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Surface treatment effect on the low temperature hydriding behavior of Mg_2Ni

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Abstract

The effects on the hydriding behavior, long term storability in air and microstructure of Mg_2Ni alloy resulting from surface treatments using (1) HCl acid (HCl-treatment), (2) F-containing solution after HCl etching (HCl + F-treatment) were determined and compared with those due to (3) F-treatment alone. Both the treatments (1) and (2) could clean up the originally contaminated surface as F-treatment did. HCl leached some pure Mg phase from the eutectic structure of the Mg-rich Mg_2Ni alloy. This resulted in an increase of specific surface area and led Mg_2Ni to partially hydride under very moderate temperature and pressure conditions. HCl-treatment alone could not form a fluorinated surface structure as F-treatment did. Instead of this, some magnesium hydroxide was formed. The fluorinated surface formed by F-treatment provided strong protection from surface contamination by long term air exposure.

Keywords: Ternary hydrides; Cycling behavior; F-treatment; Microstructure; Mg-fluorinated surface; Initial activation; Storability in air

1. Introduction

Using a fluorine-containing aqueous solution (F-treatment), Mg_2Ni alloy, which usually can only be hydrided at elevated temperature, could be easily partially hydrided under extremely moderate conditions such as 30°C and 1.0 MPa H_2 pressure [1,2]. This dramatic improvement is known to be caused by the Mg-fluorinated surface formation and also some new microcracks along the surface and interfaces between the Mg and Mg_2Ni eutectic structure in a slightly Mg-rich Mg_2Ni alloy during the F-treatment. This research is an extension of our previous investigation on the hydriding behavior of F-treated Mg_2Ni alloy and is aimed at improving the hydriding kinetics and capacity by searching for other chemical treatments that can be combined with F-treatment. It has been reported by Wang and co-workers that when etched with HCl, Mg_2Ni can be hydrided easily at room temperature, but the hydrogen absorption capacity degrades rapidly on cycling [3]. In this paper, the effects of HCl-treatment (using dilute hydrochloric acid) and HCl + F-treatment (using the standard F-containing solution after HCl-treatment) on the low temperature hydriding behavior, long term air exposure properties (H_2 absorption properties) and metallurgical microstructure of a Mg-rich Mg_2Ni alloy are summarized and compared with those of the alloy just F-treated.

2. Experimental details

The Mg_2Ni alloy was produced commercially by induction melting. In order to avoid the formation of the non-reacting $MgNi_2$ phase during solidification, this alloy sample is slightly Mg-rich from the stoichiometric composition of Mg_2Ni and is characterized by a lamellar eutectic Mg + Mg_2Ni structure in addition to the primary Mg_2Ni phase [2]. After the ingot was mechanically ground into 106–250 μm powder, the sample was treated in a 0.02 N HCl-solution with a w/v ratio of 4 g alloy to 400 ml solution for 15 min (during which the pH was dramatically changed from

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acid to alkaline), as shown in Fig. 1. Then this was followed by water washing. Part of the HCl-treated sample was given a subsequent F-treatment by using an F-containing solution with a w/v ratio of 10 g alloy to 400 ml solution. F-treatment time was 4 h and was followed by water washing and naturally drying in air. The increase in pH during F-treatment after HCl etching was much faster than that of the F-treatment without HCl etching (see Fig. 1). This might be caused by the increase of specific surface area after HCl etching.

The hydriding and dehydriding reactions were measured on a standard Sieverts volumetric apparatus. A 1 g sample mass was used for testing the hydriding reactions at 30, 45, 60 and 75°C. All the hydriding reactions were performed under an applied H_2 pressure of 1.0 MPa. Dehydriding was accomplished by evacuating the reactor at 200°C. For the initial hydriding, the treated samples were exposed to a vacuum of 1.33 Pa for 40 min at the same temperature as the hydriding test and then charged with 1.0 MPa H_2. Hydrogen storage capacities of the differently treated samples by long term storage were compared by testing the first five hydriding–dehydriding reactions at 45°C after exposing the samples to air for 4 months. Microstructures of both HCl-treated and HCl + F-treated as well as partially hydrided Mg_2Ni samples were examined by a metallurgical microscope (Olympus PMG3). Samples for microstructural analysis were prepared by mounting in a cold-curing resin mixed with fine copper powder and polishing with dry SiC paper and an oil–diamond-impregnated polishing cloth. X-ray diffraction was performed on a Rigaku RINT-1200 diffractometer using Cu Kα radiation.

