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Hydrogen absorption by nanocrystalline and amorphous Fe–Ti with palladium catalyst, produced by ball milling

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The effects of microstructure on hydrogen absorption in FeTi are reported. Powders of FeTi with different microstructures (nanocrystalline and amorphous) were prepared by high-energy ball-milling. FeTi powders were also modified with small amounts (less than 1 wt%) of palladium catalyst to eliminate activation. Enhancements in hydrogen absorption for both nanocrystalline and amorphous FeTi powders were observed.

1. Introduction

FeTi alloy is a classic material for hydrogen absorption [1]. FeTi absorbs hydrogen by the formation of intermetallic hydrides: FeTiH (at a pressure of about 10 bar at room temperature) and $FeTiH_2$ with a higher but not well-defined plateau pressure. FeTi can also retain a small amount of hydrogen in solid solution (maximum 0.1 hydrogen atom per FeTi). However, as-made FeTi does not normally absorb hydrogen and so must be activated prior to hydrogenation. Activation of FeTi (usually as a powder) involves heating to 400–450 °C in vacuum and subsequent annealing in hydrogen at a pressure of about 7 bar, followed by cooling to room temperature and exposure to hydrogen at high pressure (35–65 bar). The activation process has to be repeated several times to obtain reproducible pressure–concentration isotherms. This complicated and energy-consuming activation process is one of the disadvantages of this material; a second problem is decrepitation of the crystalline FeTi during absorption/desorption cycles. To get around these problems with FeTi, different approaches have been used. One is to use amorphous FeTi, which may be made by sputtering [2], solid-state reaction in thin films or ball milling [3, 4]. Amorphous FeTi does not decrepitate, but unfortunately, the amount of usable stored hydrogen is reduced [4–7]. An alternative approach is to use nanocrystalline FeTi, in the hope that it may combine the absorption characteristics of the polycrystalline with the mechanical characteristics of the amorphous alloy. Nanocrystalline FeTi (with crystal sizes less than 10 nm) may be readily produced by ball milling [4] starting either from elemental powder mixtures (iron and titanium) or from the pre-melted intermetallic FeTi. The mechanism of the formation of nanocrystalline FeTi from elemental powders and the role of oxygen content in producing an amorphous phase, were recently presented [4]. Preliminary results of the hydrogen absorption by nanocrystalline FeTi [8] showed that the absorption mechanism was very sensitive to microstructure of the material and could be controlled by its modification (crystal size, amount of amorphous phase, etc.). Activation of the ball-milled FeTi powders was much easier than that for polycrystalline material [8]. Recently published results by Aoki *et al.* [9] on hydrogenation of ball-milled FeTi showed that FeTi absorbed hydrogen at room temperature without activation, when the powders were ball-milled in an inert gas atmosphere or in vacuum, and were not exposed to air before hydrogenation.

2. Experimental procedure

Nanocrystalline and amorphous FeTi powders were fabricated from elemental powders of iron (99.9%) and titanium (99.9%) by high-energy ball-milling technique. The milling was carried out using a high-energy ball mill from SPEX (Spex 8000). Powder mixtures were sealed in the WC vial under an argon atmosphere. Details of the experimental conditions for the formation of nanocrystalline and amorphous powders are presented elsewhere [4].

The powders of nanocrystalline and amorphous FeTi were modified with small amount of palladium catalyst during the course of ball-milling. A similar method for the fabrication of compositionally graded amorphous metallic materials was proposed by Harris *et al.* [10]. Ball-milled powders were characterized by X-ray diffraction technique using Nicolet–Stoe powder diffractometer (CuK_α and MoK_α radiation). Transmission electron microscopy was performed with a Philips CM20 (200 kV) combined with an energy-dispersive X-ray analyser (EDAX 9900) with a thin beryllium window. Hydrogen-sorption properties of the ball-milled powders and of the polycrystalline compound prepared by arc-melting were investigated by an automated gas titration system controlled by computer, similar to that described elsewhere [5].

