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Combinational Effect of Charged Particle Irradiation and Alkaline Pretreatment on Hydriding Property of a Mm-Ni Based Alloy

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Abstract

This study deals with surface modifications of a misch metal-nickel (Mm-Ni) based hydrogen storage alloy. This alloy is widely used as negative electrode of nickel-metal hydride (Ni-MH) battery. The surface modification was conducted by electron irradiation. The initial hydriding rate of the alloy was measured. Results are compared among those at different irradiation conditions, and also for additional surface alkaline pretreatment using a KOH solution [1,2]. The electron irradiation on the alloy surface was found effective to increase the initial hydrogen absorption rate.

1 Introduction

Recently, global environmental issues such as greenhouse effect, climate change and air pollution are serious matters to be solved. The use of clean hydrogen energy technologies is one of the most prominent solutions to reduce CO_2 emission presumably causing greenhouse effect.

The application of hydrogen storage alloys may contribute to energy saving and the reduction of CO_2 emission as is proven by hybrid vehicles which are drive both an electric motor and a combustion engine. Most of these hybrid vehicles use Ni-MH rechargeable battery. In 1988, Tokai University proved that a Ni-MH rechargeable battery can be use more than 1000 charge and discharge cycles. Since that time, we have been involved in improving kinetic of electrode performance by surface modifications.

The alkaline pretreatment of the alloy surface using LiOH, NaOH or KOH was found to accelerates the rate of the initial activation [1,2]. Alkaline atoms in the surface oxides lower the work function of electron of the surface, and this facilitates the rate of dissociation of H_2 or H_2O molecules, resulting in the acceleration of hydrogen absorption. In addition, the surface modification of materials, ion/electron irradiation was found to be a quite useful method [3,4]. Then, ion/electron irradiation onto the surface of a metal effectively induces defects such as vacancies, dislocations and micro-cracks in the surface region of the materials.

In this study, we adopted electron as charged particles, and applied electron irradiation to surface modifications of the electrode of the Ni-MH battery. And the effect of electron irradiation on the initial rate of hydriding of Mm-Ni based alloys was investigated in electrochemical process.

2 Experimental Process

2.1 Mm-Ni based alloy sample

In this study, a negative electrode material of NI\MH battery a Mm-Ni based hydrogen storage alloy, $MmNi_{3.48}Co_{0.73}Mn_{0.45}Al_{0.34}$ (Mm = $La_{0.35}Ce_{0.65}$), was prepared by arc melting. The alloy was then crushed to produce powder samples by cyclic hydriding and dehydriding treatments. The produced powder samples had an average grain size of about 38 μm. The powder was then mixed with Cu powder at a rate of alloy/Cu=1 : 3 in weight, and the pressed under a pressure of 7 t/cm^2 to prepare a pellet sample as cathode for the measurement of hydriding rate in electrochemical process.

2.2 Surface modifications

Surface modifications were made by electron irradiation and/or alkaline treatment. Electron irradiation onto the surface of a sample was made in an acceleration energy of 2 MeV, and a dose range from 5 x 10^{16} cm^{-2} to 1 x 10^{17} cm^{-2} in the atmospheric air, low vacuum (~10^{-2} Torr) or in a He gas atmosphere respectively, using a 2 MV Cockcrfoft-Walton electron accelerator in Japan Atomic Energy Agency.

Alkaline treatment was made by heating a sample at 398 K for 30 min in a 6M KOH solution. This treatment put K ions in the surface oxide layers of the alloy [3,4].

2.3 Measurement of the initial hydriding rate

The initial hydriding rate was measured in electrochemical process where a pellet sample was used as a cathode, and $Ni(OH)_2$ as an anode. An Hg/HgO electrode was used as a reference electrode in an open cell. The rate of hydriding of the sample was measured in a 6 M-KOH using the open cell at a constant voltage –0.93 V and at 298 K.

3 Results and Discussion

3.1 Effect of electron irradiation

Figure 1 shows hydriding curves for samples with and without electron irradiation before electrochemical process. Samples with electron irradiations in the air exhibit much higher hydriding rates than a sample without irradiation.

As known, electron irradiation induces vacancy type defects in the surface region of the alloy [3]. These defects may act as hydrogen trapping sites, and increase hydrogen concentration in the surface region. This may enhance the initial hydriding rate, which was similarly observed for other metals pretreated by various charged ions [4].