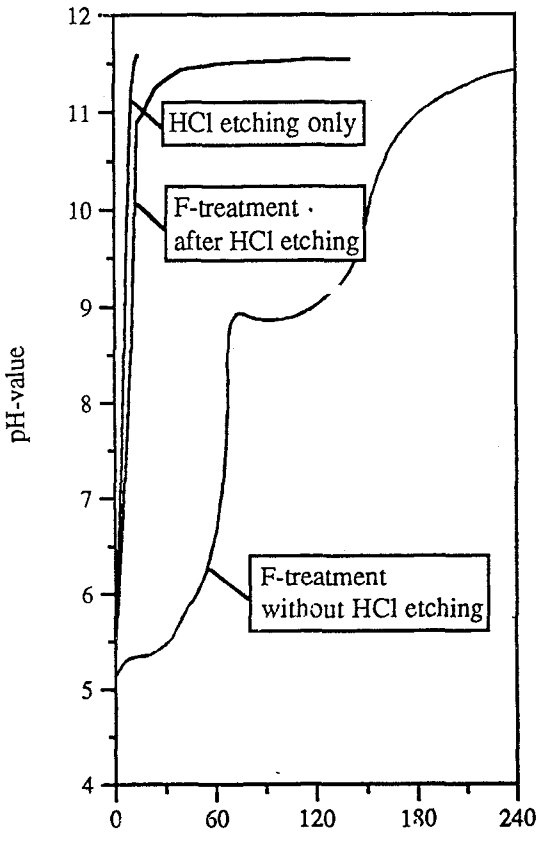

Fig. 1. Effect of HCl-etching on pH variation vs. time for Mg_2Ni during F-treatment.

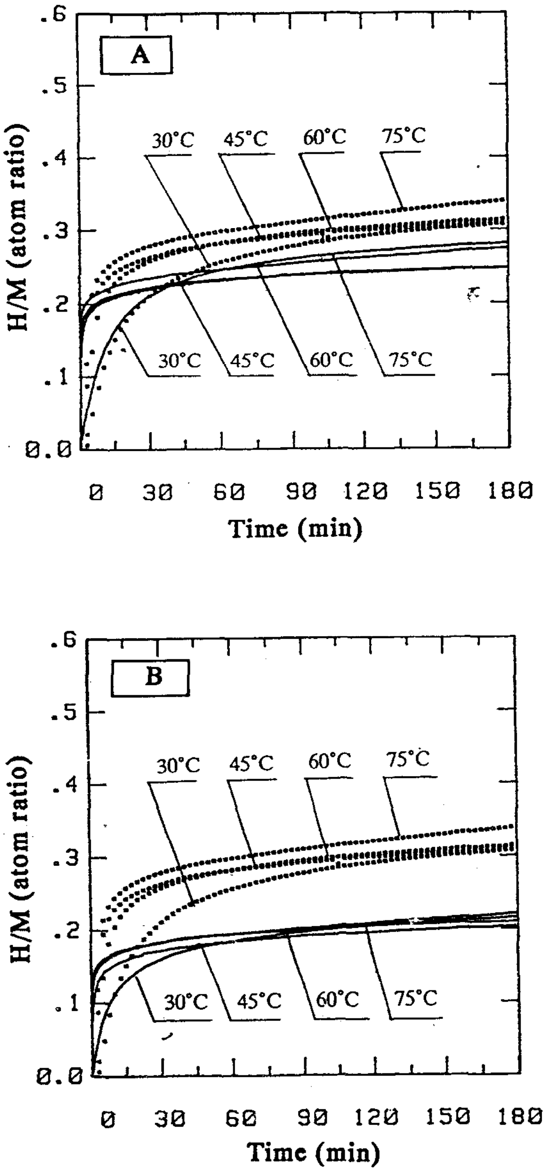

Fig. 2. Effect of temperature on the initial activation vs. time curves for HCl-treated and HCl + F-treated Mg_2Ni compared with those of F-treated alone: (A) HCl-treated (———) and F-treated (— — —); (B) HCl + F-treated (———) and F-treated (— — —).

