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Hydriding characteristics of palladium and platinum alloyed FeTi

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Effect of alloying on the hydriding characteristics of FeTi with noble metals such as platinum and palladium (5% by weight) has been investigated. It is observed that palladium has a favourable effect with respect to easy activation, decreased hysteresis and lower plateau pressures for hydrogen absorption and desorption process. For Pd/FeTi, a saturation composition of Pd/$FeTiH_{1.85}$ having the γ-phase, has been obtained. Unlike this, for Pt/FeTi, the total hydrogen absorption is decreased significantly and a saturation composition of Pt/$FeTiH_{1.5}$ having only β_2 phase, is observed.

1. Introduction

FeTi is proposed to be a potential hydrogen-storage material due to its low cost, relatively large value of $H/M \approx 1.0$ and reversible character for hydriding and dehydriding. A number of research workers have investigated the hydrogen storage characteristics of FeTi [1–3]. The two major drawbacks of this material are its difficult activation for hydrogen absorption and sensitivity to impurities in the hydrogen gas. A variety of substitutions both at iron and titanium sites, including excess titanium compositions, such as $FeTi_{1+x}$ with $x \leq 0.15$, have been investigated in detail to overcome both these problems [4–6]. It has been concluded that, in general, any substitution leads to an easy activation but its capacity for hydrogen storage is reduced. The nature of active centres responsible for hydrogen dissociation and the significance of the secondary phase produced for certain substituents, and dispersed in the FeTi matrix, in facilitating the hydride formation, has been discussed by many authors [7–9]. The existence of iron metal centres on the surface of FeTi and their role for initial hydrogen dissociation has been emphasized in a number of studies [10, 11].

Some of the important characteristics of any hydrogen-storage material which need to be considered for application, are the equilibrium plateau pressure for hydrogen absorption and desorption, the total hydrogen absorption capacity and the kinetics of hydride formation, which is a sensitive function of surface characteristics of the intermetallic compound. For FeTi and related systems, in general, two well-defined plateau pressures corresponding to α–β and β–γ hydride phase formation have been reported by most of the workers. From our earlier studies it is known [12] that for pure FeTi samples, the first plateau pressure for α–β hydride phase formation occurs at ≈ 8 atm hydrogen pressure followed by second plateau at ≈ 15 atm, corresponding to β–γ phase formation. Further, approximately 12–13 cycles of activation (comprising heating at ≈ 675 K in vacuum for 4 h followed by heating in hydrogen for 1 h and cooling to room temperature in a hydrogen atmosphere) are required to achieve the saturation composition of $FeTiH_{2.0}$ under a hydrogen pressure of ≈ 30 atm. For practical application, the system should show, in addition to a high value of hydrogen concentration, a lower value of desorption plateau pressure for β–α phase transformation preferably at ≈ 2 atm, and a minimum amount of pressure hysteresis between the absorption and desorption cycles.

Bronca *et al.* [13] have reported a significant improvement in the hydriding characteristics of FeTi when alloyed with 4.5% Misch metal which provides clean FeTi surface produced by cracks due to differential thermal expansion during the activation of FeTi. Noble metals, such as palladium and platinum, are known to have better hydrogen dissociation efficiency and do not easily become oxidized by impurities in the hydrogen gas. It was thought appropriate to study the effect of alloying small concentrations of palladium and platinum with FeTi, on the hydriding characteristics of FeTi, because these metals will provide additional centres for hydrogen dissociation. In the present communication the hydriding characteristics of FeTi (5% Pd and Pt) are reported.

2. Experimental procedure

FeTi buttons were prepared by arc melting the constituent elements of electrolytic grade, in pure argon. The buttons thus prepared were inverted and remelted four times. The intermetallics obtained were melted together with platinum or palladium (5% by weight) and remelted four times again for homogenization and cooled to room temperature in an arc furnace. No further annealing treatment was given to these samples. Powder X-ray diffraction measurements showed the formation of single phase with no change in diffraction pattern due to palladium and platinum alloying, suggesting that they have dispersed uniformly in the FeTi matrix.