3. Results and discussion

3.1. Role of microstructure in hydrogen absorption

Hydrogen absorption is very sensitive to the microstructure of FeTi. Fig. 1 shows pressure–concentration isotherms at room temperature for FeTi powder in three different states: polycrystalline, nanocrystalline and amorphous. The polycrystalline sample (prepared by arc-melting and activated in the conventional way) exhibits absorption of hydrogen into solid solution not exceeding 0.1 hydrogen atom per FeTi. At higher pressures, formation of FeTiH occurs, as reflected by a plateau at $p = 10$ bar. The amorphous sample exhibits a typical hydrogenation characteristic for materials in the amorphous state [5–7]. Instead of the well-defined plateau pressure, related to the formation of the FeTiH hydride in the crystalline alloy, hydrogen absorption gradually increases with increasing pressure. Nanocrystalline FeTi to some extent combines the two above absorption characteristics (Fig. 1). Because the crystals are as small as 6–7 nm [4, 8], the number of grain boundaries becomes important. In this material, the grain-boundary regions are highly disordered (or amorphous-like), as discussed elsewhere [11]. These disordered regions cause significant solubility of hydrogen which can be observed at low pressures (below the plateau pressure). Crystalline cores of the nano-grains give a plateau in the pressure–concentration isotherm due to the formation of the FeTiH hydride. The pressure of the plateau is, however, slightly lower than that for the polycrystalline alloy, as discussed previously [12].

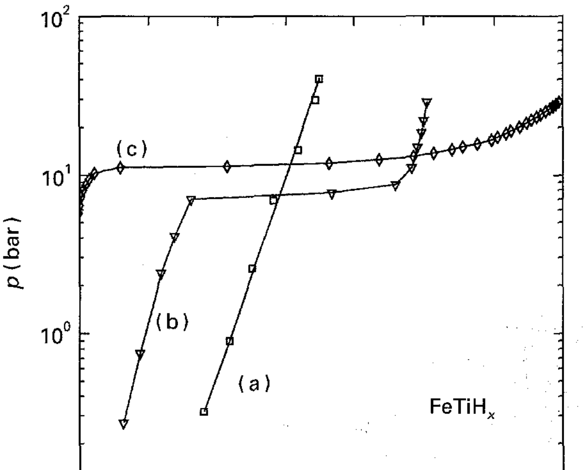

Figure 1 Room-temperature pressure–concentration isotherms (measured on absorption) for FeTi. (a) Amorphous sample showing continuous pressure increase, (b) nanocrystalline sample with crystallite size ~6–7 nm, and (c) intermetallic compound showing a plateau at ~10 bar.

It is important to note that the activation procedure prior to hydrogenation is much easier in the case of the ball-milled materials (even after storing in air), both amorphous and nanocrystalline, than that for the polycrystalline material. A single anneal at 400 °C for 1 h in vacuum was sufficient for nanocrystalline samples and annealing at 300° C for 0.5 h for amorphous samples. Easier activation of the ball-milled powders may be explained by the fact that ball-milling constantly creates new surfaces and ball-milled powders exhibit a high surface-to-volume ratio which enables the hydrogen to penetrate more easily.

3.2. Modification of FeTi with palladium catalyst

To improve hydrogen absorption of the ball-milled material, the powders were modified by introducing small amounts of palladium during the course of ball-milling. Microstructures of the powders were characterized by TEM. Nanocrystalline materials showed a particle size of about 0.5–2 μm. Each particle consisted of an agglomerate of very fine crystals of about 6–7 nm in size (consistent with the X-ray diffraction estimation from broadening of the peaks, after subtracting a contribution from strain). The presence of palladium was also revealed. Fig. 2 shows a transmission electron micrograph of the nanocrystalline material with a small particle of palladium attached to FeTi. The palladium particle consists of small (though several times larger than FeTi nanograins) crystallites of about 30 nm. It appears to be "mechanically attached" (cold-welded), without any evident alloying zone between palladium and FeTi. Analogously, palladium particles have been found on the surfaces of the amorphous FeTi powders, as shown in Fig. 3. Fig. 4 presents EDX spectra for the FeTi powder and for the palladium particle.

The addition of palladium to the ball-milled FeTi significantly enhances its hydrogenation characteristics. The FeTi amorphous or nanocrystalline powders (ball-milled and then stored in air) do not require any activation annealing. The powders are able to absorb hydrogen at room temperature with no need for protection against oxidation during handling and storing. Moreover, the kinetics of the hydrogen absorption are exceptional even during the first hydrogenation cycle, as shown in Fig. 5. Absorption of more than 0.3 hydrogen atom per FeTi is attained in 20 s and the maximum capacity of the absorbed hydrogen reaches 0.96 H/FeTi at a pressure of 12 bar. Pressure–concentration isotherms for the as–ball-milled nanocrystalline FeTi with palladium and for the palladium-free activated nanocrystalline powder (at 400° C, 1 h) are shown in Fig. 6. The absorption of hydrogen by the as-ball-milled FeTi with palladium is already high at low pressures, and the hydrogen uptake is about 0.6 hydrogen atom/FeTi at pressures lower than 1 bar. The origin of the absence of the well-defined plateau for the nanocrystalline sample with palladium is discussed elsewhere [11].

