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Improvement of initial activation of a Ti–Cr alloy by surface modification with potassium (K)

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Abstract

The alkaline treatment of the surface of a Ti–Cr hydrogen storage alloy was made by sticking potassium (K) metal onto the alloy block surface or by milling the alloy powder with K metal blocks instead of the use of KOH solution. This dry surface treatment was found effective to reduce the work function of electrons of the alloy surface and to ease the rate of hydrogen dissociation, resulting in an accelerated activation rate. The K atoms were found distributed in the surface oxide layer; however, X-ray photo spectroscopy (XPS) analyses in the vicinity of Fermi level suggest rather the induction of a metallic feature of the surface modified by K atoms.

Keywords: Hydrogen storage materials; Photoelectron spectroscopes; Catalysis; Kinetics

1. Introduction

In previous papers [1–6], we reported that the alkaline treatment of the surface of rare earth based hydrogen storage alloys with LiOH, NaOH or KOH enhances the initial rate of hydriding. And we elucidated that the treatment induces the distribution of the alkaline atoms in the surface oxide layers, and that the presence of the alkaline atoms in the alloy surface strongly reduces the work function of electrons of the surface. In recent studies [5,6], we concentrated our study on the effect of K atoms on the improvement of the initial activation of La–Ni based alloys, because among these alkaline atoms K atoms reduce the work function and enhance the initial rate of hydrogen absorption most effectively. And we found that the work function becomes decreased linearly over 1.0 eV with the increasing surface concentration of K atom, and that the activation energy of the initial rate of the hydrogen absorption becomes markedly decreased over 70 kJ (mol $H_2)^{-1}$ as the work function is decreased over 0.6 eV [6]. No decrease in the work function or the enhancement of the initial rate was measured by the surface treatment with NH_3–H_2O. This means that the presence of alkaline atoms in the surface region is responsible for the enhancement of the initial reaction rate, and that partial disintegration of the alloy surface by the alkaline solutions does not contribute to the enhancement of the initial reaction rate.

In the surface process of hydrogen, the dissociation of hydrogen molecules on the alloy surface is the first partial step of the over all reaction. And the dissociation of hydrogen molecules often becomes rate controlling step [7,8]. The occurrence of the exchange of electrons between the covalent gas molecules and the metal surface is crucial to induce the dissociation of covalent gas molecules.

Based on these results and facts, we proposed a model that the reduction of the work function by the presence of the alkaline atoms eases the uptake of electrons from the alloy surface by the hydrogen molecules, and this accelerates the dissociation rate of hydrogen molecules, resulting in the enhancement of the initial activation.

So far, the surface modification with the alkaline atoms was made using LiOH, NaOH or KOH for La–Ni based alloys. However, such hydroxides solutions sometimes markedly modify the surface of some alloys, and no enhancement of the rate can be observed. For example, the alkaline treatment of a Ti–Cr based alloy with a KOH solution is found to induce a marked dissolution of alloy elements into the solution, and no effect was observed. In this study, in order to avoid such surface disintegration by a wet method, we tried to modify the alloy surface with K atoms by dry methods, and which was found very effective

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to induce a distribution of K atoms in the surface, to reduce the work function and the enhancement of the initial rate of hydrogen absorption by a Ti–Cr alloy.

2. Experimental procedure

A Ti–Cr based hydrogen storage alloy was manufactured by the Japan Steel Works (JSW), Japan, with a hexagonal structure of Laves C_{14} and a composition of $Ti_{0.44}Zr_{0.56}Cr_{0.86}Fe_{0.68}Ni_{0.21}Mn_{0.25}Cu_{0.03}$. This alloy was developed for the use of MH refrigerators at low temperatures. The effect of the surface modification of this alloy was examined by the measurement of the initial rate of hydrogen absorption by a rectangular block sample with a size $10\times10\times3$ mm, or a powder sample with diameters smaller than 150 μm produced by ball milling in a hexane for 6 h. The surface modification was made in such a way: the surface of a block sample was stuck firmly and covered with potassium (K) metal in an Ar gas atmosphere, and subsequently immersed in a hexane solution for 6 h at 298 K, and then K metal was peeled off. A powder sample was ball milled with K metal block pieces with a diameter about 3 mm in a hexane for 6 h. The mixture ratio of the alloy and K metal was 10:1 in mole ratio. These treatments were found effective to induce distributions of K atoms on the alloy surface by analyses of electron depressive X-ray spectroscopy (EDX) on the surface and X-ray photo spectroscopy (XPS) in the depth profile. Fig. 1 shows the images of (a) secondary electron microscopy (SEM) and (b) EDX for the surface of a block sample after the K treatment, respectively. The clear distribution of K atoms can be seen on the surface. For a powder sample, the adhesion of K metals to the surface was confirmed by EDX analysis.