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An all stainless steel apparatus was used for hydriding and dehydriding experiments. A freshly crushed sample weighing approximately 2–3 g was placed in the hydriding reactor, evacuated and heated at 675 K for 2 h with continuous evacuation. It was then exposed to hydrogen gas at ≈ 10 atm pressure for 1 h at 675 K. The sample was subsequently cooled to room temperature and loaded to 40 atm hydrogen pressure and kept under this pressure for 18 h for initial hydriding. In order to achieve the saturation hydrogen composition, the above procedure was repeated many times. The extent of hydrogen in the sample was also estimated by heating the sample to 775 K in a small quartz tube and measuring the volume of the hydrogen released. The hydrided samples were passivated at liquid nitrogen temperature using oxygen, before removal from the reactor. The kinetics of hydride formation was studied by applying a hydrogen pressure of ≈ 26 atm. X-ray diffraction and ^{57}Fe Mössbauer spectra were used to identify the hydrided phases formed. Mössbauer spectra have been least-square fitted using Lorenzian line shape to obtain the values of various Mossbauer parameters for different hydride phases. All isomeric shift values are reported with respect to iron metal at room temperature.

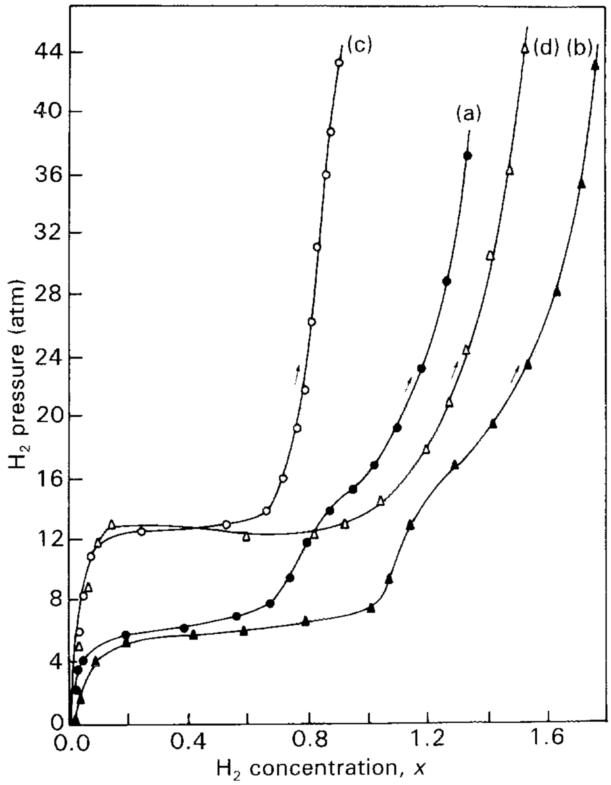

Figure 1 Hydrogen absorption curve for (a) Pd/FeTi for first cycle (●), (b) Pd/FeTi for third cycle (▲), (c) Pt/FeTi for first cycle (○) and (d) Pt/FeTi for fifth cycle (△).

3. Results and discussion

The unannealed sample of Pd/FeTi started absorbing a significant amount of hydrogen just after completion of the second activation cycle and attained a saturation composition of Pd/FeTi$H_{1.8}$ after the third hydriding and dehydriding cycle, as can be seen from Fig. 1a and b. For both these curves, clear indications of the α–β and β–γ phase formation are seen and the first plateau for α–β phase is observed at ≈ 6 atm. Unlike this, the unannealed sample of Pt/FeTi required about six cycles of activation before it started absorbing an appreciable amount of hydrogen with a saturation composition of Pt/FeTi$H_{0.9}$ at about 40 atm hydrogen pressure. This sample attained a saturation composition of $x \approx 1.55$ after the fifth cycle of hydriding and dehydriding. Further, there was no indication of β–γ hydride phase formation, as observed for Pd/FeTiH_x samples. The single plateau corresponding to α–β hydride phase formation is observed at ≈ 12 atm hydrogen pressure (Fig. 1c and d). A comparison of these results with those reported for FeTi by different authors, suggests that palladium alloying has favourably altered the hydriding characteristics of FeTi, compared to platinum alloying.