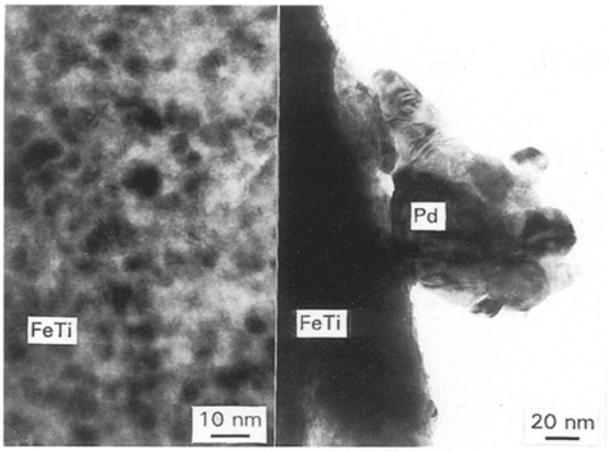

Figure 2 Transmission electron micrograph for nanocrystalline FeTi powder with a particle of palladium.

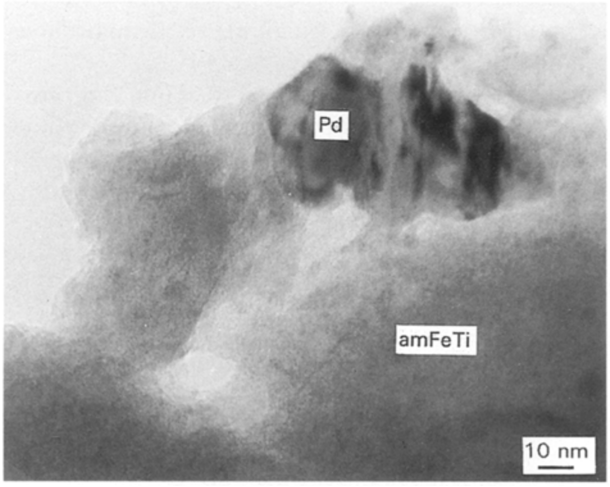

Figure 3 Transmission electron micrograph for amorphous FeTi with a palladium particle.

Palladium also enhances hydrogen absorption in ball-milled amorphous FeTi and eliminates the necessity for activation. Fig. 7 shows pressure–concentration isotherms for the as-ball milled amorphous FeTi with palladium (a) and without palladium (activated before hydrogenation at 300 °C for 0.5 h, b). For the as–ball–milled sample with palladium, the pressure–concentration isotherm is shifted towards a higher hydrogen concentration (by about 0.1 H/FeTi), which implies easier hydrogen absorption at lower hydrogen pressures.

The microstructure of the powders was examined by X-ray diffraction and TEM before and after hydrogenation cycles to check for crystallization or grain growth, caused by hydrogen absorption. No apparent degradation of the material occurred. The amorphous sample did not crystallize and the crystal sizes in the nanocrystalline samples remained the same. The particles of palladium also remained unchanged (Fig. 8) and could still be effective in the subsequent hydrogenation cycles. The effects of relaxation on hydrogen absorption in ball–milled FeTi with palladium catalyst will be presented in a forthcoming paper [11].

ELEM	INT	AT % ELEM
TIK	66.9	49.4
FEK	73.2	50.6

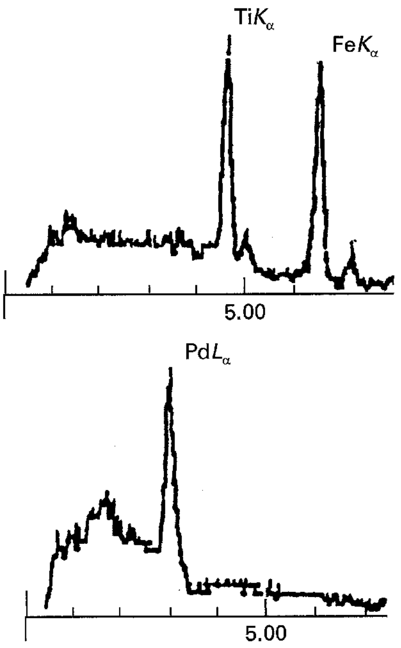

Figure 4 EDX spectra for the FeTi powder and for the palladium particle.

