ELECTROREFINING OF MAGNESIUM IN CHLORIDE MELTS

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ABSTRACT

Electrorefining of Mg in molten chloride has been investigated. A mixture of MgCl₂, CaCl₂ and NaCl was used as molten salt bath. The electrochemical behaviors of Fe, Cr and Ni were examined by voltammetry, because they are typical impurities in Mg and seriously debase Mg metal. The results being referred, the electrorefining of Mg was carried out. Magnesium moved electrochemically from anode to cathode with a good current efficiency. Iron was enriched in the residual Mg metal at anode, whereas the Fe content in the Mg electrodeposit at cathode was less than that in the Mg metal supplied originally. The dependence on some electrolytic conditions being discussed, it was found that the anode potential should be essential for elimination of Fe from Mg. It was concluded that the electrorefining process was promising for purification of Mg metal.

INTRODUCTION

Magnesium metal and alloys are used in a wide range of applications because of their superior characteristics. However, their corrosion resistance is usually poor so that the usage is still limited. Some impurity elements, such as Fe, Cr and Ni, are reported to lower the Mg metal of corrosion resistance (1). The levels of these elements must be kept very low for some purposes. The elimination of the impurities will be necessary.

Electrorefining in molten salt has been applied to Al purification, and Al metal of very high purity is produced. The similar process should be applied to the purification of Mg metal. Electrorefining can be also used to the recycling of Mg metal, which is a key technology for expanding the usage of Mg metal in the future. The study of the electrochemical behavior of impurity elements is very important in order to control their contamination level in Mg metal made from these processes. Many researchers have investigated the electrochemical behavior of metallic elements in some molten salt systems (2). However, sufficient studies of the electrochemical behavior of metallic elements has not been reported in the molten salt system used for Mg electrolysis. Moreover, the electrorefining of Mg itself has been rarely studied.

In this study, the electrochemical behavior of FeCl₂, NiCl₂ and CrCl₃ were examined by voltammetry in a MgCl₂-CaCl₂-NaCl melt. The anodic dissolution of these metals was also examined in the melt. Based on these results, electrorefining was carried
out under potentiostatic conditions. The behavior of impurities was examined, and the
dependence on some electrolytic conditions, for example the potential of electrode and
temperature, was discussed.

EXPERIMENTAL

The experimental cell is schematically shown in Figure 1. A mixture of MgCl$_2$-
CaCl$_2$-NaCl in the weight ratio of 2:3:5 (m.p. $\sim$760K) was used as bath. The mixture
was vacuum-dried at 373K for one day, and then fused in a quartz glass crucible for
dehydration. The dehydration was carried out by bubbling dry Cl$_2$ gas in the fused
mixtures. The dehydrated mixture was degassed by vacuum, and solidified once. The
solidified mixture was transferred to an Ar-filled glove box without exposure to the air.
Electrolysis was carried out in a carbon crucible, which was placed in an airtight
container in the Ar-filled glove box. The container was heated by an electric furnace
externally, and the cell was purged with Ar gas of high purity during the experiment.
Ferrous chloride, NiCl$_2$ or CrCl$_3$ was added to the melts to examine their electrochemical
behavior. All the compounds were commercial anhydrous reagents of reagent-grade.
The temperature of the melt was measured by an alumel-chromel thermocouple protected
by an alumina tube.

Voltammetric measurement was carried out to investigate the cathodic behavior
of FeCl$_3$, NiCl$_2$ and CrCl$_3$ in the melt. A Mo wire covered with a high purity alumina
sheath (active area: $\phi$1mmH5mm) was used as a working electrode (3). A carbon rod
($\phi$4mm) or a Mg rod ($\phi$10mm) was used as a counter electrode. The reference electrode
was a Ag/AgCl(5mol%)-(MgCl$_2$-CaCl$_2$-NaCl) couple separated from the bath with mullite
membrane. The electrodes were burnished with emery paper, rinsed with acetone and
dried at 373K.

An Fe rod ($\phi$3.2mm), a Cr plate (1.5mmH3mm) and a Ni rod ($\phi$4mm) were
immersed for 20mm into the melt. After electro-etching, these metals were polarized
anodically with slow potential scan rate to measure their anodic behaviors. A Mo plate
was used as a counter electrode, and the Ag/AgCl reference electrode was applied.

