Dynamic P-c-T relations of the La-incorporated/fluorinated AB$_2$ hydriding alloys

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Abstract

Pressure–composition–temperature (P–c–T) relations of the La-incorporated and fluorinated AB$_2$ alloy, $Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Co_{0.1}Ni_{1.1}$, were studied under isothermal dynamic conditions of 313 K and 343 K. The La-incorporation and fluorination effectively improved both the significant deviations existing in the static and dynamic P–c–T relations of conventional metal hydrides. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: AB$_2$ type alloy, P–c–T curves; Dynamics, Fluorination treatment

1. Introduction

P–c–T relations under dynamic conditions deviate considerably from the static P–c–T relations under equilibrium conditions. For instance, the dynamic pressure–composition (P–c) relations at a given isothermal condition exhibit a much larger pressure difference between absorption and desorption pressures than those under equilibrium states.

Those dynamic P–c relations were studied experimentally by Nagel by using a coupled reactor system [1–3]. There has also been reported an extensive work on the dynamic studies on P–c–T relations of Mg-hydrides by Friedelmeyer [4,5]. Such a dynamic relation can be defined as the P–c–T relations under non-equilibrium conditions during hydrogen being absorbed or desorbed where the system pressure varies depending on the hydrogen transfer rates, i.e. the hydriding/dehydriding kinetics. As the reaction kinetics are greatly dependent on the pressure difference between the system pressure and the equilibrium pressure, the dynamic pressure during hydrogen transfer does exceed the equilibrium absorption pressure during hydriding reactions.

The reaction kinetics are significantly governed by the heat transmission characteristics of the reaction bed, i.e., the configuration of a reactor as the heat exchanger, the thermal conductivity of metal hydride bed, the over-all heat capacity of a container system, and the overall heat transfer coefficient between the outer surface and the reaction bed [6]. The dynamic pressure profiles as a function of hydrogen concentration were well correlated with the heat transmission characteristics of the reaction bed by a computational simulation [7].

In engineering devices such as refrigerators and heat pumps in which the hydrogen and heat transfer is accompanied between a coupled reactors, the performance of the system is governed by the dynamic P–c–T relations and it is of essential importance to know such dynamic P–c–T relations in designing thermodynamic devices.

La-incorporation into the typical AB$_2$ compounds has been studied for improving reaction kinetics and the fluorination of the AB$_2$ particle surface and has been found to be effective for improving reaction kinetics and for reducing pressure hysteresis between hydriding/dehydriding pressure and composition isotherms [8]. Roles of surfaces covered by LaF$_3$ after removing oxides were reported by Liu [9], and those of metallic Ni reduced from F-solution are reported by Liu [10]. Particle surfaces covered by oxides such as La$_2$O$_3$ and ZrO$_2$ exhibit very poor hydriding kinetics when compared with those of the fluoride-covered surface [11].

In this study, an AB$_2$-type of Laves phase alloy, $Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Co_{0.1}Ni_{1.1}$, was chosen for evaluating the effects of La-incorporation and fluorination on the dynamic P–c–T relations. The pressure profiles under dynamic conditions were taken by measuring isothermal composition changes as a function of reaction time elapsed at various initial pressure conditions during hydriding and

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dehydriding processes. And the fluorination effects on the initial activation characteristics and the dynamic P–c behaviors are confirmed through this simple experimental study.

2. Experiments

2.1. Sample preparation

A small amount of La was incorporated during a re-melting procedure in an arc furnace and the samples were annealed at 1100°C for 8 h. The average particle size before fluorination treatment was less than 26 m and the samples were hydrided and dehydrided 13 times in a small reactor under hydrogen pressure of 2.0 MPa at 313 K.

2.2. Fluorination treatment

Depending on the types of alloys and applications, various fluorination techniques have been developed in order to improve surface properties and characteristics of conventional hydrogen storage alloys [11]. An F-treatment was applied for removing the oxide layer and implanting metallic Ni on the surface. A mass of 25 g of sample was treated for 30 min at 343 K in an aqueous solution of HF and KF, which contains 4.0 g of NiF_2/1000 ml to maintain the pH-value at 5.0. A significant increase in specific surface area has been observed during those F-treatments due to the volumetric expansion caused by the hydriding reaction generating fine cracks and channels increasing surface areas [11].

2.3. Experimental set-ups

An automatic P–c–T unit of Sievert type was used to measure the dynamic pressure changes as a function of time elapsed during hydriding and dehydriding reactions at 313 K and 343 K. The experimental runs were repeated at several different initial pressure conditions between 0.1 and 3.0 MPa. The equilibrium (static) P–c–T relations were determined isothermally at 313 K and 343 K by measuring the P–v–T relations where the compressibility factor (z=PV/RT) was taken into consideration for correcting the non-ideal behavior of hydrogen gas at its super critical conditions.