3.2 Effect of alkaline pretreatment

Figure 2 shows hydriding curves for samples with and without electron irradiation. After the electron irradiations in air, samples were treated in an alkaline solution of 6 M KOH. Samples with electron irradiations show higher reaction rates that a sample without irradiation. The reaction rates for samples with both the irradiation and the alkaline treatment are much higher than those of samples only with electron irradiations (Figure 1). After the irradiation, samples were exposed to air before the measurement of electrochemical hydriding rate. In this step, surface oxidation of samples surely took place. Therefore, the additional alkaline treatment was effective to enhance the rate, because the alkaline treatment induces the K atoms in the surface oxides, and reduces the work function of electron of the surface to facilitate the dissociation of H_2O and the subsequent hydriding rate [1,2], .

3.3 Effect of electron irradiation conditions

Figure 3 shows hydriding curves for samples irradiated under different conditions. A sample irradiated in the air exhibits a higher hydriding rate than the other samples irradiated in low vacuum or in a He atmosphere. According to surface analyses using ESCA, samples treated under different conditions showed the presence of complicated oxides of alloy components. Since Mm consists mainly of La and Ce, the contribution of conductive rare earth oxides like CeOx or LaOx to the fast kinetics [5-10] should be taken into account to explain the different kinetic behaviors measured in this work. In this study, we report limited information for surface of samples examined.

ESCA analyses revealed that the sample irradiated in a He atmosphere was found to have rather reactive surface conditions with thinner surface oxide layers than the sample irradiated in low vacuum. All samples were exposed to air before electrochemical hydriding process. As well known, even at room temperature, surface oxidation proceeds more profound for a metal with a clean surface than for a metal covered with thin oxide layers [11]. Therefore, the sample with reactive surface was heavily oxidized during the air exposure. And this resulted in a subsequent low H_2O dissociation and hydriding rates. The sample treated in low vacuum was covered by stable oxide layers after the irradiation, and this seems to have inhibited the subsequent H_2O dissociation and hydriding.

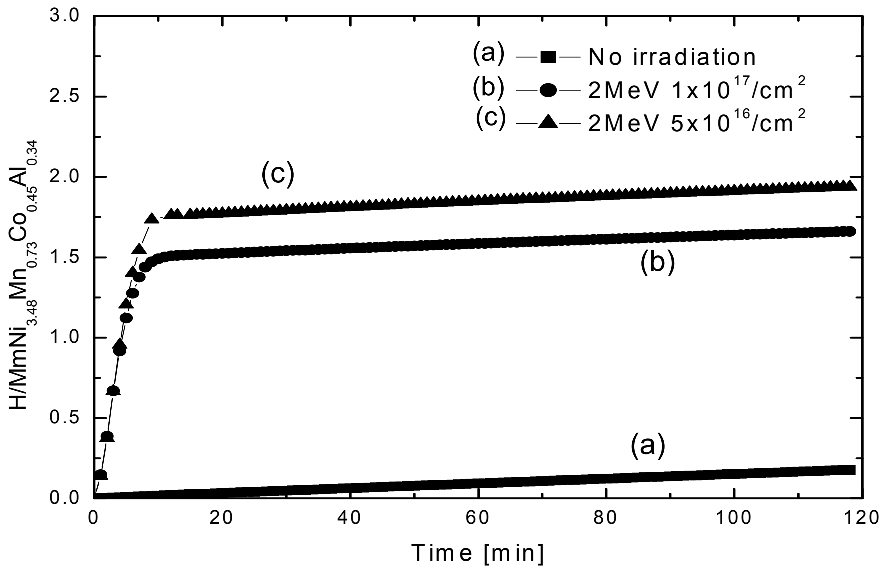

Figure 1: Hydriding curves for samples with and without electron irradiation.

