FORMATION OF
MG-BASED HYDROGEN ABSORPTION THIN FILM
BY ELECTRODEPOSITION AND DIFFUSION PROCESS
IN MOLTEN CHLORIDE

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The hydrogen absorption alloys were formed as a film by using the electrodeposition and diffusion process. Magnesium was electrodeposited from a NaCl-KCl-CaCl2-MgCl2 molten salts on the Ni or Cu substrates to form Mg-Based hydrogen absorption alloy such as MgNi or MgCu, respectively. The experiments were conducted at 803 - 1073K with 0.02 - 0.10Acm^-2 for 1.8 - 18ks. After the formation of the alloy, the specimens were subjected to the X-ray diffraction patterns and EPMA line analysis to identify the compounds and to measure the thickness. In the Mg-Ni system, the hydrogen absorption alloy Mg2Ni was obtained with 20 μm thickness (electrodeposited with 0.10Acm^-2 for 3.6ks at 1023K). In the Mg-Cu system, Mg2Cu was obtained, but other intermetallic compound MgCu2 was obtained at the same time. The hydrogen absorption-desorption properties were examined in 30mass% KOH solution at 298K.

INTRODUCTION

Much attention was paid to the hydrogen absorption alloys, because their batteries are clean and safe in terms of the low environmental impact and have high-capacity. Hydrogen absorption alloy are usually produced by the melting method of pure metals in a furnace. It is reported that mechanical alloying method or sputtering method were used to make hydrogen absorption alloy as a powder or a thin film, respectively (1, 2). As a new process, we have applied electrodeposition and diffusion process in molten salts to prepare hydrogen absorption films. This method has the following advantages: (i) Hydrogen absorption film is formed on substrate in direct process from chloride, fluoride or oxide resources without using the costly reduced metals (e.g. lanthanum, calcium and magnesium) (ii) The mass production of the film is easy. We have previously reported the hydrogen absorption films such as LaNi5, CaNi5 and TiFe by using this method (3, 4).

Mg-based hydrogen absorption alloy, Mg2Ni, is superior to the LaNi5-type alloy or Laves-phase alloys in material cost and theoretical hydrogen absorption capacity (5). Electrodeposition and diffusion process to form Mg-based hydrogen absorption alloys, Mg2Ni and Mg2Cu, is presented in this paper.
EXPERIMENTAL THEORY

The schematic illustration of the formation process of the intermetallic compound on substrate is shown in Fig. 1. When the substrate B is dipped into the molten salts with A ions and the cathodic current is imposed, metal A is electrodeposited on the substrate B (Fig. 1 (1)). If the mutual-diffusion and the chemical reaction occur between the electrodeposits A and the substrate B (Fig. 1 (2)), the intermetallic compound A-B is formed (Fig. 1 (4)). In the alloying process between A and B, the mutual-diffusion of A into B or B into A is the rate-determining step, the metal phase A must remain on the metal compound on the specimen (Fig. 1 (3)). The rate-determining step in the reaction determines whether the A-B alloy layer consists of single- or multi-layer. That is to say, the alloy phase formed on the substrate should be determined by the experimental temperature and time period (i.e. the rate of the diffusion and the reaction time).

EXPERIMENTAL

Magnesium electrolysis was conducted in NaCl-KCl-CaCl₂ (15-55-30 mol%) molten salts with 10mol% MgCl₂ on Ni or Cu substrate (15x15 mm², 0.1mm thickness) as a working electrode. The constituent salts were accurately weighed, mixed, dried for 2 days at 373K and dehydrated by slowly heating up to 1073K and for 1 hour. The substrate was polished, degreased and heated in molten salts for 0.5 hour at 973K. The pre-electrolysis was carried out in order to remove some impurities and moisture from the molten salts. Experimental temperature was from 803 to 1073K under constant current density. Reference electrode was a silver wire dipped in NaCl-KCl-CaCl₂(15-55-30mol%) containing 10mol% AgCl in a mullite tube. Counter electrode was a graphite rod (6mm in diameter). After the electrolysis, the specimen was cooled in a furnace under Ar atmosphere for about 7 hours to room temperature. The specimens were subjected to the XRD and EPMA line analysis to identify the phase in the alloy film and to measure the thickness. The surface was also observed by SEM.

