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Effects of ion irradiation on hydriding rate of Mm based hydrogen storage alloy

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Abstract

The effect of ion irradiation on the rate of the electrochemical hydrogen absorption by Mm–Ni based alloy was investigated. Since the low-energy ion irradiation is quite useful for surface modification of materials, it is expected that the hydriding properties of Mm samples were improved by ion irradiation. The research, which aimed at the improvement in occlusion ability of Mm alloy using ion irradiation, is the first trial in the world. In this study, the ion irradiation was made with H^+, Ar^+ and K^+ in the acceleration energy range of 350 keV, up to a dose of 1×10^{16} cm^{-2} using Takasaki Ion Accelerators for Advanced Radiation Application (TIARA) in Japan Atomic Energy Research Institute (JAERI). The initial hydrogen absorption rate was increased as the ion dose was increased. These results clearly suggest that the ion irradiation induces a high concentration of vacancies that trap high concentration of hydrogen atoms at the initial stage of the reaction. The induction of a high concentration of vacancies in metal by the ion irradiation is found effective to enhance the initial activation in the electrochemical hydriding process of $MmNi_5$.

Keywords: Hydrogen storage materials; $MmNi_5$; Defects; Ion irradiation

1. Introduction

Mm based hydrogen storage alloys are applied to the negative electrode of the Ni–H batteries and other hydrogen storage systems. In such practical applications, various surface processes of hydrogen molecules are often becoming control of hydriding rate. Therefore, the surface modifications are crucial to improve the reactivity of hydrogen with alloys and it is indispensable to improve the hydrogen absorptivity in the materials. We have reported that the alkaline pre-treatment of the alloy surface using LiOH, NaOH or KOH accelerates the rate of the initial activation [1]. In this study, we aimed at investigating the effect of ion irradiation (H^+, Ar^+ and K^+) on the electrochemical hydriding rate of the alloy. The H^+ and Ar^+ irradiated the $MmNi_5$ according to the circumstances. Already, we performed ion irradiation to palladium (Pd) sample, and acquire the data of hydriding rate about the hydrogen absorption experiment of Pd [2,3]. It glared from the K^+ irradiation activating the sample surface, consequently improvement in hydriding ability being expected. Then, it succeeded surface modification of Pd sample by ion irradiation. Surface modifications are crucial to improve the reactivity of hydrogen with metals because the dissociation of the H_2 molecules in the gas phase or the dissociation of the H_2O molecules in electrochemical process is the first step of the overall reaction of the hydrogen absorption by metals [4]. The dissociation of the H_2 or H_2O molecule becomes markedly influenced by surface conditions of a metal. So far, we have systematically investigated the effect of surface oxide layers on the kinetics of hydrogen absorption by hydrogen absorbing metals [4,5] and reported several methods of surface modifications, such as metallic coatings [6], fluorination treatment [7,8] and alkaline treatment [9]. Using the ion beam, ion irradiation can effectively induce the formation of vacancies in the surface region of alloy. Furthermore, ion irradiation onto the surface of a metal effectively induces defects, such as vacancies, dislocations, micro-cracks or impurities in the surface region

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of the metal trapping hydrogen atoms. Marked effects of the trapping on the diffusivity of metals with hydrogen atoms are reported [10]. The hydrogen trapping effects, for example, induce a marked increase in the hydrogen solubility and the heat of hydrogen solution of alloy [11]. Hydrogen trapping sites act as the center of segregation of hydrides even in hydrogen solid-solution region [12]. Oxide/metal interfaces also tend to act as hydrogen trapping sites and form hydrides in the course of hydrogen absorption, and a marked effect of surface oxidation on the hydriding kinetics of La–Ni based hydrogen absorbing alloys was reported [12–14]. Based on these facts, we intentionally induced vacancies with high concentrations by ion irradiation in the surface region of alloys, and investigated the effects of the vacancy formation on the initial rate of hydrogen absorption by $MmNi_5$.

2. Experimental

The samples used in this study were $MmNi_{3.48}Co_{0.73}Mn_{0.45}Al_{0.34}$ ($Mm = La_{0.35}Ce_{0.65}$) pellets, with a size of 13 mm Ø and 2 mm thickness. Ion irradiation was made with H^+, Ar^+ and K^+ in an acceleration energy range of 350 keV with a dose range from 1×10^{14} to 1×10^{16} cm^{-2}, respectively, at the room temperature, using the TIARA 400 kV ion implanter in JAERI. Hydrogen absorption measurements were also performed for the irradiated and un-irradiated samples. An electrolytic cell with Mm cathode apparatus shown in Fig. 1 was used to characterize hydrogen storage of samples [15,16]. The Hg/HgO electrode was used as the reference electrode in an open cell [1]. The rate of the hydrogen absorption of a sample was measured electrochemically in the 6 M KOH using an open cell as the change of current density mA (g alloy)$^{-1}$ at a constant potential of −0.93 V at 298 K. The hydrogen concentration absorbed by the negative electrode was calculated. In all reactions measured, no bubbles were observed during the hydriding.

