/s . Scanning potential from -0.3 V to -2.0 V (vs. W wire), there only was a single peak, and it was respond to result of Cyclic Voltammetry. At about -0.9 V potential, the electrochemical formation of Al-Sc alloys on Al electrodes begun. Compared to the Cyclic Voltammetry, the Linear Sweep

Voltammetry showed more details of the electrochemical reaction because the scanning speed was very low.

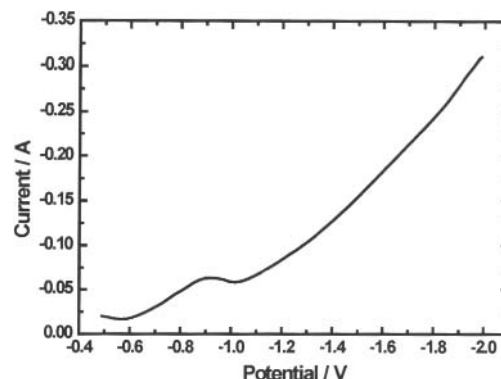
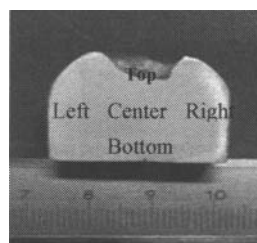


Figure 10. Typical LSV of the KF-AlF_3 melts containing of Sc_2O_3 on liquid Al electrodes at 1023 K ($750\text{ }^\circ\text{C}$). Scan rate: 20 mV/s . Tungsten wire as reference electrodes.

Electrolysis with ultrasound

Figure 11 shows 1 hour electrolysis alloy sample profiles produces with the electrolyte temperature $750\text{ }^\circ\text{C}$, the current density 1 A/cm^2 , and the ultrasonic frequency 20 kHz . Chemical analysis drilled five different parts: top, bottom, center, left, right, then Sc content has been determined by ICP-AES. The table in right reveals that Sc content of sample with ultrasonic treatment during electrolysis reaches about $1.10\text{ wt.}\%$. However, Sc content is just $0.73\text{ wt.}\%$ in normal non-ultrasonic electrolysis experiment. Comparing the results with non-ultrasonic electrolysis, ultrasonic treatment during electrolysis effectively improved the content of Sc in alloys.

Few literatures on ultrasound aided electrolysis process was reported, so the mechanism of ultrasound increasing the alloy element contained is unclear. We inferred that ultrasound intensifies mass transfer of Scandium atoms in liquid Al cathode, and reduces the reduction of Scandium atoms dissolved back to melts. Generally, ultrasonic treatment during electrolysis undoubtedly increases the alloy element.



Section	ICP analysis %
Top	1.18
Bottom	1.10
Left	1.14
Right	1.15
Center	1.14

Figure 11. The different sections of Al-Sc alloy by electrolysis with ultrasound.

Conclusions

1. Al-Sc alloys are prepared on liquid Al cathode in $\text{KF-AlF}_3\text{-Sc}_2\text{O}_3$ ($\text{CR}=1.22$) melts at $750\text{ }^\circ\text{C}$, in which Sc contents are 0.44 and $0.73\text{ wt.}\%$ with current density of 0.5 and 1.0 A/cm^2 , respectively.

2. SEM and EDS analysis indicate that the main phases in the alloy samples are α -Al base and Al_3Sc particles. The primary Al_3Sc has highly faceted cubic morphology. Most of Al_3Sc particles are distributed on grain boundaries, and a few of them become nuclear core of the grains.

3. Electrochemical investigation shows that the reduction of Sc^{3+} takes place at potential value (-0.9 V) on a liquid Al electrode, and Al_3Sc formation is electrochemically irreversible.

4. With ultrasonic treatment during electrolysis process, Sc content in alloys increases up to 1.10 wt.%, compared to 0.73 wt.% under the same operating conditions without ultrasound. This shows a potential application for ultrasound-assisted electrolysis making Al-Sc alloys.

Acknowledgement

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