# Preparation of aluminum-magnesium alloy from magnesium oxide in RECl₃-KCl -MgCl₂ electrolyte by molten salts electrolysis method

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## Abstract

Aluminum-magnesium alloys were prepared from magnesium oxide by molten salt electrolysis method. 10w%RECl₃-63.5w%KCl-23.5w%MgCl₂-3w%MgO was taken as electrolyte. The results showed that RE could be attained in aluminum-magnesium alloy, and it was proved that the RE was reduced directly by aluminum. Magnesium in the alloy was produced by electrolysis on cathode. The content of RE in the alloy was about 0.8wt %-1.2wt%, and the content of Mg in the alloy was 1wt%~6wt% with electrolytic times. The highest current efficiency was 81.3% with 0.8A/cm2 current density. The process of electrolysis was controlled together by electrochemical polarization and concentration polarization.

## Introduction

As the lightest of all the commonly used metals, magnesium is very attractive for applications in transportation. It also has other advantageous features, such as good ductility, better damping characteristics than aluminum, and magnesium alloys are readily casting, particularly by high-pressure die casting and exhibit good mechanical properties, they have been promoted as a desirable component for use in many fields, such as aerospace industry, electrical industry, car manufacture and so on. Aluminum-magnesium alloys, in particular, are used wider than others. Aluminum-magnesium alloys containing about 5% magnesium are used in welded structures, such as in ship building and construction field [1~3].

However, commercial applications of magnesium alloys are limited because of poor creep resistance and poor tensile properties at elevated temperatures above 120°C. Rare earths are important alloying elements to magnesium alloys, which can improve casting characteristics, high temperature properties and corrosion resistance without affecting the electrical conductivity of the base alloys. Rare earths have been used in magnesium alloys for many years, whereas the alloys of Mg–Al–RE system have been developed recently. Some investigations have been done on the precipitation, morphology, structure, thermal stability and strengthening mechanisms of inter-metallic phases when RE were added to Mg–Al alloys[4~6].

There are many impossible ways for resolving the contradiction between increasing need of magnesium alloys and high cost of its production, but the best way is to prepare the Al-Mg alloys from MgO by molten salt electrolysis method[7-10]. For many years, many researchers have studied and attained some exciting results on this field[11-19]. Therefore, the method of preparation Al-Mg-RE alloy by molten salt electrolysis is promising way to solve the problems of large productive scale and low productive cost.

This paper focus on preparation of Al-Mg alloys by molten salt electrolysis from magnesium oxide, reduction mechanic was investigated by electrolytic experiments and no-electrolytic experiments.

## Experiment

### Experimental apparatus and agents

The purity of rare earth oxide was above 99w%, and its elemental content was shown as table 1:

Table 1 Content of elements in mixed rare earth (w/%)

| Elements | La | Ce | Pr | Nd | Others |
|---|---|---|---|---|---|
| Content | 24.6 | 50.8 | 5.2 | 17.4 | 2 |

RECl₃6H₂O was prepared by RE₂(CO₃)₃ dissolving in chlorhydric acid, and it was dehydrated at 350°C after amount of ammonium chloride added, RECl₃ was prepared by this way. MgCl₂ was prepared from MgCl₂·6H₂O at 350-400°C in resistance furnace by vacuum dehydration way.

Super low-frequency oscilloscope(SBD6B), Resistance furnace(2kw);Temperature controller(DWK-702); KCl(analytic agent); MgO(analytic agent);MgF₂(analytic agent);LiF(analytic agent)
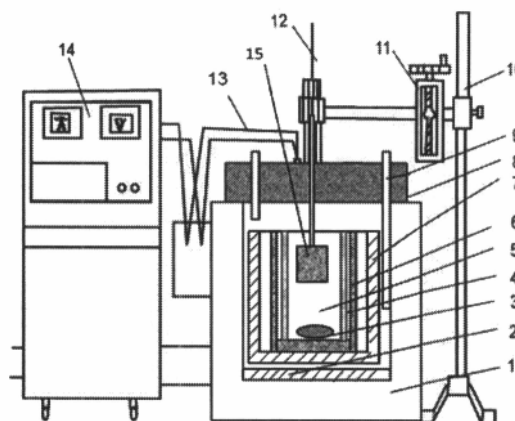
### Experimental installing