The hydrogen absorption and desorption properties were examined electrochemically in alkaline 30mass%KOH solution at 298K. The reference electrode and the counter electrode were a Hg/HgO electrode and a Pt-coil, respectively. Cycle tests were performed at 298K by repeating an absorption for 10 min with 0.01A cm⁻², a rest for 10min and a desorption with 0.01A cm⁻².

RESULTS AND DISCUSSION

The Mg-Ni System

Figure 2 shows the XRD and the EPMA results for the cross section of the specimen electrodeposited with 0.10A cm⁻² for 3.6ks at 1023K. Intermetallic compound, Mg₅Ni, is observed on the Ni substrate. The thickness of electrodeposited film is about 22 μm and the current efficiency calculated from the thickness is about 18%. Although MgNi₂ was formed between Ni substrate and Mg₅Ni layer at 1073K, MgNi₂ was not detected at 1023K. Since Mg₅Ni melts at 1073K (m.p. of Mg₅Ni: 1033K), only the solid MgNi remained co-existing with the liquid phase.

Mixed phase consisting of Mg and Mg₂Ni was formed in the electrodeposition at
low temperature of 873K with 0.10Acm\(^2\) for 3.6ks. It means that the rates of reaction and diffusion at 873K between the electrodeposited Mg and the Ni substrate was slower than that of 1023K. So, Mg phase remained on the surface and formed the mixed phase.

Only Mg\(_2\)Ni was formed with 29 \(\mu\)m thickness after the electrolysis with low current density, 0.02Acm\(^2\) for 18ks at 873K. This is caused by the slow deposition rate of Mg and long electrolysis time enough to react with Ni substrate.

The Mg-Cu System

Figure 3 shows the XRD and the EPMA results of the specimen electrodeposited with 0.10Acm\(^2\) for 3.6ks at 833K. The thickness of the film was about 40 \(\mu\)m and the current efficiency was 31.5%. The intermetallic film consists of two layers. The layer I is only MgCu\(_2\), the layer II is, on the other hand, Mg\(_2\)Cu with a MgCu\(_2\) dispersion. It is considered that the dispersion MgCu\(_2\) in the layer II was precipitated during the cooling.

Hydrogen Absorption-Desorption Properties

All alloy films absorbed hydrogen without initial activation treatment. The hydrogen ratio (H/M) in the Mg-Ni film is 2.4 and in the Mg-Cu is 1.6, respectively. In both systems, hydrogen desorative property was insufficient. Nearly all of the absorbed hydrogen remained in the film (about 5% of absorbed hydrogen was desorbed in the both systems). These properties in 30mass%KOH at 298K are inferior to the LaNi\(_5\) film examined previously. It is said that the absorption and desorption reaction of Mg-based hydrogen absorption alloy occurs only when the temperature is raised to about 573K (6) and it may be difficult to apply in 30mass%KOH at 298K.

CONCLUSION

The formation of the hydrogen absorption film such as Mg\(_2\)Ni and Mg\(_2\)Cu was attempted by using the electrodeposition and diffusion process in the molten salts. The formed intermetallic compound film was examined by the XRD analysis and the EPMA and SEM observations and the hydrogen absorption-desorption properties were tested by the electrochemical method. The following results were obtained:

(1) Hydrogen absorption film, Mg\(_2\)Ni, was obtained in the Mg-Ni system. The mixed phase consisting of Mg and Mg\(_2\)Ni was also formed on the surface electrodeposited with high current density of 0.10Acm\(^2\) for 18ks at 873K. Only Mg\(_2\)Ni phase was obtained with low current density of 0.02 Acm\(^2\) or at high temperature 1023K.

(2) Both phases of Mg\(_2\)Cu with hydrogen absorption property and MgCu\(_2\) were obtained in the Mg-Cu system. Mg\(_2\)Cu and MgCu\(_2\) formed mixed phase.

(3) Although the phases of Mg\(_2\)Ni and Mg\(_2\)Cu produced by the electrodeposition process absorbed hydrogen in 30mass% KOH, little amount of charged hydrogen was released.

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**Fig. 1** The schematic illustration of the formation of the intermetallic compound.

**Fig. 2** XRD and EPMA results of the specimen electrodeposited with 0.10Acm⁻² for 3.6ks at 1023K.
Fig. 3 XRD and EPMA results of the specimen electrodeposited with 0.10Acm⁻² for 3.6ks at 833K.