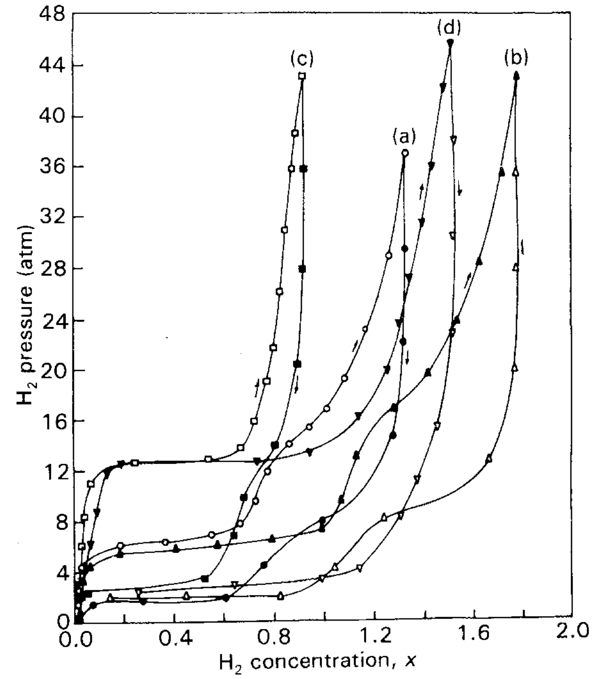

Figure 2 Hydrogen absorption–desorption curves for (a) Pd/FeTi for first cycle (○, ●); (b) Pd/FeTi for third cycle (▲, △); (c) Pt/FeTi for first cycle (□, ■) and (d) Pt/FeTi for sixth cycle (▼, ▽).

Fig. 2a and b show the typical results of hysteresis observed for Pd/FeTi samples in the first and third cycles of hydriding and dehydriding. From the figure it is clear that both during absorption and desorption cycles, clear plateau pressures corresponding to the α–β and β–γ phase formation are seen. The desorption plateau for β–α phase transformation observed at ≈ 2 atm is a very favourable feature from the application point of view. The representative hysteresis results observed for Pt/FeTi samples after the first and sixth cycle of hydriding and dehydriding are shown in Fig. 2c and d which exhibit much larger hysteresis effects compared to the Pd/FeTi system. Further, both hydrogen absorption and desorption results of Pt/FeTi suggest that the γ hydride phase is not formed for platinum alloyed samples despite the fact that a saturation composition of Pt/FeTiH$_{1.55}$ has been achieved.

Defects in the FeTi matrix are known to play an important role in its hydriding and dehydriding characteristics, because they affect the diffusion of hydrogen in the bulk material. Fig. 3a shows the typical hydrogen absorption curve for an unannealed and activated sample of Pd/FeTi and Fig. 3b shows the results obtained for the same sample after annealing it at 1075 K for 4 h in vacuum. A distinct change in the absorption pattern is observed and there is no indication of the two well-separated plateau pressures. Rather, a continuous variation in composition with hydrogen pressure is observed over the same region. The subsequent cycles of hydriding and dehydriding clearly showed the occurrence of two plateau pressures, as can be seen from Fig. 3c and d, which are quite similar to the curve shown in Fig. 3a. These results suggest that a direct conversion of α phase to γ hydride phase occurs as the diffusion of hydrogen in the annealed sample of Pd/FeTi sample is reduced, due to elimination of defects. This leads to the formation of γ phase on the surface with α phase inside the bulk matrix which transforms to γ phase with increase in hydrogen pressure and duration of hydriding. Unlike this, the material with lattice defects facilitates the migration of hydrogen through the bulk, and conversion of α phase to β phase followed by γ phase formation takes place on increasing the hydrogen pressure. This observation is in agreement with the results reported by Reilly *et al.* for FeTi [14].