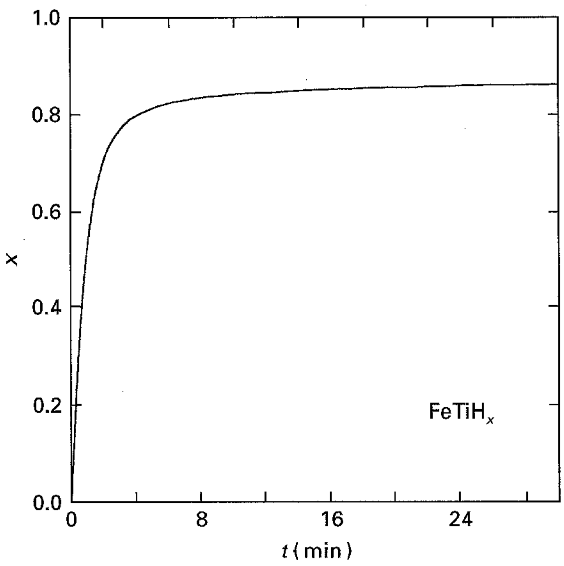

Figure 5 Rate of hydrogen absorption in the first hydrogenation cycle for nanocrystalline FeTi modified with palladium (room temperature, $p = 12$ bar).

The mechanism of palladium catalysis may be considered as based on the "spillover" effect [13, 14]. Palladium catalyses the dissociation of hydrogen molecules, and the adsorbed hydrogen atoms can then be "spilled over" on to the surface of the material. This mechanism of palladium catalysis eliminates the problem of surface contamination, which typically poisons the metal surfaces. Therefore, both preparation and handling of the material can be undertaken without too much concern about oxygen. The powders can be stored in air without any protection against oxygen

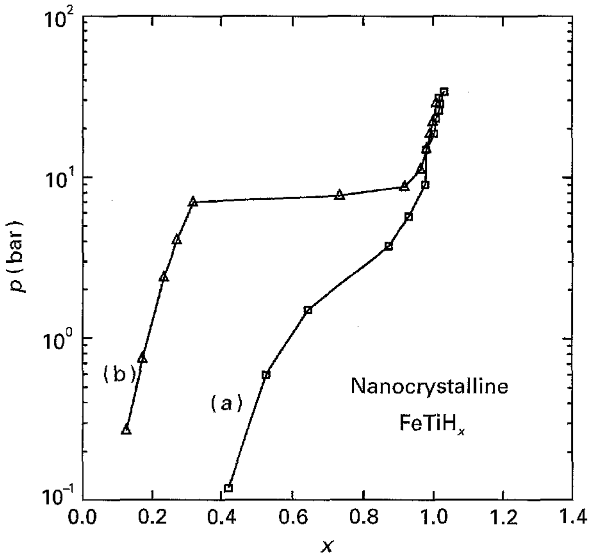

Figure 6 Room-temperature pressure–concentration isotherms for nanocrystalline FeTi (a) in the as-produced state (with palladium) and (b) annealed at 400 °C (without palladium).

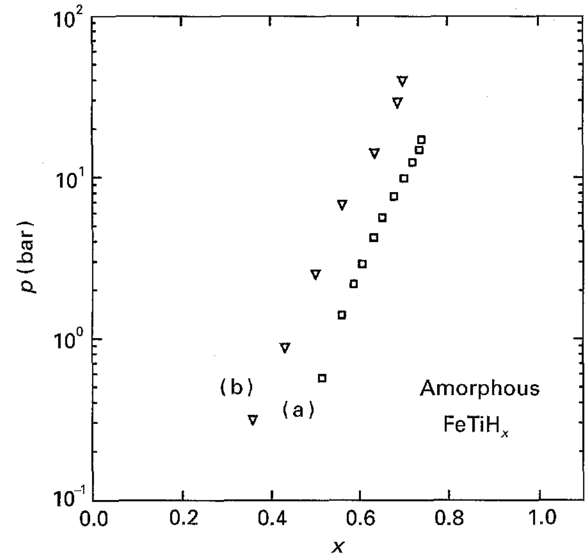

Figure 7 Room-temperature pressure–concentration isotherms for amorphous FeTi (a) (□) in the as-produced state (modified with palladium) and (b) (▽) activated at 300 °C (without palladium).

