Electrorefining of Magnesium in Molten Salt and Its Application for Recycling

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Electrorefining of Mg has been investigated in a molten salt system, and the electrolysis conditions for the effective purification have been discussed. A purified mixture of MgCl_2 – NaCl – CaCl_2 was used as an electrolytic bath. Magnesium metal was dissolved anodically by potentiostatic electrolysis, and purified Mg was electrodeposited at the cathode. A certain degree of cathodic overpotential was required for the effective electrodeposition of Mg metal, while large anodic overpotential directly caused the deterioration in the purity of Mg electrodeposit; it was necessary for the anodic overpotential to be less than 1.0 V for good purification. In addition to the electrode potentials, some factors affected the electrorefining of Mg metal. Under the suitable electrolysis condition, the Fe content in the Mg electrodeposit was less than 10 ppm. A couple of subjects on recycling Mg metal and its alloys have been also studied: purification of Mg alloy by an electrorefining technique and distinction of Mg alloys. It was shown that pure Mg metal was electrodeposited at the cathode by the electrorefining of Mg alloy. X-ray fluorescence analysis was applied to distinction of Mg alloys, and the measuring conditions were discussed. It was concluded that the electrorefining process and X-ray fluorescence analysis were usable for the recycling of Mg metal and alloys.

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1. Introduction

Magnesium metal and its alloys are used widely 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 corrosion resistance of Mg metal¹⁾ so that the levels of these elements must be kept very low.

The electrochemical behaviors of Fe, Cr and Ni were reported as a fundamental study for electrorefining of Mg in a MgCl_2 – NaCl – CaCl_2 .^{2,3)} The results indicate that the elements should be eliminated from Mg metal by an electrorefining process because they are much nobler than Mg electrochemically. Therefore, the electrorefining in molten salt is a candidate for the purification of Mg metal, but conditions required for good electrolysis were not known.

Recycling of Mg metal should be a key technology for expanding the usage of Mg metal in the future. The recycling from the end user must be troublesome; some metals other than Mg must be included. Since Mg is strongly debased in corrosion resistivity by some impurity elements, purification of Mg scrap must be required in its recycling. The application of vacuum distillation to the recycling was reported,⁴⁾ but a more efficient process will be desired. An electrorefining technique can be applied to the recycling though it had never been tried. The elimination of the impurities, such as Fe, is also essential in this case, and the behaviors of alloying elements must be examined besides.

Magnesium scraps from the end user are also expected to consist of many kinds of Mg alloys. They should be segregated severally for the effective purification, and easy and quick identification of Mg alloys is necessary for the segregation. X-ray fluorescence analysis should be one of the likely determination methods of Mg alloys since it is a nondestructive test without a special treatment of the sample.

In this study, electrorefining of Mg has been carried out by

potentiostatic electrolysis. The behaviors and the effects of impurities on some electrolysis conditions were discussed, and the behaviors of alloying elements in Mg alloy were investigated. Application of X-ray fluorescence analysis for distinction of Mg alloys has been also examined in this study, and the measuring conditions were discussed.

2. Experimental

The experimental cell for electrorefining is schematically shown in Fig. 1. A mixture of MgCl_2 – NaCl – CaCl_2 in the weight ratio of 2 : 3 : 5 (m.p. ~ 760 K) was used as an electrolytic bath. The mixture was vacuum-dried at 373 K for one day, and then fused in a quartz crucible for dehydration. The dehydration was carried out by bubbling dry Cl_2 gas in

Fig. 1 Schematic illustration of electrolytic apparatus. (a) Mg cathode (Mo plate), (b) Mg anode, (c) Mo wire electrode, (d) reference electrode (Ag/AgCl), (e) thermocouple, (f) molten salt (MgCl_2 – CaCl_2 – NaCl), (g) Ar-filled glove box and (h) electric furnace.

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the fused mixtures. The dehydrated mixture was degassed under vacuum, and solidified. 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 highly pure Ar during the experiment. The temperature of the melt was measured by using an alumel-chromel thermocouple protected by an alumina tube.

The cathode was a Mo plate, and the anode was Mg metal of commercial grade with a Mo lead wire. Magnesium metals at both cathode and anode were expected to float on the molten salt in a MgO or Al₂O₃ tube surrounding the electrodes. The reference electrode was a Ag/AgCl(5 mol%)-MgCl₂-CaCl₂-NaCl couple separated with mulite membrane from the bath. The electrode potentials in this paper are represented versus the potential of Mg metal deposition in the molten salt. Potentiostatic electrolysis was performed at 823 K or 943 K. The electrode deposit 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 in Mg metal was analyzed as a representative impurity element.