3. Results and discussion

3.1. First hydriding reaction cycle

Fig. 2 shows the initial activation curves of HCl-treated and HCl + F-treated Mg_2Ni alloys as a function of temperature. It was found that both treated samples could be partially hydrided at each temperature with no incubation time. A fast initial hydriding reaction for each treated sample was observed for the first 30 min that accelerated slightly with increasing temperature. However, the high initial rate soon ceased with a final hydriding capacity of nearly 20% of that of Mg_2NiH_4 after 3 h. This is because the hydride phase Mg_2NiH_4 which is easily nucleated on the clean reactive surface of particles acts as a diffusion barrier for H atoms and inhibits further growth. From Fig. 2 we can also see that both HCl-related treatments decrease the H_2 absorption capacities at all temperatures compared with those of the F-treated only alloy. This is contrary to our expectation, because one of the most important roles for HCl-treatment is to leach the pure Mg phase from the eutectic structure leaving holes or channels. These holes and channels are believed to increase the specific surface area so as to improve the low temperature hydriding kinetics. However, in fact the HCl-solution quickly becomes highly basic and results in the conversion of Mg to the water insoluble $Mg(OH)_2$, rather than completely dissolving the Mg. This has been confirmed by the X-ray diffraction patterns shown in Fig. 3. $Mg(OH)_2$ is difficult to remove from the channels even after F-treatment and serves as a source of H_2O vapor contamination.

3.2. Hydride-dehydride cycling behavior

Fig. 4 shows the hydriding behavior of HCl-treated and HCl + F-treated Mg_2Ni alloys for the first five cycles at 30 and 75°C. It is evident that the subsequent hydriding reactions could not be completely finished during 3 h at such moderate conditions, perhaps because the partial initial activation could not result in enough volume expansion to create much freshly fractured surface at this low temperature. With cycling the hydriding reaction speeds were increased, especially within the first 30 min. Cycling was more effective at 75°C. This implies that the initially hydrided Mg_2NiH_4 phase can induce local stress during the 3 h initial activation to generate some cracks; these cracks slowly propagate with cycling and will produce many more new finer microcracks. The hydride phase grows easily along these cracks from the surface to bulk, until hydriding becomes complete. This suggestion is consistent with the metallographic microstructure observations of partially hydrided HCl or HCl + F-treated Mg_2Ni alloy as seen in Fig. 5. Such a cyclic cracking growth process, as previously proposed [2], results in the hydriding capacity increase seen with increasing hydriding-dehydriding cycles and temperature illustrated in Fig. 6. However, the maximum hydrogen capacities of both HCl and HCl + F-treated Mg_2Ni at 75°C after 3 h are only about 30% of that of

