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Influence of expansion of metal hydride during hydriding–dehydriding cycles

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Abstract

The mechanical behavior of metal hydride reactor and the mechanism of the advent of strain caused by $Ti_{0.71}Zr_{0.29}Mn_{0.8}CrCu_{0.2}$ alloy expansion have been studied using pressure vessel controlled to be no pressure difference between the inner and outer wall of the reactor tube occurred. Strain gauges were set on the various locations in the reactor. The change of strain was continuously monitored using the strain analyzer. The metal hydride in the reactor after hydriding–dehydriding cycles was subjected to optical and scanning electron micrograph study, particle size analysis and the measurement of the angle of repose to investigate the flowability of metal hydride. The results indicate that once the elastic deformation of the reactor occurred during hydriding–dehydriding cycles, its deformation did not become larger anymore because the grain size of the alloy in the reactor changed to a lesser extent after subsequent cycles. The formation of metal hydride aggregates during cycling exerts a great influence on the advent of strain imposed to the reactor because the strain caused by the expansion of the aggregate becomes larger than that of the fine grain itself. The aggregate formation tends to occur easily due to the increase of cohesion and friction within the metal hydride powder during hydriding–dehydriding cycles.

Keywords: Expansion; Strain; Cycling; Grain size

1. Introduction

The large change in the specific volume of metal hydride in hydriding–dehydriding cycle often results in deformation and cracking of metal hydride reactors [1]. Previously, it was presented that an appropriate packing density, which is defined and normalized here as the volume of metal hydride powder packed in the reactor divided by the reactor volume, is needed to be below 0.4 in order not to exceed the elastic limit of the reactor, especially using rare earth series metal hydride even in the case of a horizontal tube reactor. Q. Wang et al., [2] investigated the damage on hydride containers caused by the expansion of metal hydride and the effect of admixture in metal hydrides at a pilot plant scale. T. Saito et al. [3] studied the influence of expansion of the Fe–Ti sintered pellet with copper binder. The Fe–Ti pellet expanded to some extent during activation and remained at a constant volume through subsequent hydriding–dehydriding cycles. In this paper, we have focused on the $Ti_{0.71}Zr_{0.29}Mn_{0.8}CrCu_{0.2}$ series metal hydrides, which are of particular interest because they have an ability to absorb a large amount of hydrogen, and we investigated the property of the metal hydride that was compressed due to the expansion after hydriding–dehydriding cycles and the mechanism of the advent of strain in the reactor.

2. Experimental details

The experimental apparatus is illustrated schematically in Fig. 1. The reactor was set within the high pressure vessel horizontally. The size of the stainless steel reactor was 20 mm in diameter and 150 mm in length with a wall thickness of 0.5 mm. The pressure vessel was controlled so that there was no pressure difference between the inner and outer wall of the reactor tube. The metal hydride powder which consists of $Ti_{0.71}Zr_{0.29}Mn_{0.8}CrCu_{0.2}$ alloy with initial grain size of less than 250 μm was used in this experiment. The packing density of the reactor was changed in the range 0.27–0.65 by varying the weight of metal hydride powder packed in the reactor. The packing density is defined and normalized here as the volume of metal hydride powder packed in the reactor divided by the reactor volume.

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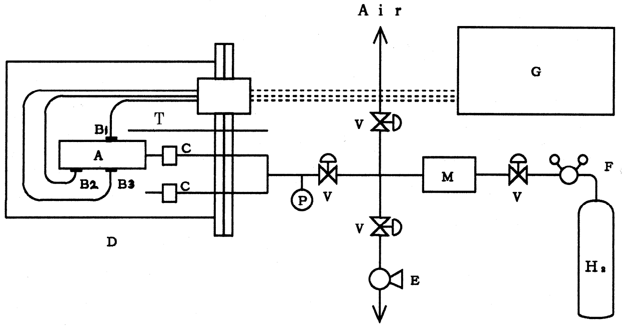

Fig. 1. Schematic diagram of the experimental apparatus. A: Sample thin tube reactor; B: Strain gauges (B1: Upper center, B2: Bottom edge, B3: Bottom center); C: Filter; D: Pressure vessel; E: Vacuum pump; F: Pressure regulator; G: Data acquisition unit and controller; M: Mass flow meter; P: Pressure transducer; V: Air-operated valve.