Fig. 4 shows two representative curves exhibiting the time dependence of the hydride formation under an initial hydrogen pressure of approximately 26 atm for both palladium and platinum alloyed samples of FeTi after the fourth and fifth cycles of hydriding and dehydriding, respectively. The behaviour for palladium- and platinum-doped samples is quite different. Whereas the palladium-doped sample attained the saturation composition of $x \approx 1.4$ in approximately 20 min, for the platinum sample an incubation period of approximately 20 min is required before it starts absorbing hydrogen appreciably. Further the kinetics is faster for the palladium-doped sample compared to that of the platinum-doped sample. The lower value of saturation composition in these experiments compared to that shown in Fig. 2, arises due to insufficient final pressure of hydrogen in the gas manifold and hydriding reactor, and is in agreement with the results reported in Figs 1 and 2, respectively.

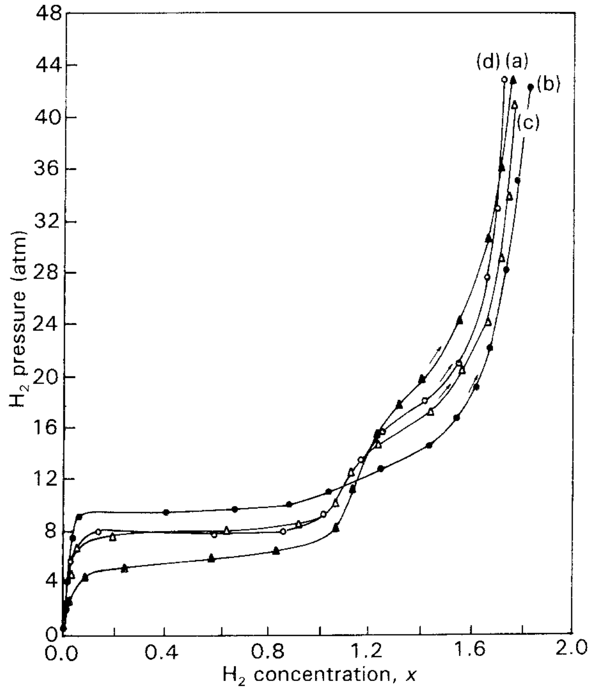

Figure 3 Hydrogen absorption curves for Pd/FeTi (a) for an activated sample after the second cycle of hydriding and dehydriding, (b) after annealing the same sample at 1075 K for 4 h, (c, d) subsequent cycles of hydrogen absorption for the same sample.

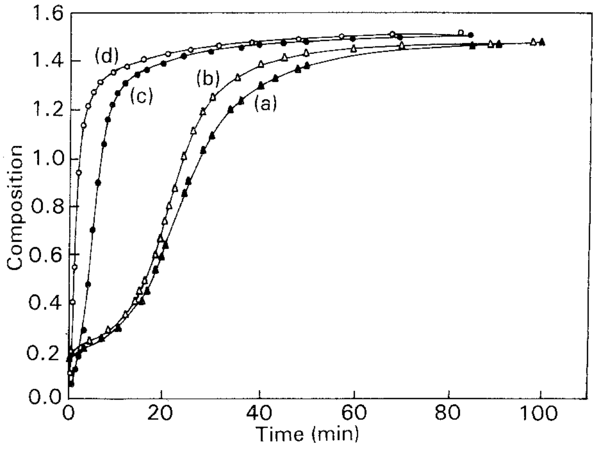

Figure 4 Time dependence of hydride formation for (a) Pt/FeTiH$_x$ (seventh cycle) (b) Pt/FeTiH$_x$ (eighth cycle) (c) Pd/FeTiH$_x$ (eighth cycle) (d) Pd/FeTiH$_x$ (ninth cycle).