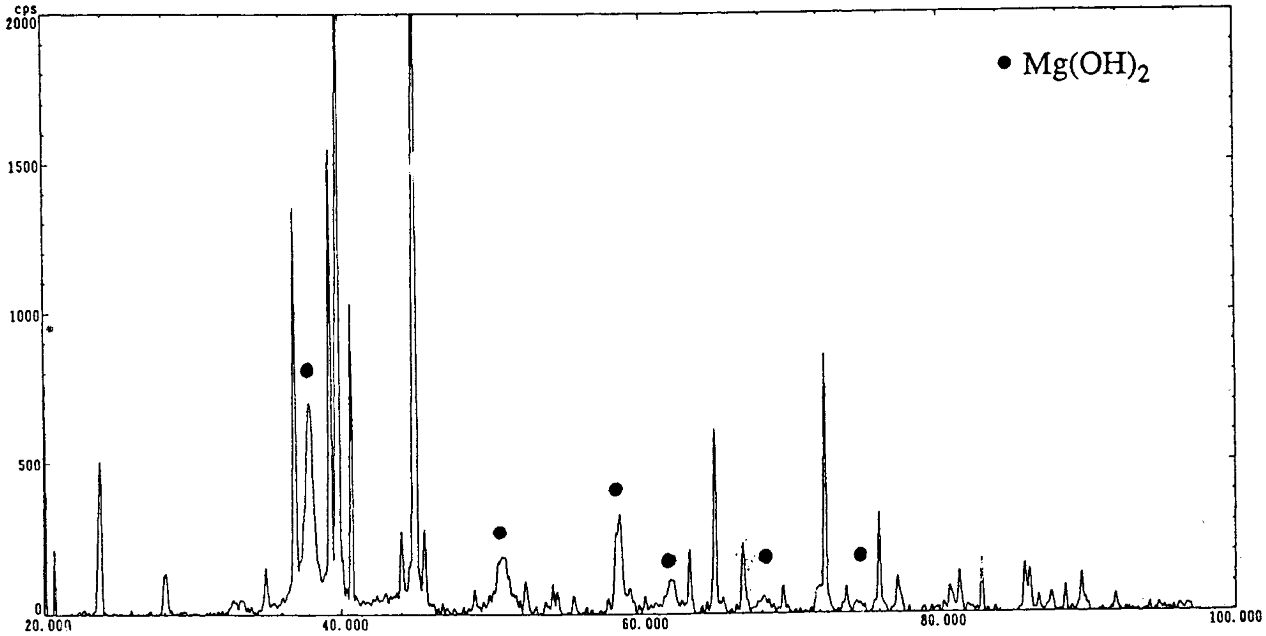

Fig. 3. X-ray diffraction patterns of HCl-treated and HCl + F-treated Mg_2Ni samples.

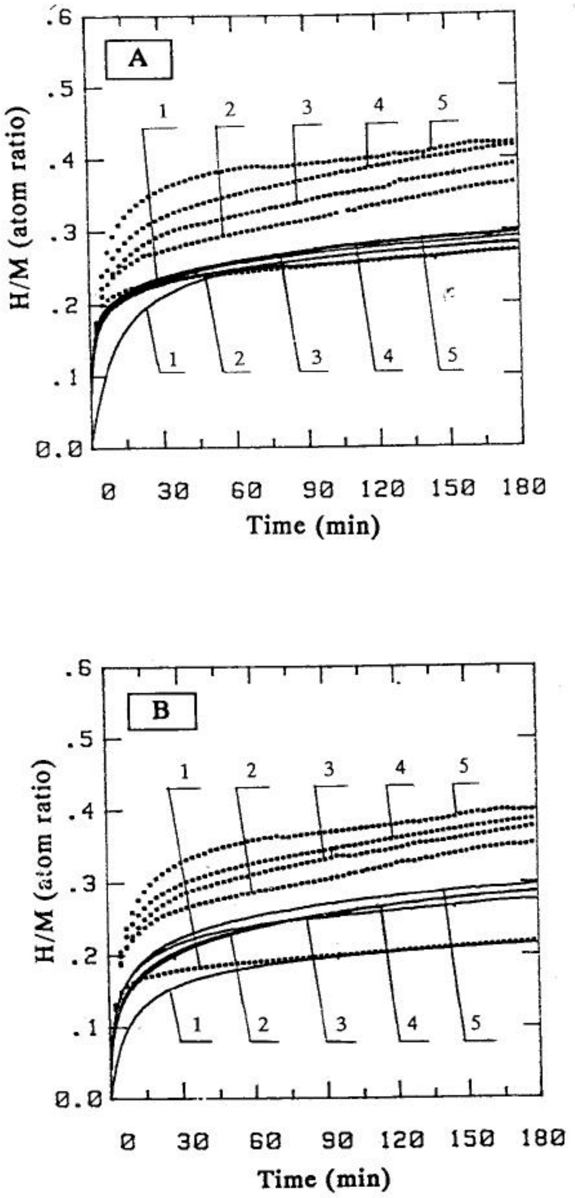

Fig. 4. Cycling behavior of HCl-treated and HCl + F-treated Mg_2Ni sample for the first five hydriding–dehydriding cycles at 30 and 75 C: (A) HCl-treated, 30°C (——) and 75°C (— — —); (B) HCl + F-treated, 30°C (——) and 75°C (— — —).