The initial rate of hydrogen absorption by the alloy samples was measured at an applied hydrogen pressure 1 MPa and 298 K using a Sieverts' type apparatus. The rate was calculated from the pressure decrease in a reaction cell as a function of time. Details of the kinetic measurement of the rate are described elsewhere [7].

The work function of the block samples was measured at 298 K by the Kelvin method [9] where an Au electrode with a work function of 5.10 eV was used as the reference material [6,10].

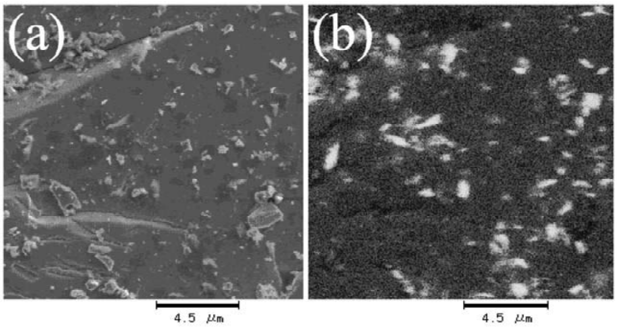

Fig. 1. Images of SEM (a) and of EDX (b) of a Ti–Cr alloy surfaced modified with potassium (K) metal.

3. Results and discussion

Typical initial activation curves of the alloy with various surface conditions are shown in Fig. 2 for powder samples and in Fig. 3 for block samples, respectively. Curves A for the samples with the surfaces modified by K atoms exhibit the highest rates for both block and powder samples. Standard samples without the K pretreatment exhibit a low rate for a powder or a delayed activation with an incubation time for a block (Curves B). In comparison, before H_2 exposures, samples were exposed to air (curves C) or

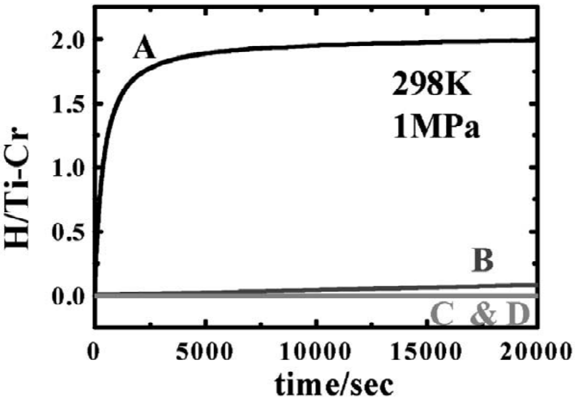

Fig. 2. Typical curves of the initial activation in the hydrogen absorption by T–Cr powder samples with various surface modifications at 298 K and an applied hydrogen pressure of 1 MPa: (A) for a sample modified with K atoms, (B) for a standard sample without K pretreatment, (C) for a sample exposed to air for 1 week at 298 K, and (D) for a sample immersed in a 8 M KOH solution at 373 K for 1 h.

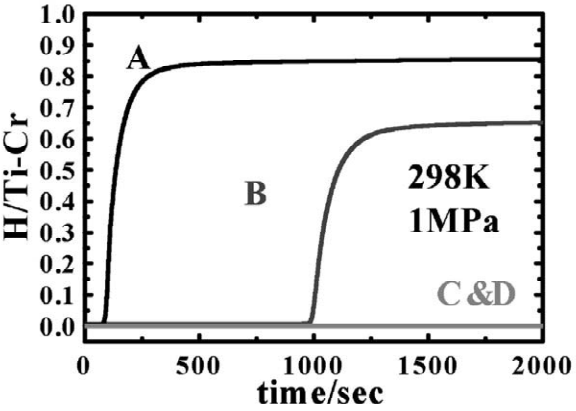

Fig. 3. Typical curves of the initial activation in the hydrogen absorption by Ti–Cr block samples with various surface modifications at 298 K and an applied hydrogen pressure of 1 MPa: (A) for a sample modified with K atoms, (B) for a standard sample without K pretreated, (C) for a sample exposed to air for 1 week at 298 K, and (D) for a sample immersed in an 8 M-KOH solution at 373 K for 1 h.

