

## Synthesis of New Recyclable Materials based on the Active Disassembly

T. Yamamoto<sup>☆2</sup>, S. Ito<sup>☆1</sup>, A. Otsuki<sup>☆1</sup>, K. N. Ishihara<sup>☆1</sup> and P. H. Shingu<sup>☆1</sup>

<sup>☆1</sup>Graduate School of Energy Science, Kyoto University, Yoshidahonmachi Sakyo-ku, Kyoto 606-8501.

<sup>☆2</sup>Fac. Eng., Osaka University, 2-1 Yamadaoka Suita 565-0871

The purpose of this research is to propose an "active disassembly" material which can be recycled. The concept of this system is to synthesize a material includes an actuator that operates under special surroundings. In this research, terbium was used as an actuator because rare earth metals have a nature of absorbing hydrogen gas and the large volume change during absorbing hydrogen gas. The iron based material was formed, which includes Tb actuator of 2at% in Fe particle boundary. The only Tb actuator was triggered under hydrogen atmosphere and pulverized itself. The recycled materials could be obtained by sintering the pulverized material again at 1673K for 600s.

Key words: active disassembly, hydrogen, embrittlement

### 1. Introduction

The purpose of this research is to propose an "active disassembly" material which can be recycled. Fig.1 shows the flow chart of this system. The "active disassembly" means to disassemble industrial products by a disconnection and a release of restriction at the end-of-life, which is triggered by a physical treatment such as rapid quench, rapid change of magnetic field and so on. The concept has reported by C. B. Boks et al on recycling technology for the electronics and automotive industry<sup>1)</sup>, but few development of self-disassembly material has been reported.

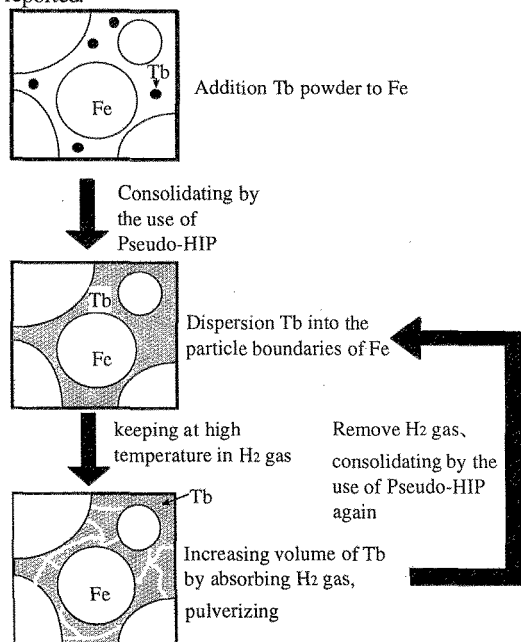


Fig.1 Flow chart of this system.

In this work, terbium was used as an actuator because rare earth metals have a nature of absorbing hydrogen gas and the volume change during absorbing hydrogen gas<sup>2)</sup>. Furthermore, it is easy to handle terbium in laboratory experiments because of the resistance of oxidation compared with other rare earth metals.

### 2. Experimental procedure

The elemental powders, Fe (-50  $\mu$  m, atomel 300M, Kobe steel ltd.) and Tb (250  $\mu$  m, Furuuch Chem. Corp.) pulverized approximately to 5  $\mu$  m by an auto agate mortar were used. The Fe-Tb powders were dry-mixed at the concentration of 2at% Tb. Cylindrical compacts (approximately 18mm in diameter and 12 mm long) were made in a stainless die with double acting rams at pressures of approximately 700MPa. The compact was then placed in the P-HIP (Pseudo-Hot Isostatic Press) equipment shown in Fig.2. It consists of a stainless steel pressure vessel 110mm inside diameter, 180mm outside diameter and 145 mm deep, filled with commercial casting sand (SiO<sub>2</sub>, average particle size: 100  $\mu$  m). Since sand is the pressure-transmitting medium and has a non-zero static shear resistance, the pressure obtained "pseudo isostatic"<sup>3)</sup>. The sample is placed in the center of vessel surrounded by a 20mm diameter Mo heating coil.