Mg_2NiH_4, i.e. $Mg_2NiH_{1.2}$, lower than that of F-treated alloy.

3.3. H_2 storage capacity after long term air exposure

For identifying the effect of the treatment process on the H_2 storage capacity of the alloy after long air exposure, the first five hydriding–dehydriding reactions of the three differently treated Mg_2Ni samples were determined at 45°C after exposing the samples to the air for 4 months. The results of the initial activation and the fifth cycle hydriding curves vs. reaction time are shown in Fig. 7. The HCl-treated alloy

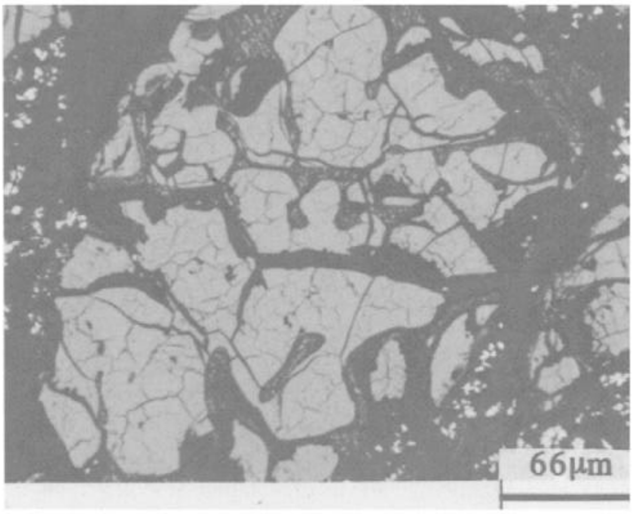

Fig. 5. Light photomicrograph of HCl-treated and partially hydrided Mg_2Ni at 75°C.

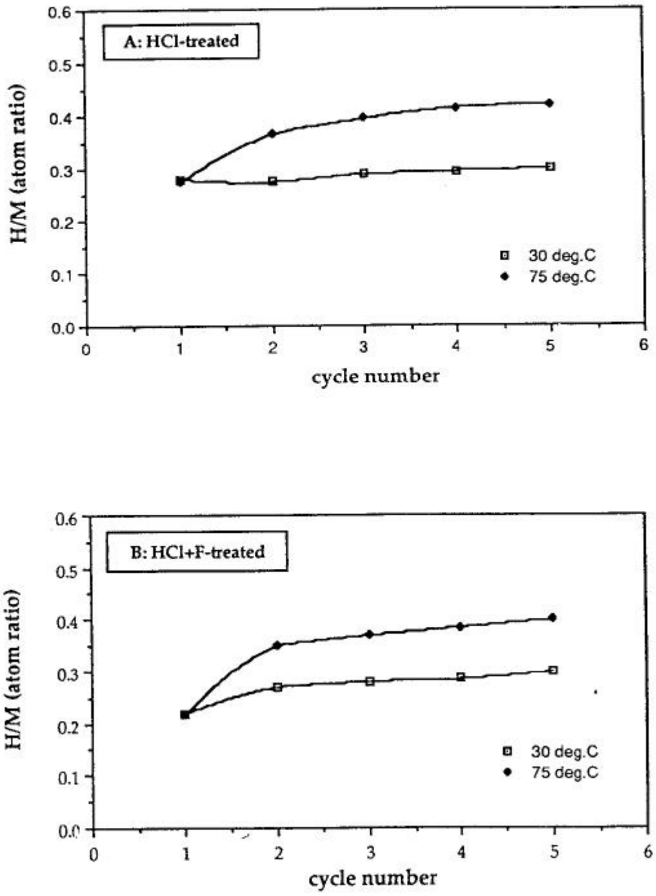

Fig. 6. Hydriding capacity after 3 h as a function of hydriding–dehydriding cycle number and temperature: (A) HCl-treated; (B) HCl + F-treated.