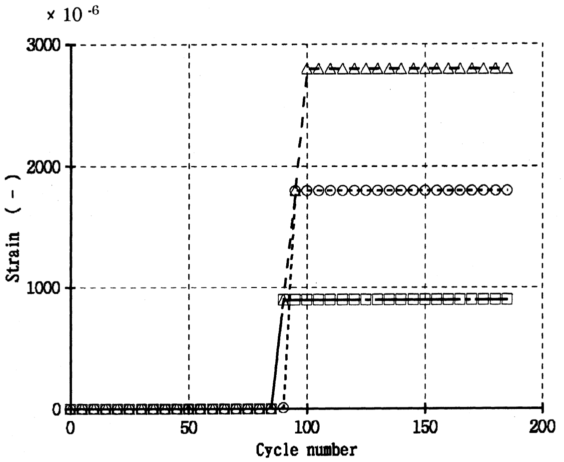

Fig. 2. The change of strain during hydriding–dehydriding cycles in the various locations of the reactor with a packing density of 0.65.

Strain gauges were set on the bottom edge, bottom center, and upper part of the reactor (see in Fig. 1). The sample reactor to be measured was evacuated using a rotary pump for 55 min. Commercial grade hydrogen (purity 99.99%) was then introduced into the sample reactor at room temperature and pressure of 9.5 kg cm^{-2}. After 55 min hydrogen was released to the atmosphere and the sample reactor was evacuated again. The air-operated valves in the system were used so as to perform cyclic measurements. The change of strain was continuously monitored using the strain analyzer. After finishing the strain measurement, the reactor was cut open. The metal hydride followed by deactivation treatment using carbon dioxide was subjected to optical and scanning electron micrograph study and particle size analysis. The angle of repose, which is the angle between the ground and the metal hydride powder surface which is just broken when rotating the reactor was measured to investigate the flowability of metal hydride using the high pressure glass-made reactor.

3. Results and discussion

The change of strain during hydriding–dehydriding cycles in the various locations of the reactor with a packing density of 0.65 is shown in Fig. 2. The packing density of 0.65, which was assumed to be a maximum density in this experiment, was obtained by tapping and vibrating while packing the metal hydride powder into the reactor. The strain variation caused by expansion of metal hydride was negligible up to the about 100 hydriding–dehydriding cycles. Beyond these cycles all parts of the reactor suddenly showed a drastic strain increase to a certain value which depended on the location of reactor. For example, the strain of the reactor bottom edge reached the value of 2800 μ-strain, which is higher than those of the other parts such as the bottom center and upper center of the reactor. Once the strain increased, its value remained constant and did not show any further increase during subsequent cycles.