To remove gases, the system was preheated to 523K for 3.6ks, while evacuating the chamber to 5Pa using a vacuum pump with a mechanical booster and applying pressure of 100MPa through the casting sand.

The sample cut to cubic pieces of 5mm and polishing the surface, Hydrogenizing was processed at 673K under hydrogen flow condition.

The temperature was measured using W-Re5%/W-Re26% thermocouples. The thermocouple outputs were monitored by using acquisition recorder (DATALOGGER R7326A/B, ADVANTEST). The microstructures of samples were observed using SEM (JSM T5200, JEOL) and optical microscopy (OPTIPHOTO, Nikon) and phases were identified using X-ray diffraction (RINT2100CMJ, Rigaku). Hydrogen absorption was confirmed using DSC measurement (PERKINELMER, DSC7) under Ar flow condition at a heating rate 0.3K/s. The mechanical properties were evaluated by compression test (crosshead speed 3  $\mu$  m/s) and vickers hardness measurements (MVK-TYPE D, AKASHI).

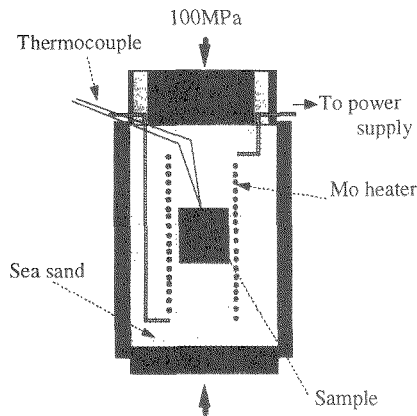


Fig.2 Schematic drawing of a Pseudo-HIP apparatus.

### 3. Experimental result

In this study, two sizes of Tb powder were used,  $5\ \mu\text{m}$  and  $250\ \mu\text{m}$  Tb, were used. Both cases, the concentration of Tb is 2 at%. In the case of  $5\ \mu\text{m}$  Tb powder, the sample was sintered at 1673K above the melting point of Tb for 600s in PHIP under vacuum condition. During sintering, Tb melted and uniformly spread into Fe particle boundary, as shown in Fig.3. In order to destruct this material as a "active disassembly" process, this sample was treated under hydrogen flow condition at 673K for 7.2ks. Fig.4 shows SEM and optical microscopic images of the sample before and after treating. Comparing the microstructure a)

with b), it can be seen that Tb operates as an actuator to crack on the sample surface. It is confirmed that only Tb rich phase (white part in the image) was pulverized [c),d)]. Furthermore, vickers hardness after treating decreased by 300MPa to 800MPa. Therefore, it indicates that the embrittlement of this sample caused by treating under hydrogen flow condition.

In order to confirm whether this material can be used again in the recycling process, this sample was pulverized using dies and was re-consolidated by PHIP. It is noted that microstructure of this sample was similar to that of Fig.3 as shown in Fig.5. It suggests that this material can be re-used by re-consolidation.

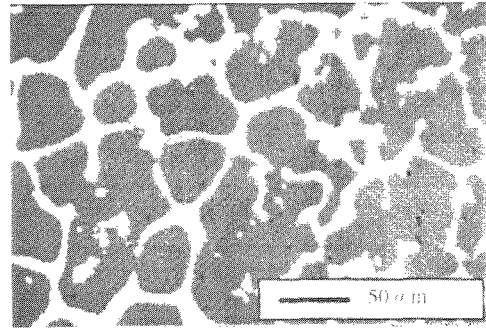


Fig.3 Scanning electron microscopic image of the sample sintered by the use of P-HIP.