The same apparatus and experimental method were applied for the electrorefining of Mg alloy. One of common Mg alloy, AZ31, was put in the anode, and the anode potential was fixed at 0.8 V at 933 K. The electrode deposit at the cathode and the residual Mg alloy at the anode were analyzed by X-ray fluorescence analysis and ICP spectrometry.

An X-ray fluorescence analyzer (Horiba, MESA-500W) was used for the distinction of Mg alloys. Plates of Mg alloys, such as AZ31B and AZ91D, were analyzed with the standard-less procedure of the analyzer under several measurement conditions. The dependence of the conditions on the measured value was investigated.

3. Results and Discussion

3.1 Electrorefining of Mg

3.1.1 Deposition and dissolution of Mg

Figure 2 shows the electrode deposits at the cathode and the residual metal at the anode after the electrolysis. The amount of Mg metal at the anode decreased with electrolysis, and the electrode deposit at the cathode was identified as Mg.

Magnesium metal was obtained by cathodic potentiostatic electrolysis at 823 K. However, the deposit was always powdery, and an electrode deposit with good morphology could not be obtained under any electrolysis condition at 823 K. It was concluded that the electrodeposition of Mg metal in solid form was difficult. Powder or small particles of Mg metal were electrodeposited at 943 K when the cathode overpotential was less than 0.5 V, while a lump of Mg metal was obtained when sufficient cathode overpotential was applied.

The changes in electrolytic current and cathode potential during anodic potentiostatic electrolysis at $E_{\text{anode}} = 1.0$ V are shown in Fig. 3. The current decreased during electrolysis because the anode potential was fixed and the amount of Mg in the anode decreased. The positive shift of the cathode potential may be as the result of decreasing current. Table 1 shows the typical Fe contents in the Mg metals and the current efficiencies. The cathodic and anodic current efficiencies were 80% and 74%, respectively. However, the cathodic current efficiency became worse under the condition where powdery Mg was deposited.

There are two ways 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 or Al₂O₃ tube. In either case, the current densities are roughly estimated at 1.0 A/cm² at the beginning of the electrolysis.

3.1.2 Behavior of impurity elements

The Fe contents in the Mg deposit at the cathode and the residual Mg metal at the anode were 15 ppm and 58 ppm, respectively, in a case shown in Table 1. The initial content of Fe in the anode was 22 ppm so that Fe was enriched in the anode and purified Mg metal was deposited at the cathode.

Fig. 2 Electrodeposits and residual Mg anode under some conditions. (a) electrodeposit at 823 K, (b) electrodeposit at $E_{\text{cathode}} = -0.5$ V at 943 K, (c) electrodeposit at $E_{\text{cathode}} = -1.0$ V at 943 K and (d) anode residue at 943 K.

Fig. 3 Changes in current and cathode potential during anodic potentiostatic electrolysis of Mg metal at $E_{\text{anode}} = 1.0 \text{ V}$ at 943 K.

Table 1 Fe contents in Mg metal and current efficiencies.

	Fe content (ppm)	Current efficiency (%)
Original Mg	22	—
Anode residue	58	80
Cathode deposit	15	74

Fig. 4 Relationship between anode potential and Fe content in Mg deposit.

The result by voltammetric measurement that Fe was much nobler than Mg in the melt³⁾ gives a reasonable explanation for the behavior of Fe in the potentiostatic electrolysis.

Figure 4 shows the Fe content in the electrodeposit, where the Mg metal at the anode originally contained about 400 ppm of Fe. Magnesium seems to be purified to a certain extent because the content of Fe in the electrodeposit is lower than that of the original metal in the most cases. From the results by the voltammetric study,³⁾ the dependence of the Fe content in the electrodeposit on the anode potential was expected as the broken line in Fig. 4 though the value of the broken line is not strict. The experimental results did not agree with the expectation, and the elimination factor of Fe from Mg is not as good as in the electrorefining of other metals, such as Al. The conditions other than anode potential

Table 2 Dependence of Fe content in Mg deposit upon electrolysis condition.

$E_{\text{anode}}/\text{V}$	Fe content (ppm)
Original Mg	398
0.3	29
0.5	83
1.0	8
1.0	34
1.5	290

sequence of electrolysis ↓

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

are not represented in Fig. 4. These conditions should affect the Fe content in the electrodeposit.

Table 2 shows the Fe content in the electrodeposit in the experimental order without changing 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 the Cl_2 gas treatment. After repeating electrolysis, the Fe content decreased to less than 10 ppm under suitable conditions. However, the purity of electrodeposit directly got worse when the anode potential was set more positively than 1.0 V. Once the electrolysis was performed at too positive anode potential, the Fe content became higher for some batches of electrolysis under any condition.