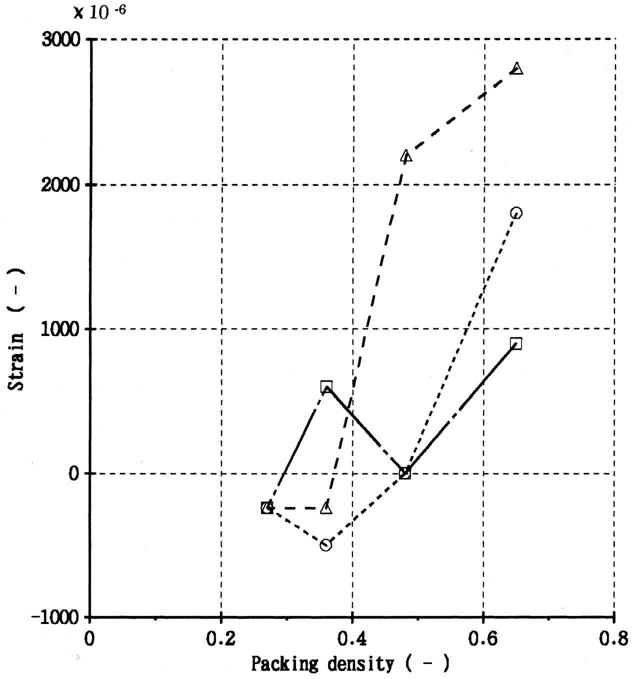

Fig. 3. The change of strain after 180 hydriding–dehydriding cycles as a function of packing density in the range of 0.27 to 0.65 in the various locations of the reactor.

The strain measured after 180 hydriding–dehydriding cycles as a function of packing density is shown in Fig. 3. The strain was increased with increasing packing density and the bottom edge was markedly affected by expansion of metal hydride in the case of a packing density over 0.48. The maximum value of 2800 μ-strain observed in this experiment was much lower than that of the maximum allowable load, which is 400 000–500 000 μ-strain for this stainless steel-made reactor wall. The value of the maximum stress in this experiment was about half that of the tensile strength of stainless steel.

Previously, it was presented that an appropriate packing density over 0.4 with rare earth series metal hydride is dangerous because the strain increases with increasing hydriding–dehydriding cycles and finally the reactor is ruptured. However, in our findings, once an elastic deformation far below the allowable limit of the reactor occurred, its deformation did not become larger anymore because the strain remained constant after some cycles. Although a much longer cycle experiment is needed to verify the strain change of the reactor, our experiment suggests, for reactor design, that a thin wall reactor which has the advantage of increasing the heat efficiency can be used for practical applications such as heat pumps.

Fig. 4 Fig. 5 show optical micrographs and scanning electron micrographs before and after 180 hydriding–dehydriding cycles of this alloy, respectively. As is shown in Fig. 4(b) and Fig. 5(b), the formation of metal hydride aggregates which consisted of a fine powder of a size of about 10 μm is recognized remarkably, after hydriding–dehydriding cycles. The particle size distribution of this alloy after 50, 180, 300 hydriding–dehydriding cycles was also measured in Fig. 6. It is shown that a relatively wide range of particle size reduction takes place during hydriding–dehydriding cycles and a mean grain diameter after 50,180,300 cycles becomes 9.8, 5.5, 5.8 μm respectively compared with an initial mean diameter of 150 μm. The grain size changes to a lesser extent after 50 cycles. This result indicates that once the elastic deformation of the reactor occurred during hydriding–dehydriding cycles, its deformation did not become larger anymore because the grain size of the alloy in the reactor changed to a lesser extent after subsequent cycles. It seems that the formation