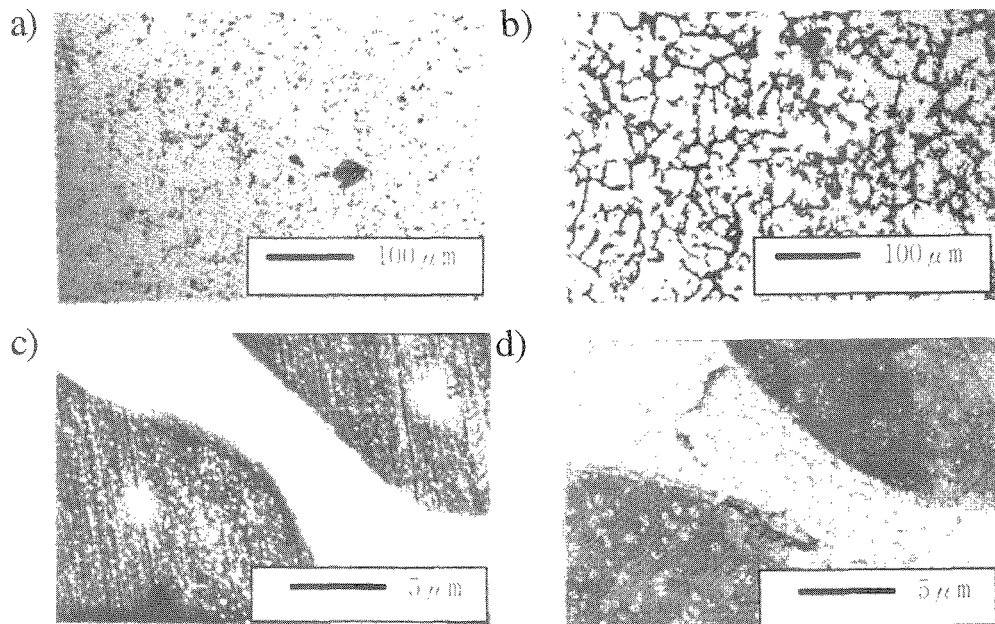


Fig.4 Optical micrographs a), c) and scanning electron microscopic images b), d) of the sample using  $5\ \mu\text{m}$  Tb powder sintered by the use of P-HIP, a)c) as HIPed and b)d) annealed under hydrogen flow condition.

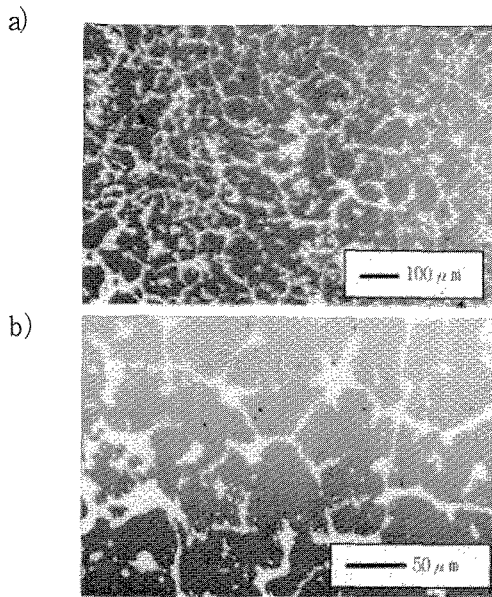


Fig. 5 Scanning electron microscopic images of the sample re-consolidated by the use of P-HIP after pulverizing a) low magnification and b) high magnification.

In the case of using 250 μm Tb powders, the sample was sintered at 1173K, below the melting temperature of Tb, for 86.4ks under vacuum condition. Fig.6 shows SEM images of the sample after hydrogen heat treatment. It is confirmed that Tb rich phase was pulverized and macro-cracks generated from Tb rich phase to Fe particle. Vickers hardness after the treatment decreased by 300MPa to 700MPa. Fracture toughness of compression after the treatment decreased by 150MPa to 300MPa as shown in Fig.7. Therefore, the sample was embrittled by treating under hydrogen flow condition in both 5 μm and 250 μm cases.