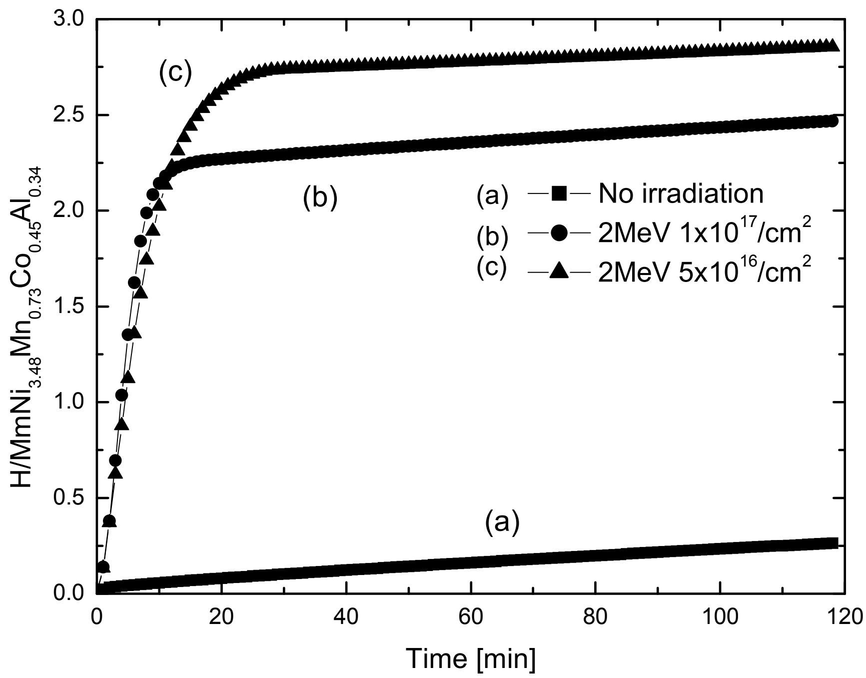

Figure 2: Hydriding curves (a) for a sample without electron irradiation and with alkaline treatment, and (b) and (c) for samples with electron irradiations and alkaline treatment.

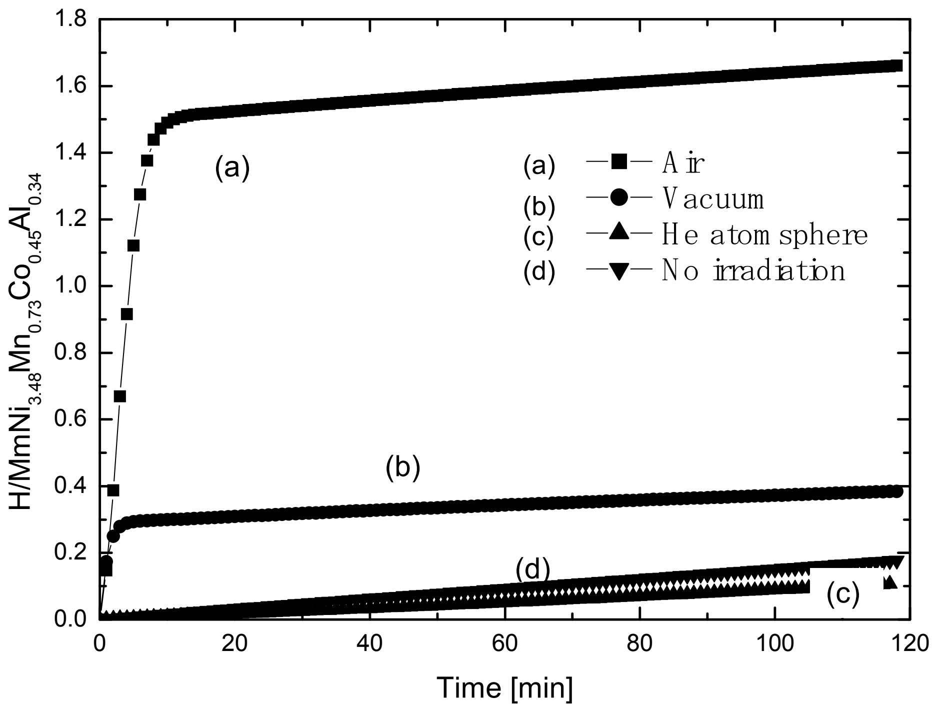

Figure 3: **Hydriding curves for samples (a) with electron irradiation in the atmospheric air, (b) with electron irradiation in low vacuum, (c) with electron irradiation in a He atmosphere, and (d) without irradiation.**

4 Conclusion

Electron irradiation onto the surface of a Mm based hydrogen storage alloy was found very effective. Additional alkaline treatment was found also to contribute to the enhancement of the hydriding rate. These effects should be interpreted in terme of the induced vacancy defects by electron irradiation, and surface oxidation of the alloy surface. Because the irradiated surface and subsequent oxidation seem to form complicated surface conditions, further investigation with surface analyses is needed.

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