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Investigation of AB_5 type hydrogen storage alloy corrosion behavior in alkaline electrolyte solutions

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Abstract

The corrosion resistance of various $MmNi_5$ (Mm: mischmetal) type hydrogen storage alloy powders in alkaline electrolyte solutions was evaluated by measuring the magnetic saturation value of ferromagnetic substances generated by selective corrosion of the alloys. The effects of heat treatment of the alloy, lanthanum content in Mm, and the degree of cobalt substitution on the corrosion resistance properties were investigated. Consequently, the following three points are clarified. (1) The effect of heat treatment on the corrosion resistance is not so significant, provided the effect on the hydrogenation induced particle disintegration rate is not taken into account. (2) The corrosion rate per surface area at 60 °C is accelerated by increasing the lanthanum content in Mm. However, this effect is not so clear at room temperature. (3) Increasing the degree of cobalt substitution causes a decrease in initial oxidation layer thickness. The pattern of corrosion progression at 60 °C shows considerable variation with the cobalt content.

Keywords: Hydrogen storage alloy; Secondary cell; Corrosion resistance; Electrode

1. Introduction

The corrosion resistance of the hydrogen storage alloys in alkaline electrolyte solutions is one of the most important factors influencing their applicability as electrode materials because alloy corrosion causes not only a decrease in negative electrode capacity but also H_2O consumption in the alkaline electrolyte solution. Therefore, it is very important to clarify the alloy corrosion mechanism in order to determine the optimal alloy composition for MH electrode materials. Chemical analysis of the corrosion products is a useful method for obtaining information regarding corrosion mechanisms [1,2]. However, chemical analysis is not well suited to the evaluation of a large number of samples because it is a complicated process, and a simpler and more convenient method is required to speed up evaluation. For this reason, the usefulness of the saturated magnetization of $MmNi_5$ alloy powders as an index of alloy corrosion has been investigated [3], and has proven to be a simple and convenient method for evaluating corrosion. In this study, the effects of alloy composition and heat treatment on corrosion resistance were investigated using this method.

2. Experimental

2.1. Theory

It is well known that the decomposition of $LaNi_5$ due to both hydrogenation and oxidation is accompanied by the formation of free Ni, and the alloy begins to show ferromagnetic properties [4–6]. As an analogy to the oxidation mechanism in air, the following oxidation reaction is expected to take place in alkaline electrolyte solutions.

$$2LaNi_5 + 6H_2O \rightarrow 2La(OH)_3 + 3H_2 + 10Ni$$

Though mischmetals are used in place of lanthanum and some of the nickel is substituted with cobalt, manganese, and aluminum, in practical alloys, the situation is not so dissimilar, because the only elements whose metallic states are stable at the hydrogen electrode potential are nickel and cobalt. Moreover, both of these elements show ferromagnetism at room temperature, in contrast with $MmNi_5$ type alloy, which shows paramagnetic properties provided the cobalt content is within the practically employed level for electrode materials. Therefore, it seems to be reasonable to estimate the progression of corrosion from the variation in magnetic saturation of alkaline treated alloy powders.

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2.2. Sample preparation

Sample alloys were prepared by induction melting under argon gas atmosphere and heat-treated, except for the alloys noted. Then these alloys were mechanically pulverized under inert gas flow condition to powders with a specified particle size distribution. As the variation in surface area of alloy powders significantly affect this measurement, the particle size distribution and surface area were measured for some sample powders to confirm that the variation was not excessive. 1.0 g of each alloy powder was weighed in a covered container, then 20 ml of alkaline electrolyte solution (4 M, 6 M, or 8 M KOH solutions) was added to the container. After bubbles were removed, the containers were sealed and stored in temperature controlled (20, 45, 60 °C) dry ovens. All containers were stirred once a day to avoid aggregation of the alloy powders. After a specified storage period, the electrolyte solution was removed with a syringe and the remaining alloy powder was washed with approximately 30 ml of H_2O, then settled and the skim removed with a syringe. This washing process was repeated three times, and finally the remaining H_2O was removed by vacuum drying at 45 °C.

2.3. Measurements

0.2 g of the sample powder was weighed accurately, placed into a cylindrical sample cup (acrylic resin, 6 mm in diameter, 3 mm in depth), then fixed by adding several drops of instant adhesive reagent. The magnetization curves were measured with a vibrating sample magnetometer (Riken Denshi, BHV-5), and the saturated magnetization of ferromagnetic substances was estimated from the difference in the interpolated parallel lines of the magnetization curves (magnetic field: ±10 kOe, sweep rate: 5 min/loop). A typical magnetization curve of alkaline treated $MmNi_5$ type alloy powder is shown in Fig. 1.