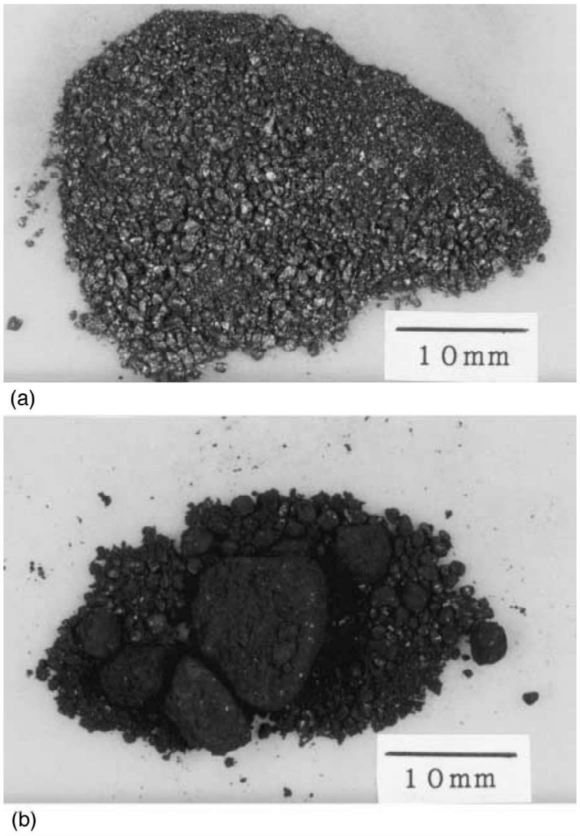

Fig. 4. Optical micrograph of $Ti_{0.71}Zr_{0.29}Mn_{0.8}CrCu_{0.2}$ alloy before (a), and after (b) 180 hydriding–dehydriding cycles.

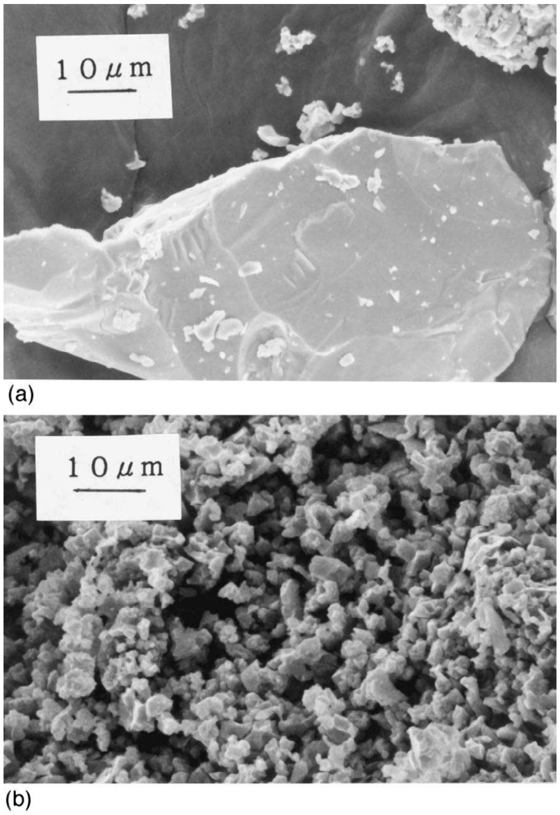

Fig. 5. Scanning electron micrograph of $Ti_{0.71}Zr_{0.29}Mn_{0.8}CrCu_{0.2}$ alloy before (a), and after (b) 180 hydriding–dehydriding cycles.

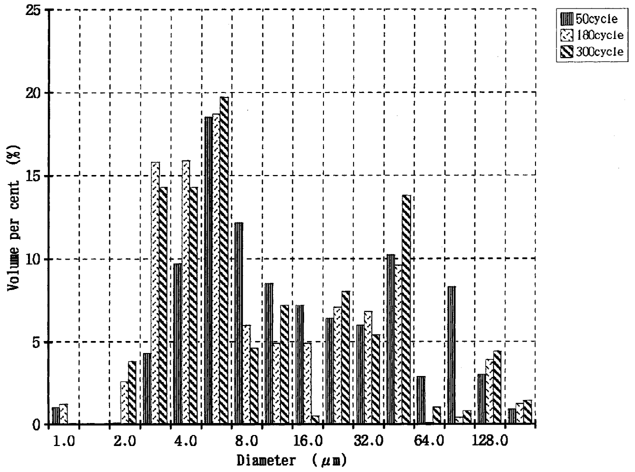

Fig. 6. The particle size distribution result of $Ti_{0.71}Zr_{0.29}Mn_{0.8}CrCu_{0.2}$ alloy after 50, 180, 300 hydriding–dehydriding cycles.

of metal hydride aggregates during cycling exerts a great influence on the advent of strain imposed to the reactor because the strain caused by expansion of the aggregate becomes larger than that of the fine grain itself. In order to evaluate the possibility of aggregate formation, we carried out the experiment to measure the angle of repose as an index of cohesion or friction properties of the metal hydride powder.