Fig. 5 shows the representative region of the X-ray diffraction pattern of FeTi samples doped with palladium and platinum before and after hydride formation. From this figure it is clear that with palladium or platinum alloying, the cell parameter has increased slightly and there is no evidence of secondary phase formation ($a = 0.2975$, 0.2984 and 0.2991 nm for FeTi, Pt/FeTi and Pd/FeTi samples, respectively). On hydriding, the palladium- and platinum-doped samples showed significantly different results. Whereas Pd/FeTiH$_x$ showed the coexistence of both γ and β phases, the Pt/FeTiH$_x$ sample showed uniform hydriding and the hydrided β phase has $a = 0.3088$ nm, $b = 0.4497$ nm and $c = 0.4382$ nm. According to Reidinger *et al.* [15] there are two discrete phases present in the orthorhombic β phase region, namely β_1 and β_2, which correspond to the hydrogen compositions of $x \approx 1.0$ and 1.4, respectively, and are formed during the desorption and absorption cycles, respectively. Unlike this, other authors [16] believe that in the β phase region, there is continuous expansion of the orthorhombic unit cell with increasing hydrogen concentration, and β_1 and β_2 phases reported by Reidinger *et al.* are the extreme compositions of the β hydride phase region. Our sample of Pt/FeTiH$_x$ is similar to the β_2 phase of Reidinger *et al.* [15]. It may be appropriate to mention that the hydrided sample of Pd/FeTiH$_x$, after exposure to atmospheric pressure for few days, was transformed to β phase with $a = 0.2881$ nm, $b = 0.4541$ nm

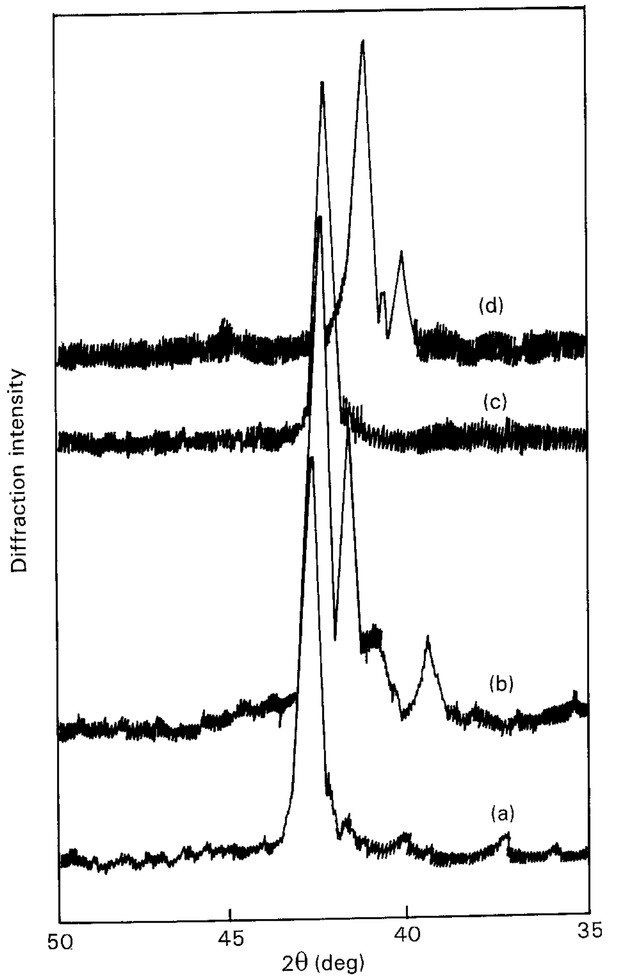

Figure 5 Selected region of powder X-ray diffraction pattern for (a) Pd/FeTi, (b) Pd/FeTiH$_{1.85}$, (c) Pt/FeTi, and (d) Pt/FeTiH$_{1.5}$.

and $c = 0.4302$ nm. These observations suggest that the samples are losing hydrogen on exposure to the atmosphere. Thus the suggestion that there is continuous variation of unit cell parameters with hydrogen composition in the β phase region is substantiated from the present results.

