ELECTROREFINING OF MAGNESIUM IN CHLORIDE MELT

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INTRODUCTION

Magnesium metal and alloys have superior characteristics, but their corrosion resistance is usually poor. Some impurity elements, such as Fe, Cr and Ni, are reported to debase Mg metal in corrosion resistance so that the elimination process should be necessary.

In this study, the electrochemical behaviors of Fe, Ni and Cr were examined by voltammetry in a $MgCl_2$-$CaCl_2$-NaCl melt. These results being referred, the electrorefining of Mg was performed in the melt.

EXPERIMENTAL

The experimental cell is schematically shown in Fig. 1. A dehydrated mixture of $MgCl_2$-$CaCl_2$-NaCl in the weight ratio of 2:3:5 was mainly used as electrolyte.

The redox behaviors of $FeCl_2$, $NiCl_2$ and $CrCl_3$ in the melt were investigated by the potential sweep method. The anodic behaviors of Fe, Cr and Ni metal were also examined voltammetrically.

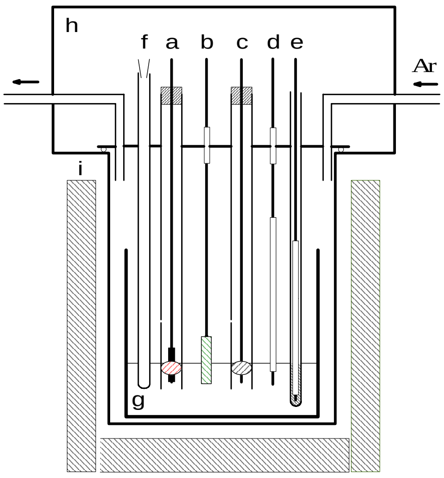
Electrorefining was carried out based on the results of voltammetry. The cathode was a Mo plate (20mm×5mm ×0.5mm) which was surrounded with MgO tube. The anode was Mg metal of commercial grade in MgO tube with a Mo lead. The Fe contents in the electrodeposit at the cathode and the residual Mg metal at the anode were analyzed by electron probed microanalyzer (EPMA) and inductively coupled plasma spectrometer (ICP).

RESULTS

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. 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.

Powdery Mg metal was electrodeposited even at 943K when cathodic overpotential was small, while a lump of Mg metal was obtained when sufficient cathodic overpotential was applied. Table 2 shows the Fe contents in the Mg deposit at cathode. At the begining of the sequence of electrolysis, Mg deposit tend to be contaminated with Fe. When the anodic overpotential was too big, the Fe content in Mg deposit increased directly. The Fe content in Mg was eliminated to 8 ppm from 400ppm under the stable condition in this study.

It was shown that Mg metal could be purified by electrorefining process. The anodic overpotential should be essential for the electrorefining of Mg; Smaller overpotential is desirable for the purification though sufficient overpotential is necessary for the good electrodeposition. The optimum condition of electrorefining must be researched for better purification of Mg metal.



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

Fig.1 Schematic illustration of electrolytic apparatus.

Table 1 Electrochemical behaviors of elements in $MgCl_2$-$CaCl_2$-NaCl melt at 823K.

	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)	!
	1.4V	$Ni^{2+} + 2e = Ni$	1.4V

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

ΔE_{anode} / V	Fe content / ppm
original	398
-0.3	29
-0.5	83
-1.0	8
-1.0	34
-1.5	290

sequence of electrolysis