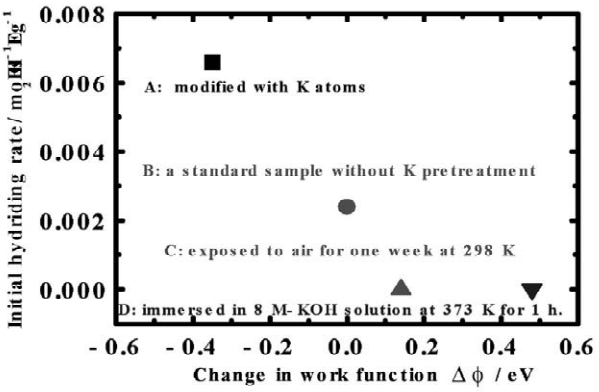

Fig. 4. The relation between the change in the work function and the initial rate of hydrogen absorption by Ti–Cr alloy samples with various surface conditions.

samples were immersed in an 8 M-KOH solution at 373 K for 1 h (curve D). These samples exhibited no reaction within 2×10^4 s during H_2 exposures.

The deviation $\Delta\phi$ of the work function ϕ from the standard value of 5.14 eV of standard sample was measured for block samples with various surface modifications. Standard block samples without K treatment were prepared by heating at 873 K in a vacuum of 5×10^{-4} Pa for 6 h, and then subjected to the work function measurement in a vacuum of 5 Pa.

Fig. 4 shows the relation between $\Delta\phi$ and the initial rate of hydrogen absorption of block samples. Sample A with K atoms in the surface exhibits a much higher rate and a reduced value of the work function with $\Delta\phi=-0.35$ eV compared with those of a standard sample B. From the XPS depth profile of K atoms in sample A in Fig. 5a, K atoms are distributed in the surface oxide. The surface of a standard sample is covered also with oxides (see Fig. 5b), however, the rate is much lower than that of sample A with a modified surface with K atoms. These results lead to the occurrence of the following surface processes that the presence of K atoms in the surface reduces the work function, resulting in an enhanced rate of hydrogen dissociation and an accelerated initial activation rate. This distribution of K atoms in the surface oxide of sample A is similar to that of the surface of La–Ni based alloys treated by KOH [6].

However, an 8 M-KOH pretreatment of the Ti–Cr alloy exhibited rather an increased value of the work function $\Delta\phi=0.48$ eV (see sample D in Fig. 4) and induced an XPS depth profile with high concentration of O atoms and low concentrations of K atoms (Fig. 5d). Compared with sample C exposed to air for 1 week before H_2 exposure, the increase in $\Delta\phi$ of sample D is much larger ($\Delta\phi=0.48$ eV for sample D and $\Delta\phi=0.14$ eV for sample C), and the surface concentration of O atoms of sample D is much higher than that of sample C exposed to air at 298 K for 1 week before H_2 exposure (see Fig. 5c and d). This indicates that the surface pretreated by KOH is covered with grown oxide layers. As shown in Figs. 2 and 3, no reaction rate was measured for samples C or D. This means that no electron exchange between hydrogen molecules and the surfaces of samples C and D may takes