Electrorefining was carried out based on the results of the voltammetry. The
cathode was a Mo plate (20mmH5mm H0.5mm) that was surrounded by a MgO tube
(inner diameter: 12mm). The anode was Mg metal of commercial grade in the MgO
tube. The Mo plate was electro-etched at +0.2V (vs. the immersion potential) for a few
minutes before electrolysis in the bath, and controlled to a planed potential. The
electrodeposit at the cathode and the residual Mg metal at the anode were cooled in the
container, and rinsed with distilled water outside the glove box. They were analyzed by
an electron probed microanalyzer (EPMA) and an inductively coupled plasma (ICP)
spectrometer. In this study, the Fe content was considered to be a representative impurity
element.
RESULTS AND DISCUSSION

Behavior of Some Metals

Two cathodic current peaks corresponding to the reduction of a Cr ion were observed at 1.5V and 1.0V (vs. Mg/Mg\(^{2+}\)) in voltammograms in the melt containing CrCl\(_3\) at 823K. The difference in standard potential between Mg/Mg\(^{2+}\) and Cr/Cr\(^{2+}\) was reported as 1.155V in LiCl-KCl eutectic melt at 723K (2) so that the cathodic peak at 1.0V (vs. Mg/Mg\(^{2+}\)) was likely due to Cr\(^{2+}\)6Cr\(^0\). The reaction corresponding to the cathodic peak at 1.5V was deduced as Cr\(^{2+}\)6Cr\(^{3+}\) from the reaction sequence and the ionic state of Cr in the bath. A cathodic current peak appeared at 1.2V (vs. Mg/Mg\(^{2+}\)) following FeCl\(_3\) addition to the bath. Based on data in the literature (2), the cathodic reaction at 1.2V (vs. Mg/Mg\(^{2+}\)) was likely Fe\(^{2+}\)6Fe\(^0\). Two cathodic current peaks appeared at 1.4V and 0.9V (vs. Mg/Mg\(^{2+}\)) by NiCl\(_2\) addition in the bath. The cathodic peak at 1.4V was considered to correspond to Ni\(^{2+}\) + 2e = Ni\(^0\) based on reported data (2). However, the cathodic peak at 0.9V could not be identified. Iron and Cr are not alloyed with Mg (4), while Ni is easily alloyed even by electrochemical processes (5). The interaction between Ni and Mg might influence the cathodic behavior of Ni.

An anodic current began flowing at 0.9V (vs. Mg/Mg\(^{2+}\)), and the anodic current increased with the increase in anodic potential of the Cr electrode. An anodic current began flowing at 1.1V (vs. Mg/Mg\(^{2+}\)) at the Fe electrode, while an anodic current began flowing at 1.4V (vs. Mg/Mg\(^{2+}\)) at the Ni electrode. Obvious traces of dissolution was seen on all the electrodes after the anodic polarization.

Table 1 shows the summary of electrochemical behaviors of the elements in the melt at 823K. The dissolution behaviors of Cr, Fe and Ni agree with the redox behavior of their chlorides. However, the behaviors of the anodic dissolution of Cr, Fe and Ni in the MgCl\(_2\)-CaCl\(_2\)-NaCl melt did not always agree with those in MgCl\(_2\)-NaCl-KCl melt (6). The bath composition could affect the electrochemical behaviors of these elements.

|       | redox of metal chloride | dissolution of metal |
|-------|-------------------------|----------------------|
|       | cathodic peak  | reaction  | potential |
| Mg    | (0.0V)         | Mg\(^{2+}\) + 2e = Mg | -         |
| Fe    | 1.2V           | Fe\(^{2+}\) + 2e = Fe | 1.1V      |
| Cr    | 1.0V           | Cr\(^{2+}\) + 2e = Cr | 0.9V      |
|       | 1.5V           | Cr\(^{3+}\) + e = Cr\(^{2+}\) | -         |
| Ni    | 0.9V (not identified) | Ni\(^{2+}\) + 2e = Ni | 1.4V      |
|       | 1.4V           | Ni\(^{2+}\) + 2e = Ni | 1.4V      |
It should be emphasized that the anodic dissolution potentials of Fe, Cr and Ni were more than 0.9V as positive as that of Mg. Therefore, these elements should remain in the anode in the electrorefining of Mg metal. The control of the anode potential should be important to eliminate these elements from Mg.

**Deposition and Dissolution of Mg**

Figure 2 shows Mg deposit at the cathode and residual Mg metal at the anode after the electrorefining process. The amount of Mg metal at the anode decreased with electrolysis, and Mg metal was electrodeposited at the cathode.

Mg metal was obtained by cathodic potentiostatic electrolysis in the bath at 823K. However, the deposit was always powdery, and an electrodeposited with good morphology could not be obtained under any electrolysis condition. It was concluded that the electrodeposition of Mg metal in solid form was difficult. Powder or small particles of Mg metal were electrodeposited at 943K when the cathodic overpotential was small, while a lump of Mg metal was obtained when sufficient cathodic overpotential was applied.

**Table 2.** Fe content in Mg deposit and current efficiencies.

|                | Fe content (ppm) | current efficiency (%) |
|----------------|------------------|------------------------|
| original       | 22               | -                      |
| anode residue  | 58               | 80                     |
| cathode deposit| 15               | 74                     |

The changes in electrolytic current and cathode potential during anodic potentiostatic electrolysis at $E_{\text{anode}} = 1.0V$ (vs. Mg/Mg$^2^+$) are shown in Figure 3. Because the anode potential was fixed and the amount of Mg in the anode decreased with electrolysis, the current decreased with electrolysis. The decrease in current seemed to lead to the positive shift of the cathode potential. The behavior under other conditions were almost similar. These results indicate the electrolysis runs steadily. Table 2 shows the typical result of Fe content in the Mg metal and the current efficiencies. The cathodic and anodic current efficiency were 80% and 74%, respectively. However, the cathodic current efficiency became worse under the condition where powdery Mg was deposited.