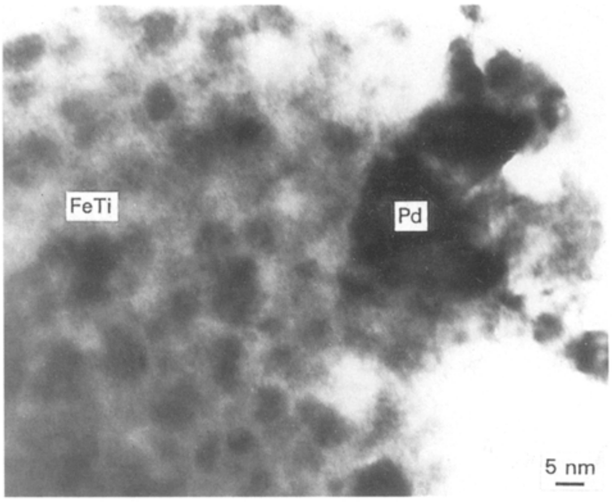

Figure 8 Transmission electron micrograph of nanocrystalline FeTi with palladium after hydrogen desorption.

contamination and humidity. More results on the catalytic effects of palladium on the hydrogen absorption (also for different ball–milled materials: Mg_2Ni, $LaNi_5$) are presented elsewhere [15, 16].

4. Conclusion

The pressure–concentration isotherms measured at room temperature for FeTi powder in three different states, polycrystalline, nanocrystalline and amorphous, were compared. The results showed that the pressure–concentration isotherms were sensitive to the structure of the absorbing material, especially in the hydrogen solubility range.

The catalytic effect of palladium gives an excellent activity for hydrogen absorption without the need for activation prior to hydrogenation, in both amorphous and nanocrystalline samples.

Enhancement of hydrogen absorption characteristics was also found for palladium-free amorphous and nanocrystalline FeTi powders in the as–ball–milled state.

References

1. J. J. REILLY and R. H. WISWALL Jr, *Inorg. Chem.* **13** (1974) 218.
2. K. NAKAMURA, *Scripta Metall.* **18** (1984) 793.
3. B. L. CHU, S. M. LEE and T. P. PERNG, *J. Appl. Phys.* **69** (1991) 4211.
4. L. ZALUSKI, P. TESSIER, D. H. RYAN, C. B. DONER, A. ZALUSKA, J. O. STRÖM-OLSEN, M. L. TRUDEAU and R. SCHULZ, *J. Mater. Res.* **8** (1993) 3059.
5. E. BATALLA, J. O. STRÖM-OLSEN, Z. ALTOUNIAN, D. BOOTHROYD and R. HARRIS, *Ibid.* **1** (1986) 765.
6. R. C. BOWMAN Jr, *Mater. Sci. Forum* **31** (1988) 197.
7. R. GRIESSEN, *Phys. Rev.* **B30** (1983) 7575.
8. L. ZALUSKI, S. HOSATTE, P. TESSIER, D. H. RYAN, J. O. STRÖM-OLSEN, M. L. TRUDEAU and R. SCHULZ, *Z. Phys. Chem.* **183** (1994) 45.
9. K. AOKI, H. AOYAGI, A. MEMEZAWA and T. MATSUMOTO, *J. Alloys Compounds* **203** (1994) L7.
10. J. H. HARRIS, M. A. TENHOVER and R. S. HENDERSON, US Pat. 4859 413 (1989).
11. L. ZALUSKI, A. ZALUSKA, P. TESSIER, J. O. STRÖM-OLSEN and R. SCHULZ, *J. Alloys Compounds* **227** (1995) 53.
12. P. TESSIER, L. ZALUSKI, Z.-H. YAN, M. L. TRUDEAU, R. BORMANN, R. SCHULZ and J. O. STRÖM-OLSEN, *Mater. Res. Soc. Symp. Proc.* **286** (1993) 209.
13. H. H. UCHIDA, H. -G. WULZ, and E. FROMM, *J. Less-Common Metals* **172–174** (1991) 1076.
14. R. KRAMER and M. ANDRE, *J. Catal.* **58** (1979) 287.
15. L. ZALUSKI, A. ZALUSKA and J. O. STRÖM-OLSEN, *J. Alloys Compounds* **217** (1995) 245.
16. L. ZALUSKI, A. ZALUSKA, P. TESSIER, J. O. STRÖM-OLSEN and R. SCHULZ, *Ibid.* **217** (1995) 289.

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