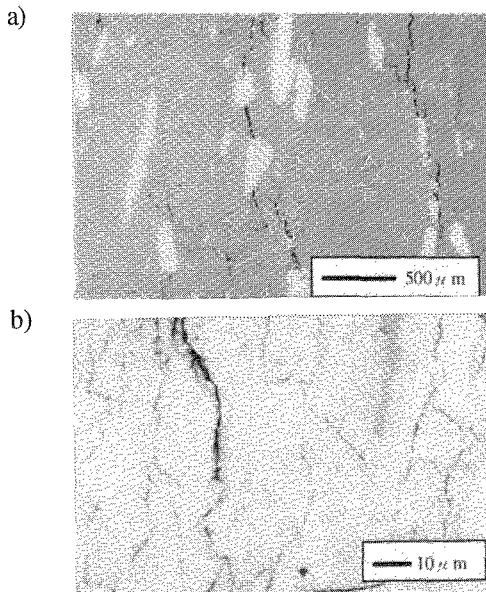


Fig. 6 Scanning electron microscopic image of the sample annealed at 673K for 1 hour under hydrogen flow condition a) low magnification and b) high magnification.

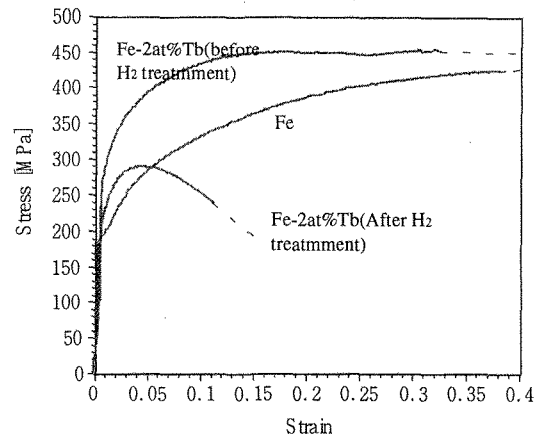


Fig. 7 Stress-strain curves of the samples using 250 μm Tb powders.

### 5. Discussion

Fig. 8 shows DSC thermograms of the sample using 5 μm Tb powder before and after treating under hydrogen flow condition. An exothermal peak attributed to the release of hydrogen gas is observed at about 573K. It suggests that hydrogen gas was absorbed in the sample during hydrogen heat treatment.

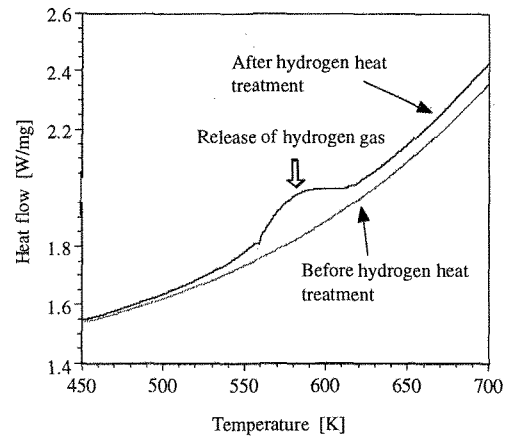


Fig. 8 DSC thermograms of sample before and after heat treatment Ar flow condition.

Fig. 9 shows cross section image of the same sample as in Fig.4. If the crack in Tb rich phase is the trace of hydrogen diffusion, this indicates that hydrogen diffused to 200 μm depth. Therefore, it is confirmed that diffusion of hydrogen was insufficient for pulverizing completely. Hence, diffusion coefficient of hydrogen into this sample was estimated. Diffusion coefficient can be calculated as follows<sup>9)</sup>,

$$x = \sqrt{2Dt}$$

where, x is diffusion distance, D is diffusion coefficient, and t is treating period. Fig. 10 shows the relationship of diffusion distance (x) and the square root of heat treatment period ( $t^{1/2}$ ). Diffusion coefficient was estimated  $0.95 \times 10^{-12} \text{ m}^2/\text{s}$ , and it means that treating for 259.2ks is needed to diffuse hydrogen to 1mm depth. According to literature, hydrogen diffusion coefficients of Fe and hydrogen storage

alloy ( $\text{LaNi}_3$ ) are  $1.93 \times 10^{-8} \text{ m}^2/\text{s}$  (673K) and  $3 \times 10^{-10} \text{ m}^2/\text{s}$  (423K) respectively<sup>7,8)</sup>. Diffusion coefficient measured in this work is smaller than those of iron and hydrogen storage alloy in spite of heating at higher temperature. Since the formation of Tb hydride should be very fast, a phase other than Fe and Tb in which the diffusion of hydrogen is slow can be formed at the interface between Fe and Tb. According to phase diagram of Fe-Tb system<sup>9)</sup>, there are four Fe-Tb intermetallics. Fe-Tb intermetallics can be formed to prevent diffusion of hydrogen though the trace of these intermetallics is not detected in XRD measurement.