The results are shown in Fig. 7(a) and 7(b) as a function of hydrogen concentration in metal hydride and particle size, respectively. The repose angle was increased with increasing the hydrogen concentration in metal hydride, on the other hand, decreased with increasing the particle size.

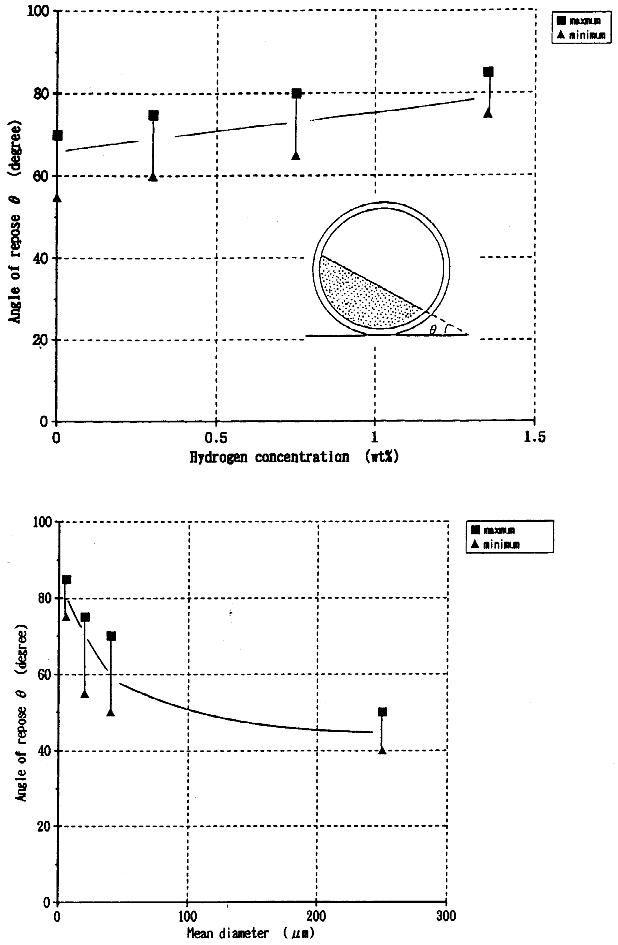

Fig. 7. The angle of repose as a function of hydrogen concentration in metal hydride (a) and particle size (b).

The aggregate formation tends to occur easily due to the increase of cohesion and friction between metal hydride powder during hydriding–dehydriding cycles.

4. Conclusion

Experimental investigations have been carried out in order to reveal the mechanical behavior of metal hydride reactor and the mechanism of the advent of strain in $Ti_{0.71}Zr_{0.29}Mn_{0.8}CrCu_{0.2}$ alloy. The conclusions can be summarized as follows.

1. Once the elastic deformation of the reactor occurred during hydriding–dehydriding cycles, its deformation did not become larger anymore because the grain size of the alloy in the reactor changed to a lesser extent after subsequent cycles.
2. The formation of metal hydride aggregates during cycles exerts a great influence on the advent of strain imposed on the reactor because the strain caused by expansion of the aggregate becomes larger than that of the fine grain itself.
3. The aggregate formation tends to occur easily due to the increase of cohesion and friction in the metal hydride powder during hydriding–dehydriding cycles.

Acknowledgments

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References

[1] F.E. Lynch and E. Snape, *Proc. 4th. Int. Hydrogen Energy. Conf.*, Vol. 3, Pergamon Press, Oxford, 1978, 1475–1524.

[2] Q. Wang, J. Wu, C. Chen and Z. Li, *J. Less-Common Met., 13* (1987) 339.

[3] T. Saito, R. Suzuki and M. Abe, *MRS Int. Mtg. Adv. Mats., 2* (1989) 143.