3. Experimental results and discussions

Composition changes as H/M at 313 K under a series of initial pressure conditions are shown for both the La-free/untreated and La-incorporated/F-treated samples in Fig. 1 (La=0) and Fig. 2 (La=0.05) as a function of time for the hydriding reactions, and for the dehydriding reactions in Fig. 3 (La=0) and Fig. 4 (La=0.05). In these figures, the
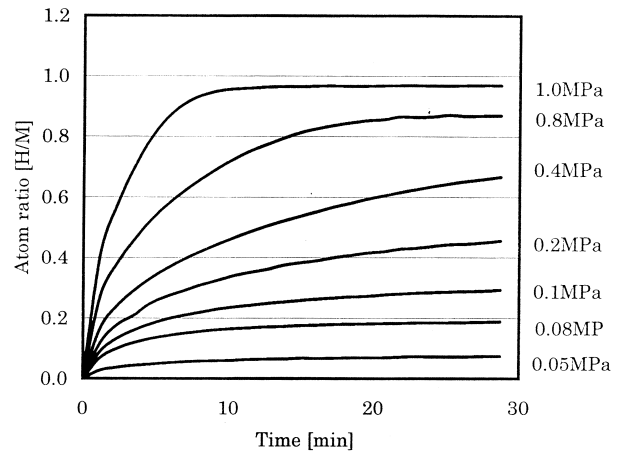

Fig. 1. Composition changes during hydriding as a function of time elapsed under various initial pressure conditions for La-free/untreated sample at 313 K.
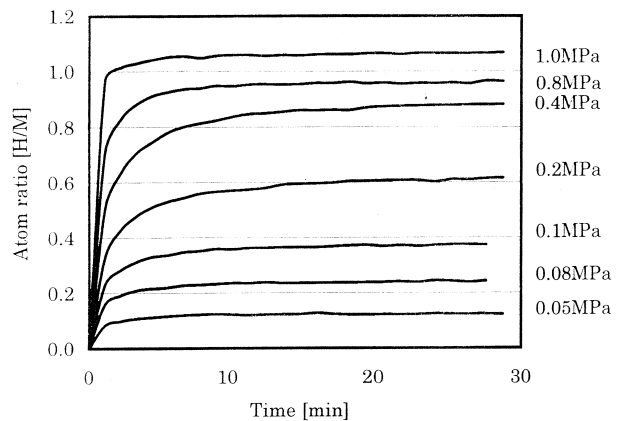

Fig. 2. Composition changes during hydriding as a function of time elapsed under various initial pressure conditions for La-incorporated/F-treated sample at 313 K (La=0.05).
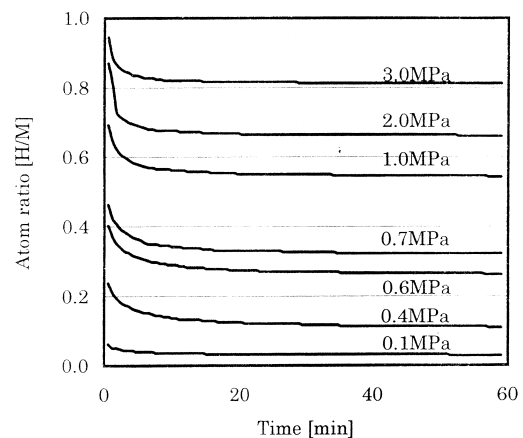

Fig. 3. Composition changes during dehydriding as a function of time elapsed under various initial pressure conditions for La-free/untreated sample at 313 K.
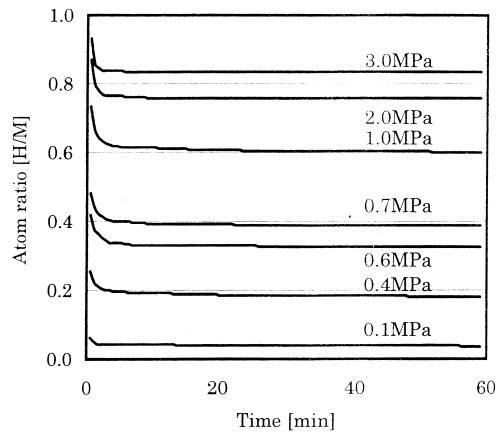
Fig. 4. Composition changes during dehydriding as a function of time elapsed under various initial pressure conditions for La-incorporated/F-treated sample at 313 K (La=0.5).

effects of La-incorporation and F-treatment on the initial activation characteristics are clearly shown at the initial parts of both the hydriding and dehydriding reactions. The effects of La-incorporation on a typical AB$_2$ type of Laves phase alloy, $Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Co_{0.1}Ni_{1.1}$, and F-treatment are reported in detail by Liu [10].