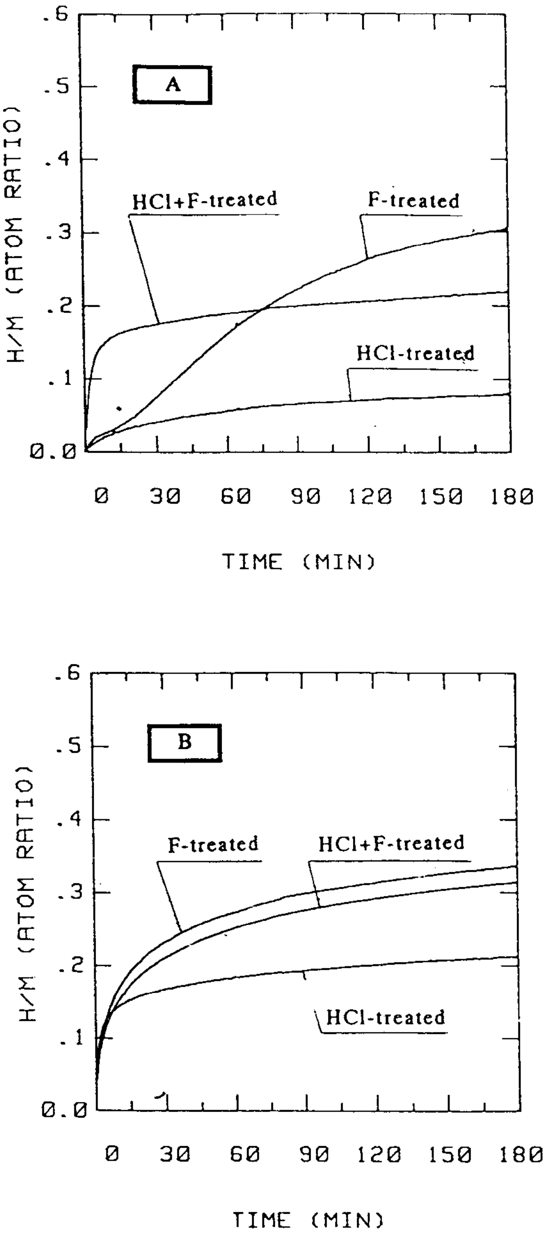

Fig. 7. Hydriding reactions of the three differently treated Mg_2Ni samples after 4 months air storage ($Ts = 45°C$, H_2 pressure = 10 atm): (A) cycle 1; (B) cycle 5.

exhibited a dramatic deterioration and could not be completely recovered even after further hydride–dehydride cycling. This is because HCl-treatment alone cannot produce a protective coating on the particles, as does F-treatment, so that the fresh surface etched by HCl-solution is easily contaminated and quickly loses its high reactivity with H_2 gas. In contrast, the HCl + F-treated alloy exhibited a slight deterioration but was easily recovered after hydride–dehydride cycling. Among the three treatment processes, the F-treated alloy alone exhibited the strongest surface protection from long term air exposure. These results clearly demonstrate the beneficial effect of F-treatment both on improving the low temperature hydriding kinetics and long term air sensitivity of Mg_2Ni.

4. Conclusions

HCl-treatment using hydrochloric acid and HCl + F-treatment using a F-containing solution after HCl-treatment showed the same etching effect as F-treatment did. Both treatments cleaned the contaminated surface and leached some pure Mg phase from the eutectic structure which results in an increase of specific surface area. This etching effect led the treated Mg_2Ni to easily partially hydride at low temperature under moderate pressure conditions. However, HCl-treatment alone could not form a fluorinated surface structure. It is unable to protect the surface from contamination during long term air exposure, as was the case for F-treated samples.

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