Mössbauer spectroscopy has been found to be an effective technique to distinguish between the different phases of FeTiH$_x$ as the values of isomeric shift and quadrupole splitting are distinctly different for the three hydrided phases. Fig. 6a, b and d show the ^{57}Fe Mössbauer spectra recorded for FeTi, Pd/FeTi and Pt/FeTi samples, respectively, recorded before hydriding. The value of isomeric shift, $\delta = -0.13$ mm s^{-1}, obtained from the analysis of these spectra is in agreement with the value reported earlier for FeTi samples. The hydrided sample of FeTi(Pd)H$_{1.8}$ showed the presence of γ phase as inferred from the observed values of $\delta = +0.26\ \mathrm{mm\,s^{-1}}$ and $\Delta_{\mathrm{Eq}} = 0.22\ \mathrm{mm\,s^{-1}}$. However, the hydrided sample of FeTi(Pt)H$_{1.5}$ showed the spectrum characteristic of β phase with $\delta = -0.02\ \mathrm{mm\,s^{-1}}$ and $\Delta_{\mathrm{Eq}} = 0.25$ mm s^{-1}. Further, the spectrum of the Pd/FeTiH$_x$ sample after storing for a few days was found to be characteristic of β phase with $\delta \approx 0.01\ \mathrm{mm\,s^{-1}}$ and $\Delta_{\mathrm{Eq}} = 0.19$ mm s^{-1}. Thus the results of Mössbauer spectroscopy are in perfect agreement with what has been observed by X-ray diffraction investigations and inferred from hydriding characteristics of these samples.

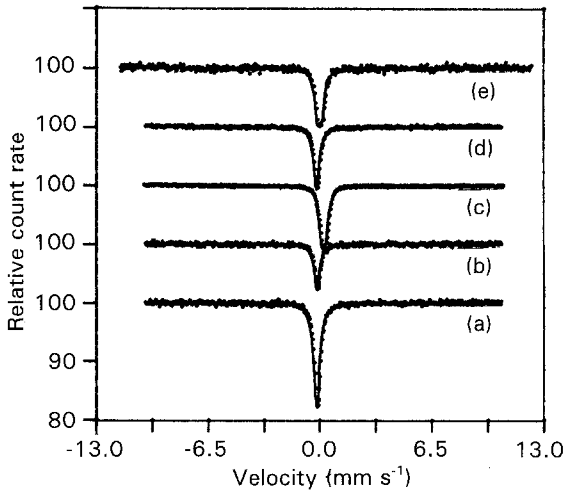

Figure 6 ^{57}Fe Mössbauer spectra of (a) FeTi, (b) Pd/FeTi, (c) Pd/FeTiH$_{1.85}$, (d) Pt/FeTi, and (e) Pt/FeTiH$_{1.5}$, recorded at room temperature.

The role of surface modifications during activation of FeTi has been discussed by many authors [17] and, based on Auger electron spectroscopy measurements, it has been suggested that during the activation process, surface segregation takes place for FeTi and the outermost few layers become richer in titanium which also takes up oxygen. Below these layers there is iron enrichment which is metallic in nature, as seen by conversion electron Mössbauer spectroscopy [18]. With a view to testing if palladium or platinum enrichment is also taking place on the surface during activation and hydriding and dehydriding process, Auger electron spectra of the original and hydrided samples have been recorded, and no evidence for the segregation of platinum and palladium on the surface was observed in this study.

An important observation of this study is the significant difference in the hydriding characteristics of palladium- and platinum-doped FeTi samples. The atomic size of the substituents is known to affect the hydrogen storage capacity and activation behaviour of FeTi, because the strains produced in the lattice by the substituents affect the diffusion of hydrogen in the matrix and the mechanism of β_1–β_2 and γ phase transformation. The substituents with atomic radii larger than that of iron or titanium show a decrease in total hydrogen absorption capacity. This may be a possible explanation for the observed difference in the behaviour of palladium and platinum alloying, because the atomic radii of palladium and platinum are slightly different.

In conclusion, the present work investigated the effect of alloying of 5% Pt and Pd on the hydriding characteristics of FeTi, and it is shown that addition of palladium has quite a favourable effect on the properties of FeTi as regards its easy activation, decrease in absorption desorption pressures and reduced hysteresis effects.

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