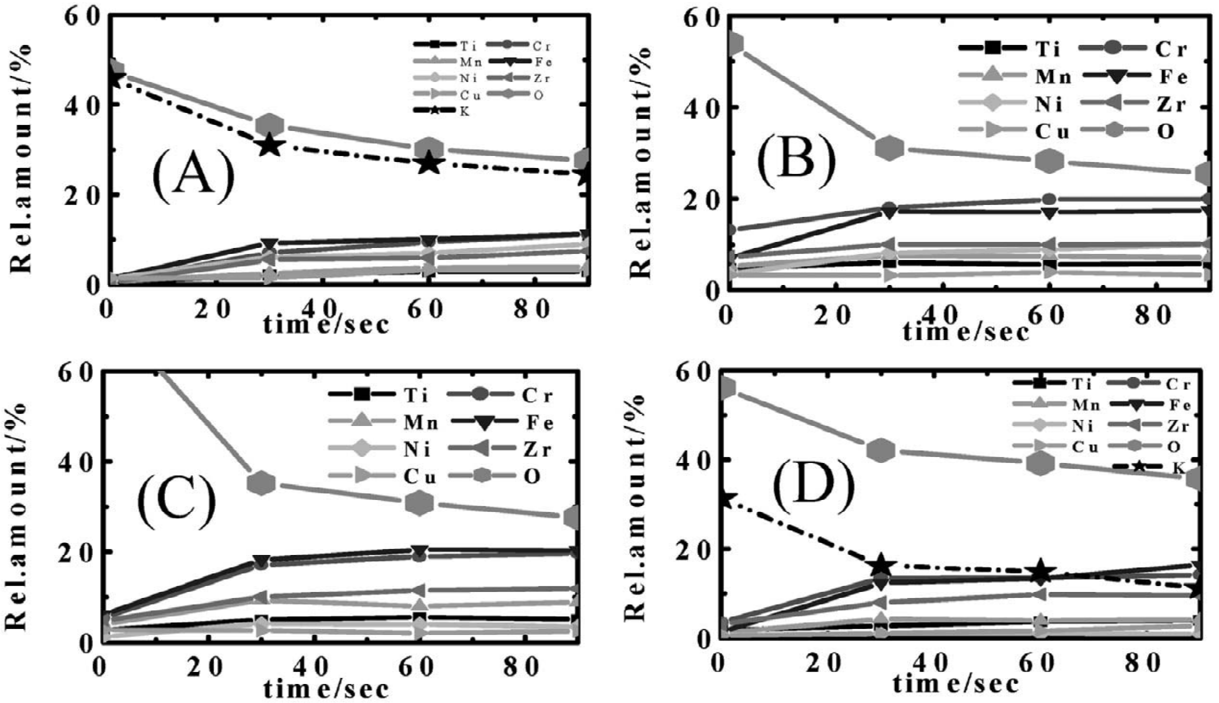

Fig. 5. XPS depth profiles of samples with various surface modifications: (A) for a sample modified with K atoms, (B) for a standard sample without K treatment, (c) for a sample exposed to air for 1 week at 298 K, and (D) for a sample modified by immersing in an 8 M-KOH solution at 373 for 1 h.

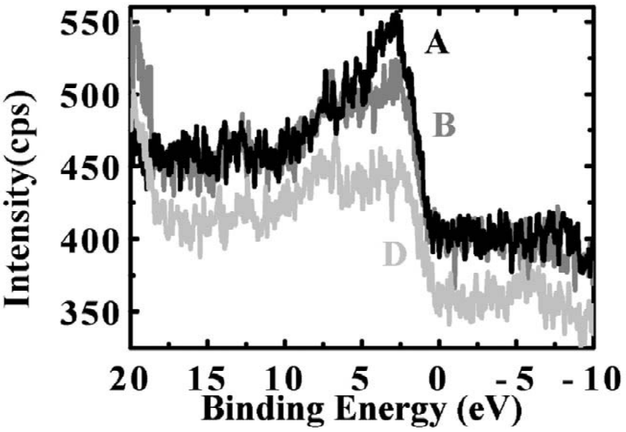

Fig. 6. XPS valence band spectra of samples with various surface modifications: (A) for a sample modified with K atoms, (B) for a standard sample without K treatment, and (D) for a sample modified by immersing in an 8 M-KOH solution.

place, and this results in no occurrence of the dissociation of hydrogen molecules or of hydrogen absorption. The KOH pretreatment of the Ti–Cr alloy induces only surface disintegration and inactive surface conditions for the dissociation of hydrogen molecules.

Fig. 6 shows XPS valence band spectra of the surface of block samples A, B and D in the vicinity of Fermi level. Standard sample B exhibits a sharp edge whereas sample D pretreated with 8 M-KOH shows rather a nonmetallic state. Sample A exhibits more sharp edge, suggesting that the surface modified by K atoms induces a more metallic features than that of sample D. These results are in good agreement with the changes in the work function of samples A and D.

4. Conclusion

K atoms can successfully be distributed in the surface region of a Ti–Cr alloy by sticking K metal firmly onto the alloy block surface, or by milling K metal blocks and the alloy powder. The measurement of the change in the work function of electrons of the alloy surface and XPS analyses of the sample surface suggest the following mechanisms of the surface process of hydrogen that the distribution of K atoms in the alloy surface accelerates the rate of electron exchange between hydrogen molecules and the alloy surface, and accordingly the rate of the hydrogen dissociation, and consequently the rate of the initial activation. However, the wet treatment with a KOH treatment induces the disintegration of the Ti–Cr alloy surface and an inactive surface by forming nonmetallic oxide layers.

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