Figure 1. Drawing of experimental installation:

1-Electrical resistance furnace; 2-Refractory brick; 3-SiC board; 4-Corundum bushing; 5-Electrolyte; 6-Graphile crucible; 7-Tungsten cathode; 8-Iron outer; 9-Furance cover; 10-Supporter; 11-Elevator controller; 12-Tungsten wine;13-Temperature wine; 14-DWK-702 temperature controller.15-Anode.

## Process of experiments

All the agents ware dried at 400°C for two hours. According to calculated ratio, the agents were weighed accurately on balance. About 280g 10w% $RECl_3$-23w%$MgCl_2$-67w%KCl electrolyte was fed into graphite cell and melted in resistance furnace. About 30g-40g aluminum was added into corundum tube. After the aluminum was melted into liquid, electrolysis could begin with liquid aluminum as cathode, magnesium oxide as raw material, and graphite as anode. During electrolysis process, amount of magnesium oxide was fed into electrolyte to guarantee stable electrolysis.

### Results and discussion

#### Reduction of rare earth

10w%$RECl_3$-23w%$MgCl$-67w%KCl as electrolyte, and liquid aluminum as reduction, experiment was carried through at 720°C ~780°C temperature, no current was loaded on electrodes from one to three hours. Content of rare earth in alloy was shown in table 2.

Table 2 Contents of Mg and RE in molten Al (w/%)

|    | 1 | 2 | 3 | 4 |
|----|------|------|------|------|
| Mg | 0.02 | 0.01 | 0.08 | 0.04 |
| RE | 1.10 | 1.02 | 0.87 | 0.90 |

The results showed that rare earth was reduced directly by aluminum, and its content in alloy was stable from 0.87-1.1w%. This could be matched with demand of practical application, because some researchers had reported that over 1w% of rare earth in alloys had no effect on material properties. Content of magnesium in alloy was very lower than 0.08w%. Therefore, preparation of Al-Mg-RE alloys could be carried out by molten salt electrolysis method, rare earth with stable content in alloy attained by reduction of aluminum, and magnesium was reduced in cell from magnesium oxide. The content of magnesium in alloys was controlled by electrolytic time.

#### Polarizing voltage and current density

Using 10w% RECl3-23w%MgCl-67w%KCl as the electrolyte, electrolysis was performed at 750°C temperatures with different current. The back electromotor force (BEMF) was measured by oscilloscope, and polarizing voltage was calculated by following equation.
$E_B=E_0+\varepsilon$      —1
$E_B$--BEMF
$E_0$--Reversible voltage
$\varepsilon$-- Polarizing voltage
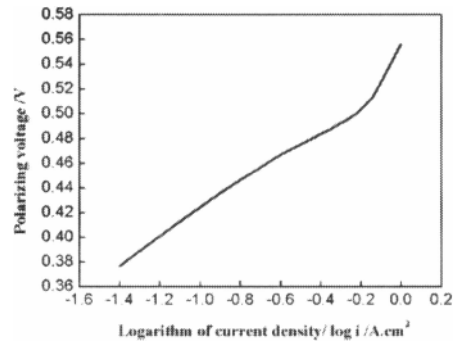The relationship between polarizing voltage and current density is shown in Figure 2.



Fig.2 Relationship between polarizing voltage and current density

Process of electrolysis was controlled by electrochemical and concentration polarization together. Under low current density from 0.04-0.6A/ cm², content of magnesium ion on cathode surface could match with need of electrolysis. Electrolysis could not be affected by depletion of magnesium ion. But, under high current density over 0.6A/ cm², content of magnesium ion on cathode surface could not match with need of electrolysis. Velocity of magnesium ion diffused in molten salts was not matched with velocity of magnesium ion precipitated on cathode, thus gradient of concentration was created from cathode surface to inner of molten salts. This was main reason of concentration polarization under high current density.