3. Results and discussion

3.1. Effect of alkaline electrolyte concentration

An alloy powder (composition: $MmNi_{3.6}Co_{0.8}$-$Mn_{0.3}Al_{0.3}$) was treated with 4 M, 6 M, and 8 M KOH solutions, respectively, at 60 °C for 8 days. Then the magnetic saturation values were measured. The results are shown in Fig. 2. Although a small amount of saturated magnetization, which was mainly due to air oxidation, was observed even before the treatment, the value was rather lower than that caused by treatment with the alkaline electrolyte solution. In addition, the reproducibility was confirmed to be within the acceptable range by comparing two independent values for samples treated under the same conditions. As a result, it was confirmed that the corrosion rates in 6 M and 8 M KOH solutions were very close, and the corrosion rate was considerably accelerated in 4 M KOH solution.

3.2. Effect of heat treatment

The flatness of the plateau in the pressure–composition (P-C) isotherms of $MmNi_5$ type alloys is known to be significantly improved by heat treatment of the alloys, and this is due mainly to increased homogeneity of the alloy composition [7]. Therefore, the corrosion resistance of hydrogen storage alloys can also be expected to improve following heat treatment. In order to estimate of this effect, two portions of the same $MmNi_{4.0}Co_{0.4}Mn_{0.3}Al_{0.3}$ alloy ingot with and without heat treatment were prepared and pulverized with a hammer mill under nitrogen gas flow

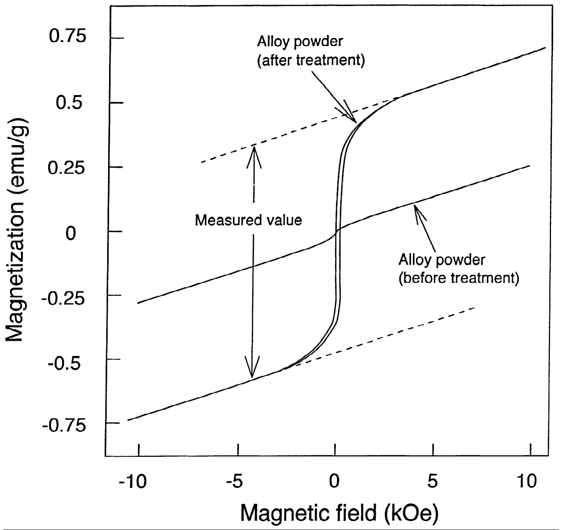

Fig. 1. Magnetization curves of $MmNi_5$ type hydrogen storage alloy powders.

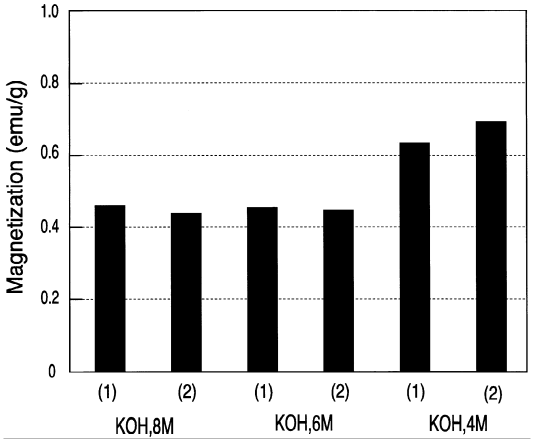

Fig. 2. Magnetic saturation values of $MmNi_{3.6}Co_{0.8}Mn_{0.3}Al_{0.3}$ powders after alkaline electrolyte (4, 6 and 8 M KOH) treatment for 8 days at 60 °C (Samples (1) and (2) were treated under each condition independently).

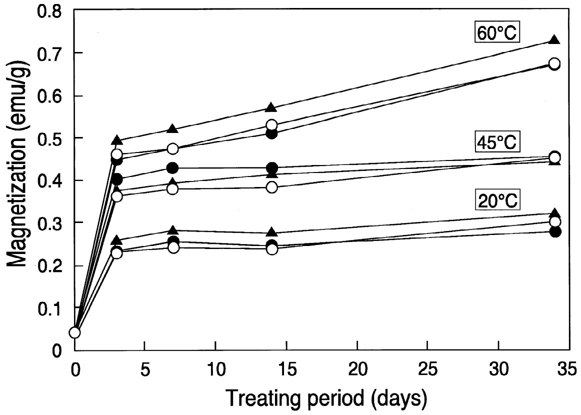

Fig. 3. Effect of alloy heat treatment on corrosion of $MmNi_{4.0}Co_{0.4}Mn_{0.3}Al_{0.3}$ alloy powder in 8 M KOH. (○, as-cast; •, H.T. 2 h; ▲, H.T. 20 h).