The pressure to composition (H/M) relations during hydriding reactions are re-plotted from Fig. 1 and Fig. 2 at some time intervals and shown in Fig. 5 for the La-free/untreated sample and Fig. 6, for the La-incorporated/F-treated sample, respectively. From these figures, it can be seen how difficult it is to attain the equilibrium state under dynamic conditions. Even after 60 min., the P–c isotherm does not reach the equilibrium isotherm for the La-free/untreated sample. However, the La-incorporated/F-treated sample reaches an equilibrium to isothermal relation much faster than the P–c relations of the La-free/untreated sample.

The dynamic P–c isotherms at 1 min after absorption

Fig. 6. Pressure changes during hydriding as a function of H/M for La-incorporated/F-treated sample at 313 K (parameters: time elapsed after starting hydriding reactions).

and desorption had being started are shown in Figs. 7 and 8 for both the La-free/untreated and the La-incorporated/fluorinated samples where the equilibrium/static P–c–T relations are shown for comparison purposes. In these figures, quite large deviations between dynamic and static absorption/desorption P–c relations can be observed, particularly in the P–c relations of the La-free/untreated sample.

The large deviation exhibited during absorption can be attributed to the heat transmission characteristics of a reactor system, i.e., the thermal conductivity and packing density of reactor bed and the overall heat transfer coefficient of a reactor (heat exchanger) packed with metal hydride powder [6,7].

However, it is not satisfactory to explain those experimental results simply by the heat transmission effects. As can be seen from the comparisons of the experimental data between the La-free/untreated and the La-incorpo-
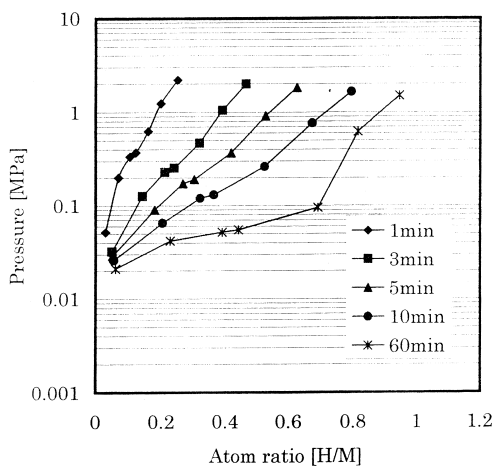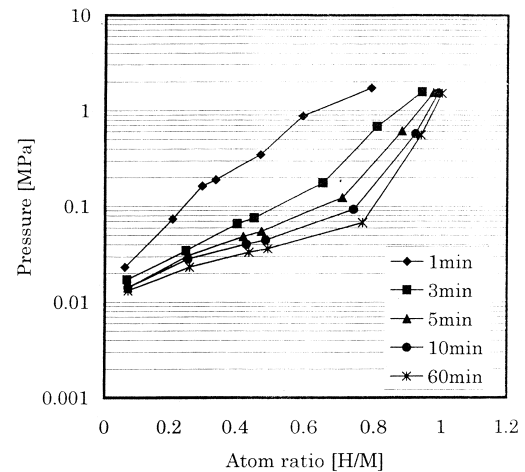

Fig. 5. Pressure changes during hydriding as a function of H/M for La-free/untreated sample at 313 K (parameters: time elapsed after starting hydriding reactions).
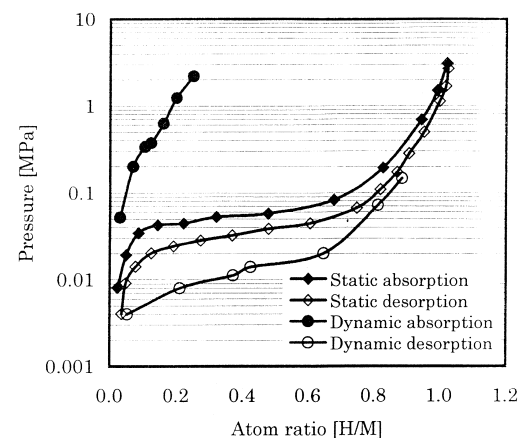