Polarizing voltage and logarithm of current density were fitted with a linear regression line by the method of least squares, and the line equation was:
$$\varepsilon_1=0.521+0.099\log I \qquad --2$$
$$\varepsilon_2=0.555+0.277\log I \qquad --3$$
"$\varepsilon_1$" was polarizing voltage with current density under 0.6 A/ cm², "$\varepsilon_2$" was polarizing voltage with current density over 0.6 A/ cm², and "I" was current density.

#### Relationship between current and back EMF, cell voltage

Electrolytic experiment was carried out in different current, and the relationship between current and back electromotor force, cell voltage was shown as Figure 3:
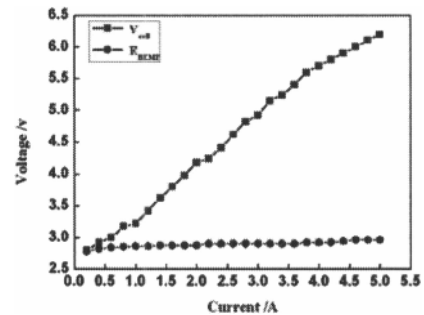


Fig.3 Relationship between current and back EMF, cell voltage

Cell voltage increased with current, but the back electromotor force almost is stable. The value of cell voltage increased from 2.8V to 6.2V, and that of BEMF was from 2.78V to 2.96V. The differences are 3.4V, 0.18V, respectively. The main reason was because the reversible voltage $E_0$ could not change at the same condition, but BEMF could increase with polarizing voltage. Polarizing voltage was influenced with two sides, electrochemical reaction and diffusion. At low current density, the process of electrode was controlled by electrochemical reaction. On the contrary, the process of electrode was controlled by diffusion at high current density. The point was correspondence with Figure 2.

Content of magnesium in alloys

Graphite as anode, aluminum as cathode, the experiment was at 760°C with 0.8A/cm$^2$ current density, the electrolytic time was 30mins,45mins,60mins,75mins and 90mins. The relationship between content of magnesium in alloys and electrolytic time was shown as figure 4
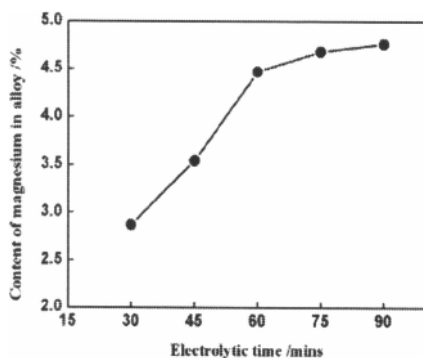


Fig. 4 Relationship between electrolytic time and content of magnesium in alloy

Content of magnesium in alloys increased with electrolytic time, but the increased value was almost at 0.2w%. In another word, content of magnesium in alloys was almost stable after a long electrolytic time. To calculate the current efficiency, the most one was 81.3% when the electrolytic time was about one hour. The phenomena was observed after one hour electrolytic time, bubbles on anode was difficulty in releasing electrolyte surface, and the electrolyte was like viscous. Further study was kept on how to control content of magnesium in alloys with electrolytic time in long operation.

**Conclusions**

It is feasible to prepare Al-Mg alloys with 0.8-1.1w% rare earth by molten salt electrolysis from magnesium oxide. The rare earth was reduced directly by aluminum, and magnesium in alloys was attained by decomposed magnesium oxide. The content of rare earth was stable 0.8-1.1w%, and that of magnesium was controlled by electrolytic time.

10%RECl$_3$-23%MgCl-67%KCl as electrolyte, the most current efficiency was in 81.3%. The content of magnesium in alloys increased with electrolytic time, the most was 4.6w%. Process of electrolysis was controlled by electrochemical and concentration polarization together.

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