Figure 5 shows the Fe content in the electrodeposit in the melt which had not been dehydrated by the Cl_2 treatment. The electrodeposit in the melt usually consisted of powder or small granular particles. The Fe content in the bath was higher in general than that in the dehydrated bath. The preparation of the molten salt bath should be important for the effective electrorefining of Mg.

It was shown that the Fe content in the electrodeposit depended upon some factors. The most important factor is the anode potential; it must be less than 1.0 V through all the batches of electrolysis. Under the suitable conditions, Fe can be eliminated from Mg effectively.

3.1.3 Behavior of alloying elements

It was shown above that the Fe in Mg metal could be eliminated by the electrorefining where the anode potential

was less than 1.0 V. The behaviors of Al and Zn in AZ31 were investigated under this condition.

Metallic deposit was obtained at the cathode by the anodic potentiostatic electrolysis, and it was identified as Mg by X-ray fluorescence analysis. Magnesium metal remained at the anode in most cases, and its amount decreased by electrolysis. Figure 6 shows typical changes in electrolytic current and cathode potential during anodic potentiostatic electrolysis at $E_{\text{anode}} = 0.8$ V, where the inner cross sections of surrounding tubes of the anode and cathode were about 2.3 cm^2 . The curves show that stable electrolysis was performed in this case; the current gradually decreased due to the consumption of Mg in the anode during electrolysis, and the cathode potential shifted positively consequently. The current efficiencies assumed the electrode reaction of

Fig. 6 Changes in current and cathode potential during anodic potentiostatic electrolysis of AZ31 at $E_{\text{anode}} = 0.8$ V at 933 K.

$\text{Mg} = \text{Mg}^{2+} + 2\text{e}^-$ were excellent as shown in Table 3; the cathodic current efficiency was 87–97%, while the anodic current efficiency was 98%. However, the electrolysis was occasionally broken because of the stop of electrolytic current. In these cases, a metallic residue was not found at the anode. A lump of Mg metal was found in the middle of the salt after experiment. It seemed the anode residue falling down from the anode. Figure 7 shows the photographs of the electrodeposit, the anode residue and the lump in the salt.

Table 3 also shows the Al and Zn contents in the Mg metals. Zinc was not detected in the electrodeposits, while its content in the anode residue was larger than that in the original alloy. From the Zn contents and the change in weight of the Mg alloy at anode, it was shown that the whole amount of Zn remained in the anode under this electrolysis condition. The lump of metal in the salt contained a few percent of Zn. It was reported that the reaction potential of $\text{Zn} = \text{Zn}^{2+} + 2\text{e}^-$

Table 3 Al and Zn contents in Mg and current efficiencies in electrorefining of AZ31.

	Al (mass%)	Zn (mass%)	Current efficiency (%)
Original Mg	3.5 (3.9)	0.73 (0.7)	—
Batch 1 cathode dept.	0.0006 (ND)	0.0026 (ND)	97
Batch 1 anode residue	(no residue)		
Batch 2 cathode dept.	0.25 (ND)	0.004 (ND)	87
Batch 2 anode residue	4.2 (4.2)	1.5 (1.5)	98
Metal lump in salt	(ND)	(2.3)	—

Measured by ICP spectrometry and X-ray fluorescence analysis in ().

Fig. 7 Electrodeposit, anode residue and metal lump in salt after electrorefining of AZ31 at $E_{\text{anode}} = 0.8$ V at 933 K. (a) electrodeposit, (b) anode residue and (c) metal lump in salt.

is about 1.1 V nobler than that of $\text{Mg} = \text{Mg}^{2+} + 2\text{e}^-$ in a $\text{MgCl}_2\text{--KCl}$ eutectic melt at 748 K.⁵⁾ Since the anodic overpotential in this study, 0.8 V, was less than the potential deviation, Zn should remain in the anode.

The content of Al in the electrodeposit was lower than that in the original alloy. However, the value varied with an experimental batch, and a small amount of Al was contained in the electrodeposit. The reaction potential of $\text{Al} = \text{Al}^{3+} + 3\text{e}^-$ was reported about 0.76 V nobler than that of $\text{Mg} = \text{Mg}^{2+} + 2\text{e}^-$ in a $\text{MgCl}_2\text{--KCl}$ eutectic melt at 748 K.⁵⁾ Aluminum in the anode should have dissolved partly and moved to the electrodeposit because the anode overpotential in this study was close to the potential deviation. Actually, the mass-balance of Al in the anode indicated that a part of Al in it was lost with electrolysis. However, the amount of Al contained in the electrodeposit could not be compensated for the amount of Al dissolved from the anode. Large amount of Al dissolving from the anode should have remained in the melt, and also a part of Al in the salt might escape as vapor of Al_2Cl_6 .