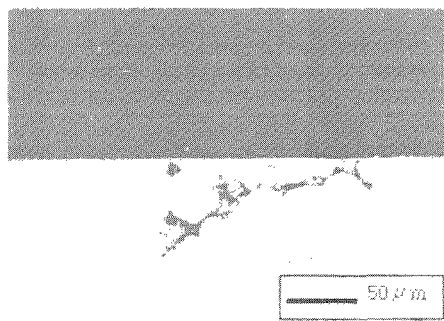


Fig. 9 Scanning electron microscopic image of cross section the sample using  $5 \mu\text{m}$  Tb powders after hydrogen heat treatment.

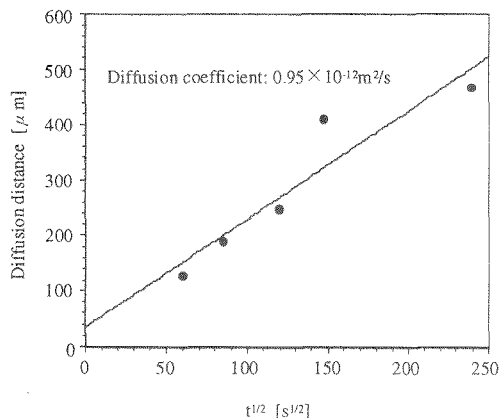


Fig. 10 Relationship of hydrogen diffusion distance and  $t^{1/2}$  in the sample using  $5 \mu\text{m}$  Tb powders.

## 6. Conclusion

It was observed that only Tb rich phase was pulverized and embrittlement of the sample in Fe-2at%Tb during hydrogen heat treatment.

It was possible to recycle the sample using  $5 \mu\text{m}$  Tb powder by pulverizing by the use of dies and re-consolidating.

## 7. Acknowledgment

This research was supported by "Distributed Autonomous Urban Energy System for Mitigating Environmental Impact (JSPS-RFTP97P01002)" in JSPS research project.

One of the authors (T. Y) wish to thank JSPS for cooperation.

## Reference

- 1) C. B. Boks, E. Tempelman: "Final report of the Delphi study on future disassembly and recycling technology for the electronics and automotive industry", TU Delft April 1997.
- 2) H. Uchida, T. Kuji: "Hydrogen storage alloy consisted of rare earth element", *Metal & Technology*, Vol.68, No.1, pp.29.
- 3) P. H. Shingu: "Internally heated Pseudo-HIP process", *New ceramics*, 2 (1990) 85-88.
- 4) P.H.Shingu, K.N.Ishihara: "A pseudo-HIP process applicable for the near-net-shape synthesis of inter-metallic compounds", *J. Jpn. Soc. Powder Powder-Metall. (Japan)*, 37(1990) 670-673.
- 5) T.Yamamoto, A.Otsuki, K.Ishihara, P.H.Shingu: "Synthesis of near net shape high density TiB/Ti composite", *Mater. Sci. Eng. A239-240* (1997) 647-651
- 6) N. Takeuchi, H. Ino and H. Furubayashi: "Metal physics", *NIKKAN KOUGYOU SHINBUN*, (1992) 37-38.
- 7) C. A. Ward, B. Farahkhsh, R. D. Venter: "Absorption Rate at the Hydrogen-Metal", *Z.Phys.Chem. Neue Folge*, 147(1986) 89-101.
- 8) E. Fromm, H. Speck, H. Jehn, G. Horz: "Physik Daten(Physics data.)" Karlsruhe: Fach informations zentrum Energie, Physik, Mathematik GmbH, Nr.5-13(1981).
- 9) H. Okamoto, P. R. Subramanian, L. Kacprzak, T. B. Massalski: "Binary Alloy Phase Diagrams", W. W. Scott, Jr, *ASM int.*, vol.2 (1993) 1778-1779

(Received December 16, 1999; accepted February 7, 2000)