There are two way of estimating current density in this case: dividing the current by the actual surface area of the electrode and by the inner-cross section of the MgO tube.
In either case, the current densities are roughly estimated at 1.0A/cm² at the beginning of the electrolysis. Though this value seems large enough even for industrial electrolysis, the so-called “three-layer” electrolysis should be preferable to perform a more effective electrorefining.

Electrorefining of Mg

The Fe contents in the Mg deposit at the cathode and the residual Mg metal at the anode were 15ppm and 58ppm, respectively, in the case shown in Table 2. Because the Fe content in the Mg metal supplied as the anode originally was 22ppm, Fe was enriched in the anode and purified Mg metal was deposited at the cathode. The behavior of Fe agrees with that observed in the voltammetric measurements.

Table 3. Dependence of Fe content in Mg deposit upon electrolysis condition.

| ΔEanode / V | Fe content / ppm |
|------------|-----------------|
| original   | 398             |
| 0.3        | 29              |
| 0.5        | 83              |
| 1.0        | 8               |
| 1.0        | 34              |
| 1.5        | 290             |

Figure 4 shows the Fe content in the electrodeposit, where the Mg metal used for the anode originally contained about 400ppm of Fe. Because the content of Fe in the electrodeposit is lower than that of the original metal in the most cases, Mg seems to be purified to a certain extent consequently. However, the elimination factor of Fe from Mg is not as good as in the electrorefining of other metals, such as Al. The dependence on the anode potential, which should be an essential parameter for Fe elimination, is not clear, either. It is suggested that other factors affect the electrorefining of Mg.

Table 3 shows the Fe content in electrodeposit in experimental order without change of the melt. Just after the melt was prepared and the electrolysis was started, the purity of the electrodeposit was always poor. A small amount of impurity could not be removed from the salt even by dry Cl₂ gas treatment. After repeating electrolysis, the Fe content decreased to less than 10ppm under suitable conditions. However, performance deteriorated when the anode potential was set more positive than 1.0V (vs.Mg/Mg²⁺). Once the electrolysis was performed at too positive anode potential, the Fe content became higher for some electrolysis under any condition. The poor dependency of the Fe content on anode potential shown in Figure 4 could be caused by these factors. In other
words, Fe can be eliminated from Mg effectively by electrorefining only under the suitable conditions.

Figure 5 shows the Fe content in electrodeposit in the melt which had not be dehydrated by dry Cl₂ gas treatment. The electrodeposit in the melt usually consisted of powder or small granular particles, and the electrodeposition of Mg metal was more difficult than in the dehydrated melt. The Fe content was higher in general than that in the dehydrated melt. The preparation of the molten salt bath should be important for the effective electrorefining of Mg.

CONCLUSIONS

The electrochemical behavior of Cr, Fe and Ni in the MgCl₂-CaCl₂-NaCl melt was investigated. Electrorefining of Mg was carried out, and the dependence on some electrolysis conditions was discussed. The results are summarized as follows:

1. Iron, Cr and Ni are electrochemically more positive than Mg in the melt, and their anodic dissolution potentials are more than 0.9V as more positive than that of Mg. Therefore, these elements should remain in the anode in the electrorefining of Mg metal. The control of the anode potential should be essential in eliminating these elements from Mg.
2. The electrorefining of Mg should be performed above the melting point of Mg metal because only the powdery deposits are obtained below its melting point.
3. Magnesium metal can be purified by the electrorefining process. The anodic overpotential is essential for the electrorefining of Mg; smaller overpotential is desirable for the purification though sufficient overpotential is necessary for good electrodeposition.
4. Proper preparation of the molten salt bath is important for the effective electrorefining.
5. To perform the effective electrorefining of Mg, the so-called “three-layer” electrolysis should be preferred. The choice of magnesium alloy as anode is important for this type of Mg electrolysis.

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Figure 1. Schematic illustration of electrolytic apparatus
a: Mg cathode (Mo plate)
b: anode for metal dissolution (Fe, Cr, Ni)
c: Mg anode
d: Mo wire electrode
e: reference electrode (Ag/AgCl)
f: thermocouple
g: molten salt (MgCl$_2$-CaCl$_2$-NaCl)
h: Ar-filled glove box   i: electric furnace
Figure 2. Photographs of electrodeposit and residual Mg anode under some conditions.

Figure 3. Change in current and cathode potential during anodic potentiostatic electrolysis. (ΔE_{anode}=1.0V, 943K)
Figure 4. Relationship between anode potential and Fe content in Mg deposit.

Figure 5. Relationship between anode potential and Fe content in Mg deposit in melt without dehydration.