condition to obtain the samples used for this comparison. Then the alloy powders were treated with 8 M KOH at various temperatures. The results are shown in Fig. 3, and the P-C isotherms of the corresponding alloys (as cast alloy and 1000 °C, 20 h treated alloy) are shown in Fig. 4. Plateau regions were observed in all curves for the samples treated under 20 °C and 45 °C conditions after the rapid initial oxidation which occurred within a few days following alkaline electrolyte immersion. These findings suggest that surface oxidation occurs quickly following immersion of the particles in the electrolyte solution, and that the surface layer formed effectively prevent further oxidation. However, in the case of 60 °C treatment, a gradual increase in the magnetic saturation value was observed even after the initial oxidation period. This finding suggests that the thickness of the surface oxidation layer required to prevent further corrosion reaction at 60 °C is significantly greater than that at 20 °C or 45 °C. It was found that both the treatment time dependence and the temperature dependence of corrosion were quite similar between alloy powders with and without the heat treatment, even though the flatness of the P-C isotherms differed significantly. Similar results were also observed for alloy powders treated at different temperatures. Therefore, corrosion resistance was found not to be much improved by heat treatment of the alloy. Therefore, the improved cycle life which is often observed in electrodes employing heat treated alloys appears to be due not to an increase in corrosion resistance but to the suppression of particle disintegration during the charge discharge cycle.

3.3. Effect of lanthanum content in mischmetal

The increase of lanthanum content in the mischmetal composition is empirically known to result in a reduction in electrode cycle life. To clarify the effect of lanthanum content on corrosion resistance properties, the variation in magnetic saturation in the treatment of $MmNi_{3.6}Co_{0.8}Mn_{0.3}Al_{0.3}$ alloy powders with lanthanum contents varying from 60 wt. % to 90 wt. % was investigated. The results are shown in Fig. 5. It was found that both the pattern of corrosion progression and the magnitude of saturated magnetization occurring in 20 °C treatment were not so different from each other. However, the corrosion rate in 60 °C treatment after the initial rapid oxidation was found to be accelerated by an increase in lanthanum content. Therefore, the accelerated degradation of the alloy with high lanthanum content appears to be due, to some extent, to faster corrosion of the alloy itself. The disintegration rate may also play a part because the difference in corrosion rate does not appear to be large enough to result in a significant difference in cycle life.

3.4. Effect of cobalt content

It is well known that the cycle life of $MmNi_5$ type alloy electrodes is markedly prolonged by increasing the cobalt content of the alloy composition [8]. In this case, alloy

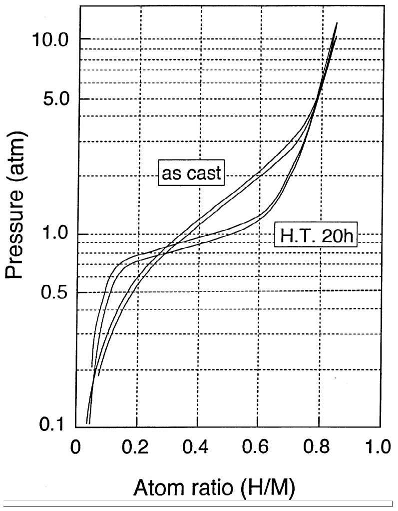

Fig. 4. P-C isotherms of as-cast and heat treated alloys.

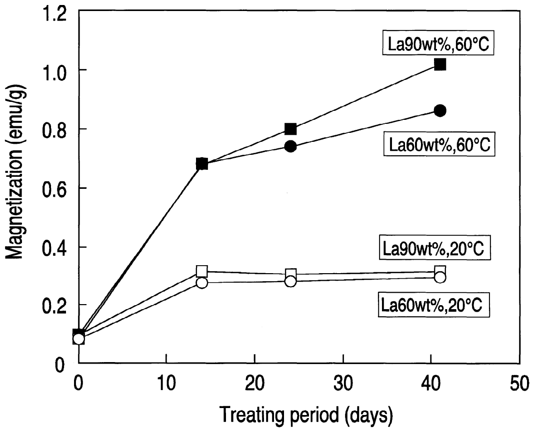

Fig. 5. Effect of La content on (La rich mischmetal) $Ni_{3.6}Co_{0.8}Mn_{0.3}Al_{0.3}$ alloy powder corrosion in 8 M KOH measured by increase of magnetization.