Fig. 7. Composition of static and dynamic P–c isotherms at 1 min after the hydriding reaction had been started for La-free/untreated sample (313 K).
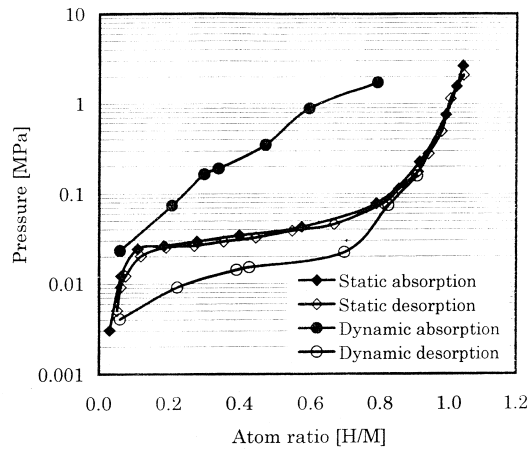
Fig. 8. Composition of static and dynamic P–c isotherms at 1 min after the hydriding reaction had been started for the La-incorporated/F-treated sample (313 K).

rated/F-treated samples, the La-incorporation and fluorination treatment is found to be effective on the initial activation characteristics and on the dynamic P–c–T relations. La forms LaF3 and the fluorination treatment removes the oxide layer and works for increasing the specific surface area and these are contributed to provide the gateway and the capture site for incoming and outgoing hydrogen at the extreme surface [11].

The contact area between particles and the surface conditions of contact points influences heat transmission characteristics of the metal hydride bed. Oxide layers act not only for decelerating the reaction kinetics but also for reducing the thermal conductivity between particles.

From this experimental study, the dynamic P–c–T relation is shown to be affected both by the heat transmission characteristics of a reactor system as reported by
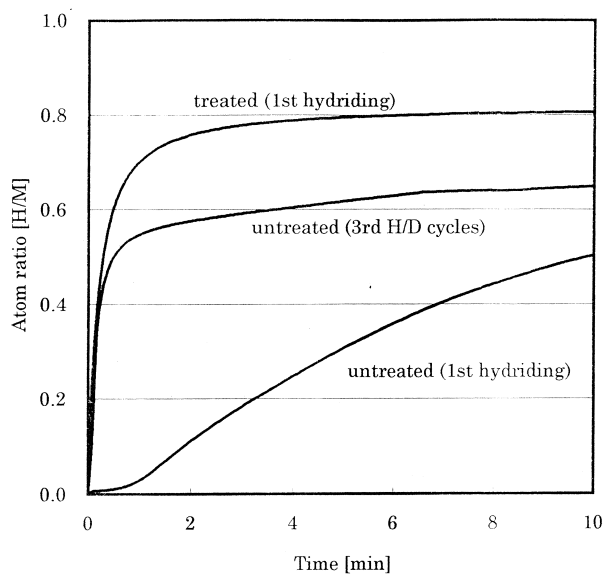

Fig. 9. Isothermal activation characteristics of La-free/untreated and La-incorporated/F-treated $Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Co_{0.1}Ni_{1.1}$ hydride (313 K).

Bjurström [6,7] and by the surface conditions of the metal hydride particles.

It should be noted that the actual pressure difference in a paired set of reactor systems where the hydrogen gas is transferred between the dehydriding- and the hydriding reactors is extremely smaller than that can be calculated by using the van't Hoff P–T relations at two different temperature conditions. The hydrogen flow-rate is unexpectedly smaller at such smaller differential pressure conditions and as a result, the estimated efficiencies and performances for any thermal energy conversion devices will lead to great failures if those effects of heat transfer and surface functions were not taken into consideration.

Finally, the initial activation characteristics of $Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Co_{0.1}Ni_{1.1}$ are shown in Fig. 9 as the H/M to time relations measured at 313 K for both the La-free/untreated and La-incorporated/fluorinated samples. The La-incorporation and fluorination effects on the dynamic behaviors are clearly exhibited in this figure.

4. Conclusion

In this work, the dynamic P–c–T relations is found to deviate greatly from the relations under equilibrium and static conditions and the effects of La-incorporation and the fluorination are demonstrated experimentally in this work. In connection with the heat transmission effects on the dynamic behaviors studied earlier by Bjurström [6,7], the deviations are correlated with the effects of La-incorporation in a Laves phase AB_2 and of the fluorination treatment.

In an energy conversion device, the amount of hydrogen transferable between a coupled reactor system per unit time determines the amount of heat, and then it determines the thermal efficiency of the device. From such a view point, it is pointed out that design information based upon the static P–c–T relations will mislead us to impractical directions in designing thermal energy conversion devices, even for the design of hydrogen storage tanks or reservoirs for hydrogen-fueled hybrid cars and fuel cell cars.

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