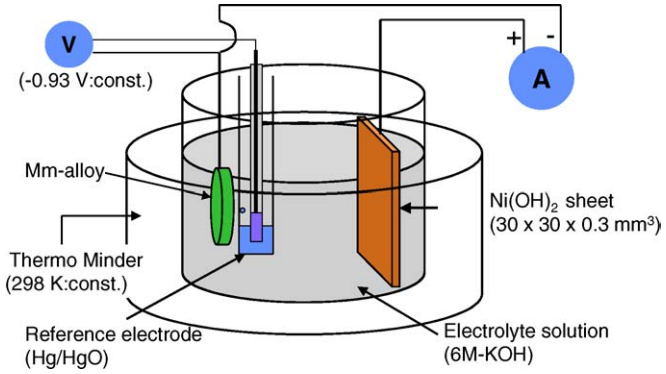

Fig. 1. An electrolytic cell with Mm cathode apparatus.

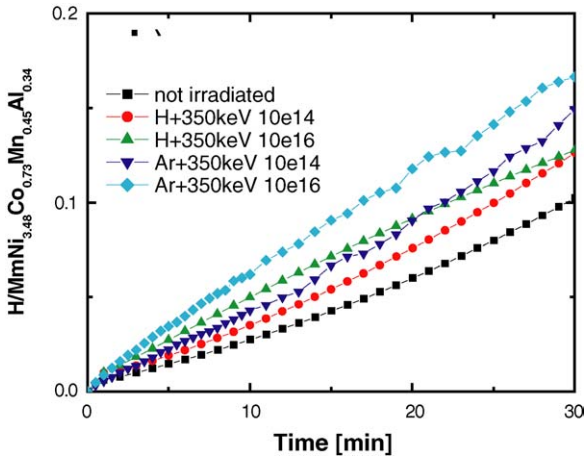

Fig. 2. Value of H/Mm of H^+ and Ar^+ irradiated Mm sample.

3. Results and discussion

The curve of the initial hydrogen absorption by Mm–Ni based alloy samples irradiated at two different doses of 1×10^{14} and 1×10^{16} cm^{-2} of H^+ and Ar^+ (Fig. 2). The initial rate of all irradiated samples were high, 1.44 times maximum, compared with that of the un-irradiated sample. At the initial stage (within 30 min from the start of each reaction), the rate of irradiated samples was increased as the ion dose was increased from 1×10^{14} to 1×10^{16} cm^{-2}. Compared with the result of H^+, the samples irradiated with Ar^+ exhibited higher initial rates. Similar results were obtained for Pd metals [3]. It is derived form TRIM calculation that Ar^+ ions produce much higher concentrations of vacancy in the surface than H^+ ions. The higher concentrations of vacancy lead to increased numbers of hydrogen trapping sits, and resulting in the acceleration of the rate of hydride nucleation and growth in the surface region.

Fig. 3 shows the result of the K^+ irradiation effects on the hydriding rate of the $MmNi_5$ alloy when the irradiation was made at an energy of 350 keV at a dose of 1×10^{16} cm^{-2}. In the measurements, hydrogen absorption and results obtained for K^+ irradiation are found to differ from those for H^+ and Ar^+ irradiations. That is, in comparison with the un-irradiated sample, the irradiated sample exhibited a very high hydriding rate. In addition, the value of H/Mm in the irradiated sample at an elapsed time of 350 min was three times as high as that in the un-irradiated one. Of the ions used in this study, the K^+ irradiation was found to be the most effective in improving the initial hydriding rate.

The improvement of the hydriding rate of the Mm–Ni based alloy due to K irradiation cannot be explained only by the production of vacancy-type defects in the surface region. Chemical reactions with K atoms implanted near the surface might be related to the increase in the hydriding rate. Further investigations are necessary to clarify the mechanisms behind the improvement of the hydriding rate by K irradiation.