Magnesium metal was electrodeposited with good current efficiency by the electrorefining. Zinc remained in the anode under the electrolysis condition in this study, while some of Al was dissolved. A smaller anode overpotential should be applied to eliminate Al from the electrodeposit. On the other hand, Al and Zn in the anode can be transferred to the electrodeposit at higher anode potential, though higher anode potential should cause the contamination of the impurity elements in the electrodeposit.

It was found that the Mg alloy fell down from the anode with the progress of electrolysis. It should be because the density of alloy increased with the selective dissolution of Mg by electrolysis. The so-called “three-layer” electrolysis, where a Mg alloy anode of higher density was set in the bottom of the electrolytic bath and electrodeposited Mg floating on the bath was used as cathode, should be preferred for the continuous treatment of Mg alloy by electrorefining.

3.2 Distinction of Mg alloy

Figure 8 shows the measured values of the Al and Zn contents in the Mg alloys finished with Al_2O_3 powder by the

Fig. 8 Al and Zn contents in AZ31 and AZ91 by X-ray fluorescence analysis (finished surface).

Table 4 Composition of Mg alloys.⁶⁾

	AZ31B	AZ91D
Al	2.5–3.5	8.3–9.7
Zn	0.6–1.4	0.35–1.0
Mn	0.20–1.0	0.15 min.
Fe	0.005 max.	0.005 max.
Si	0.10 max.	0.10 max.
Cu	0.05 max.	0.03 max.
Ni	0.005 max.	0.002 max.
Ca	0.04 max.	
Mg	bal.	bal.
		(mass%)

X-ray fluorescence analyzer. Some pieces of the scrap were used and several points of each piece were analyzed. The compositions of the Mg alloys were given as shown in Table 4,⁶⁾ and the Al and Zn contents were measured by ICP spectrometry as 3.5 mass% and 0.73 mass% respectively. The measured values by X-ray fluorescence analysis agreed well with these values, though the measured values varied to some extent. A circle area of about $\Phi 5$ mm was irradiated with X-ray in the analyzer so that the dispersion of the value was due not to segregation in the sample but to measurement error. The dispersion became larger with decrease in measuring time, but the Al and Zn contents in Mg alloy could be measured even in 10 s. The analysis could be accomplished when the sample was inclined at 5°, whereas it was hardly done by the inclination of 10°. AZ31 and AZ91 could be easily distinguished with the measured values of Al and Zn in them as long as the values were obtained.

Figure 9 shows the measured values of the Al and Zn contents in Mg alloys of which surface were covered with oxide scale. The Al and Zn contents in AZ31 with scale were somewhat larger than those in the finished sample, while the Al content in AZ91 with scale was slightly lower than that in the finished sample and the Zn content was slightly larger. Although the composition of the scale should be different from that of the base metal, AZ31 and AZ91 could be easily distinguished by X-ray fluorescence analysis. Moreover, AZ31 and AZ91 could be distinguished by X-ray fluores-

Fig. 9 Al and Zn contents in AZ31 and AZ91 by X-ray fluorescence analysis (surface covered with oxide scale).

cence analysis in a short time even if the alloys with fresh surface and with scale were mixed. All the values were obtained under vacuum in this study. However, the analysis should be also possible in the atmospheric pressure if the parameters for the standard-less measurement are corrected.

The results above indicate that X-ray fluorescence analysis is usable for the distinction of Mg alloys.

4. Conclusion

Electrorefining of Mg was carried out, and the dependence on some electrolysis conditions was discussed. The subject related to recycling of Mg scrap was also investigated: determination of Mg alloys by X-ray fluorescence analysis and application of an electrorefining technique to Mg alloy. The results are summarized as follows;

- (1) The electrorefining of Mg should be performed above the melting point of Mg metal.
- (2) Magnesium metal can be purified by the electrorefining process. The control of the electrode potential is essential; smaller anodic overpotential is desirable for the purification though sufficient cathodic overpotential is necessary for the good electrodeposition.
- (3) Proper preparation of the molten salt bath is important for the effective electrorefining.
- (4) By the electrorefining of Mg alloy, AZ31, Mg metal was electrodeposited at the cathode with good current efficiency. Zinc remained in the anode, while Al in the anode was dissolved partly.
- (5) Magnesium alloys can be distinguished in a short time by X-ray fluorescence analysis even when the alloys with fresh surface and with thick oxide film were mixed.

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