disintegration, which is caused by a change in volume accompanied by hydrogen absorption desorption cycles, is also known to be significantly suppressed by increasing the cobalt content of the alloy. However, the influence of cobalt on corrosion resistance is not yet clear because it is difficult to separate the contributions of the corrosion rate per surface area and the increase in surface area accompanied by the alloy disintegration. To obtain information concerning this point, $MmNi_{4.4-x}Co_xMn_{0.3}Al_{0.3}$ ($x=0.4$, 0.6, 0.8) sample powders were treated in 8 M KOH and compared. The results are shown in Fig. 6. To be exact, the magnetization saturation values are influenced by the cobalt content in the alloy, because the magnetic saturation of cobalt is approximately three times larger than that of nickel. In addition, some of the cobalt may migrate from the alloy surface because of its relatively high solubility in concentrated alkaline aqueous solution. However, the variation of absolute magnetic saturation caused by the same degree of corrosion seems to be not so significant in this experiment, because the variation of cobalt content in these alloy samples is within 1/10 of the nickel content. Therefore, direct comparison of magnetic saturation values of these three alloys is useful, so long as the possible error is taken into account. To clarify the composition of metallic substances caused by the corrosion, further data such as the Curie point of the formed ferromagnetic substances seem to be necessary. In the case of tracing the corrosion progression of an alloy, the variation of cobalt content does not cause any problem, because the composition of metallic substance formed on a certain alloy surface must be constant, at least in early stage corrosion, as occurred in this experimental condition. In Fig. 6, the curve for a coarse $x=0.4$ alloy powder, which shows the same degree of initial increase in magnetization at 60 °C as that of $x=0.6$ or $x=0.8$ standard powders is also shown. Comparing the magnetic saturation values observed for samples with the same particle size, the magnitude of initial oxidation was markedly suppressed with increasing cobalt content under both 20 °C and 60 °C conditions. However, a suppressive effect appeared more clearly at 20 °C, as was made obvious by comparing the magnetization plateaus of $x=0.4$ coarse powder and $x=0.6$ powder, which showed approximately equal initial magnetization in 60 °C treatment. As the magnetic saturation values of all alloy samples showed a plateau within the first few days of the initial oxidation period at 20 °C, it appears that the surface oxidation layer developed quickly in all alloy compositions, and the surface layer formed, effectively prevents further oxidation. However, the thickness of the surface oxidation layer varied with the cobalt content of the alloy. In the case of 60 °C treatment, corrosion continued at a significant rate even after the formation of the initial oxidation layer, and the rate was influenced by the cobalt content. The alloys with $x=0.6$ and 0.8 showed a markedly faster increase after the 14th day compared with the alloy with $x=0.4$, and the magnetic saturation values at 34 days of treatment were not so different from each other. Although the mechanism is not clear, the corrosion progression after the formation of initial surface oxidation layer in high temperature alkaline electrolyte seems to be significantly influenced by the cobalt content of the alloy. As a result, the increase in cobalt content reduced the thickness of the initial oxidation layer. However, the corrosion resistance at a temperature of 60 °C or higher is not so much improved by increasing the cobalt content of the alloy.

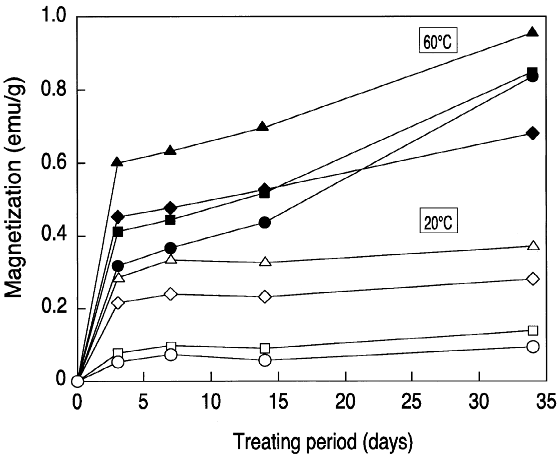

Fig. 6. Effect of Co content on corrosion of $MmNi_{4.4-x}Co_xMn_{0.3}Al_{0.3}$ ($x=0.4$, 0.6 and 0.8) alloy powder in 8 M KOH. △ ▲ $X=0.4$, ○ ● $X=0.6$, □ ■ $X=0.8$ ◇ ◆, $X=0.4$ (coarse powder).

4. Summary

The corrosion rates of various hydrogen storage alloys in concentrated alkaline electrolyte solution were investigated by monitoring the increase in ferromagnetic substances. The main findings of these experiments are summarized below.

1. Heat treatment of $MmNi_5$ type alloy does not significantly affect the corrosion resistance of the alloy itself.
2. An increase in lanthanum content in the mischmetal composition accelerates the corrosion at temperatures of 60 °C or higher. However, the degree of acceleration is not particularly great.
3. An increase in cobalt content of the alloy composition leads to a thinner initial surface oxidation layer.
4. The mechanism of the progression of corrosion at temperatures of 60 °C or higher temperature appears to be influenced by the cobalt content of the alloy.

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