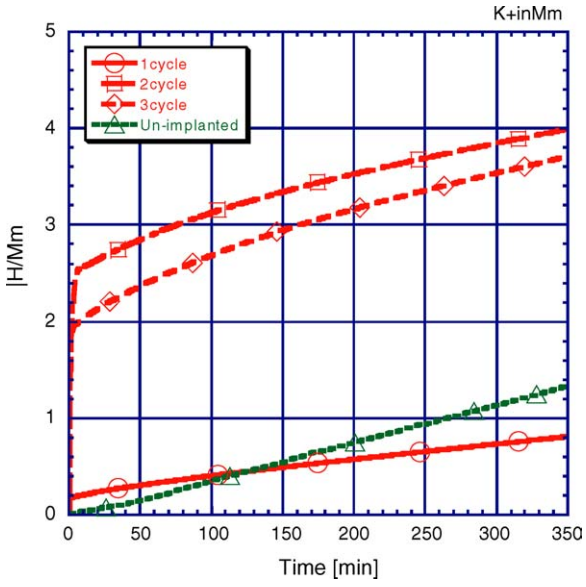

Fig. 3. Hydriding rate of 350 keV K^+ irradiation.

4. Conclusion

The ion irradiation using H^+, Ar^+ and K^+ can enhance the initial rate of electrochemical hydrogen absorption by $MmNi_5$. The induction of a high vacancy concentration in the surface of the alloys seems to be responsible for the enhancement of the initial rate. The increasing ion beam energy and the increasing ion dose are effective to enhance the initial rate. The results obtained suggest that the intentional induction of high concentration of vacancies in metals by the ion implantation is useful for the activation treatment of hydrogen absorbing alloys. The ion irradiation not only introduces a lot of vacancy-type defects but also introduces the irradiated ion inside of a sample. Therefore, the Mm–Ni based alloy surface caused the catalyst reaction by K^+ irradiation. Then, it is thought that the amount of occlusion of Mm based alloy increased.

References

[1] H.H. Uchida, Y. Watanabe, Y. Matsumura, H. Uchida, J. Alloys Compd. 231 (1995) 679–683.
[2] H. Abe, H. Uchida, Y. Azuma, A. Uedono, Z.Q. Chen, H. Itoh, Nucl. Instrum. Methods B 206 (2003) 224–227.
[3] H. Abe, A. Uedono, H. Uchida, A. Komatsu, S. Okada, H. Itoh, Mater. Sci. Forum 363–365 (2001) 156–158.
[4] H. Uchida, Int. J. Hydrogen Energy 24 (1999) 861–869.
[5] H. Uchida, Y. Ohtani, M. Ozawa, T. Kawahata, T. Suzuki, J. Less Common Met. 172–174 (1991) 983–996.
[6] E. Fromm, Poisoning of hydrogen reactions, in: Kinetics of Metal–Gas Interactions at Low Temperatures, Springer-Verlag, Berlin, 1998, ISBN 3-540-63975-6, p. 126.
[7] H. Uchida, T. Inoue, T. Tabata, S. Seki, H.H. Uchida, F. Aono, T. Nakazawa, H. Kikuyama, R. Hirayama, J. Alloys Compd. 253–254 (1997) 547–549.
[8] H. Uchida, F. Aono, T. Iwamoto, T. Matsu, M. Ito, T. Nakazawa, T. Tabata, A. Kosuge, Proceedings of the 13th World Hydrogen Energy Conference, vol. 2, 2000, pp. 1088–1092.
[9] H. Uchida, K. Yamashita, M. Goto, J. Alloys Compd. 330–332 (2002) 622–626.
[10] E. Hayashi, Y. Kurokawa, Y. Fukai, Phys. Rev. Lett. 80 (1998)5508.
[11] T.B. Flanagan, The thermodynamics of hydrogen solution in perfect and defective metals and alloys, in: V.A. Goltsov (Ed.), Progress in Hydrogen Treatment of Materials, Donetsk State Technical University, Ukraine, 2001, ISBN 966-7418-71-5, p. 37.
[12] G.H. Kim, A.G. Lee, K.Y. Lee, C.H. Chun, J.Y. Lee, Acta Metall. Mater. 43 (6) (1995) 2233.
[13] H. Uchida, A. Hisano, K. Terao, N. Sato, A. Nagashima, J. Less Common Met. 172–174 (1991) 1018–1027.
[14] S. Seta, H. Uchida, J. Alloys Compd. 231 (1995) 448–453.
[15] H. Uchida, M. Sato, W. Cui, T. Tabata, M. Kumagai, H. Takano, T. Kondo, J. Alloys Compd. 293–295 (1999) 30–33.
[16] H. Uchida, K. Yamashita, T. Tabata, H.H. Uchida, M. Iwase, Y. Katoh, J. Alloys Compd. 293–295 (1999) 751–754.