Journal of Alloys and Compounds 253–254 (1997) 238–240

Hydrogenation characteristics of $TiFe_{1-x}Pd_x$ ($0.05 \leq x \leq 0.30$) alloys

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Received 13 August 1996

Abstract

Pseudobinary $TiFe_{1-x}Pd_x$ ($0.05 \leq x \leq 0.30$) alloys have been investigated on their crystal structure and hydriding behavior. The lattice constant increased with an increase in the substituted amount of Pd with maintaining the CsCl type crystal structure. The partial substitution by Pd with superior catalytic and hydriding natures were effective for mitigation of their activation conditions to a considerable extent. The substitution resulted in lowering the plateau pressures ascribed to formation of the monohydride in the PCT diagrams.

Keywords: TiFe-based alloy; Palladium; Metal hydride; Hydriding property; Activation condition

1. Introduction

Intermetallic TiFe alloy has been a prime candidate material for hydrogen storage in the form of a metal hydride since Reilly and Wiswall found its hydrogen-absorbing capability [1]. However, the alloy generally requires heating to about 670 K under a high pressure of hydrogen for initial activation. Although it has been suggested that metallographic modifications by addition or partial substitution with the constituent or other elements and surface modifications with catalytically active elements such as palladium are effective for facilitating the initial activation [2–7], the difficulty in the activation treatment is still a major drawback for TiFe-based alloys. In the present study, partial substitution for the Fe by Pd having superior catalytic and hydriding natures has been examined in an attempt to improve hydrogenation characteristics of TiFe alloy.

2. Experimental

Alloy samples were prepared from the component metals of titanium (99.8% purity), iron (99.9%) and palladium (99.9%) by arc-melting in an atmosphere of a high purity argon. The ingots were turned and remelted several times, and then annealed under vacuum ($<1.33 \times 10^{-4}$ Pa) at 1273 K for 24 h to be homogenized. The pulverized alloys with particle sizes from 100 to 150 μm and those below 100 μm were used for hydrogen absorption measurements and crystal structure examinations by X-ray powder diffraction (XRD) analysis, respectively. For activation, the pulverized alloys were heated in a reactor for more than 2 h at a hydrogen pressure of 3.5 MPa and temperatures from 423 to 723 K. The pressure–composition isotherms (PCT diagrams) were measured at temperatures from 273 to 353 K and pressure from 1.0×10^{-3} to 3.3 MPa by use of an automated Sieverts' type apparatus.

3. Results and discussion

Fig. 1 shows the XRD profiles of $TiFe_{1-x}Pd_x$ ($0.05 \leq x \leq 0.30$) alloys. A typical diffraction pattern of the CsCl type (B2) structure was observed for each alloy. As shown in Fig. 2, the lattice constants increased with an increase in the amount of Pd, varying along a straight line connecting between the two lattice constants of TiFe ($a = 0.2976$ nm) and β-TiPd ($a = 0.3180$ nm) alloys. From these results, it is evident that the lattice volume is expanded by the partial substitution by Pd for the Fe without changing the crystal structure.

Temperatures above 453 K were required in order to activate the Pd-substituted alloys in an atmosphere of hydrogen at 3.5 MPa. Fig. 3 shows hydriding curves at 273

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PII S0925-8388(96)02925-8

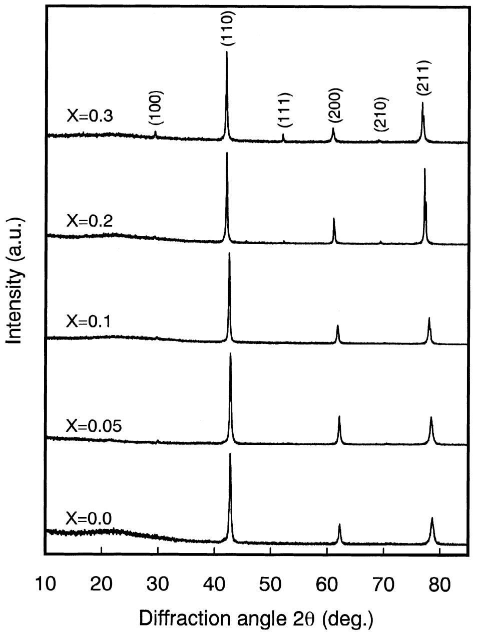

Fig. 1. X-ray diffraction pattern of $TiFe_{1-x}Pd_x$ ($0 \leq x \leq 0.3$) alloys.

K for TiFe, $TiFe_{0.95}Pd_{0.05}$ and $TiFe_{0.9}Pd_{0.1}$ alloys which were treated under the condition of a hydrogen pressure of 3.5 MPa and a temperature of 453 K for 2 h. Both the $TiFe_{0.95}Pd_{0.05}$ and $TiFe_{0.9}Pd_{0.1}$ alloys were immediately hydrogenated to form their hydrides with an atomic hydrogen to metal ratio above 0.8 within 12 min, whereas, the TiFe alloy did not react with hydrogen. Owing to the presence of Pd with superior catalytic and hydriding characteristics, passivating oxide layers on $TiFe_{1-x}Pd_x$ alloy surfaces would be more easily activated by surface segregation and chemical reduction than those on TiFe alloy surfaces. It has been confirmed that the partial substitution by Pd for the Fe is much effective for mitigating the initial activation condition of TiFe alloy.

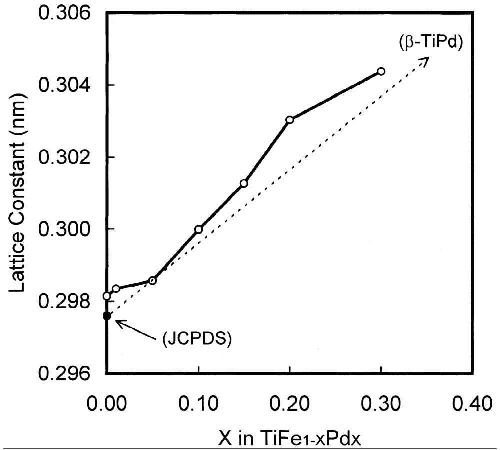

Fig. 2. Change in the lattice constant with Pd concentration (x) for $TiFe_{1-x}Pd_x$ alloys. Dotted line connects the lattice constants of TiFe and β-TiPd alloys.

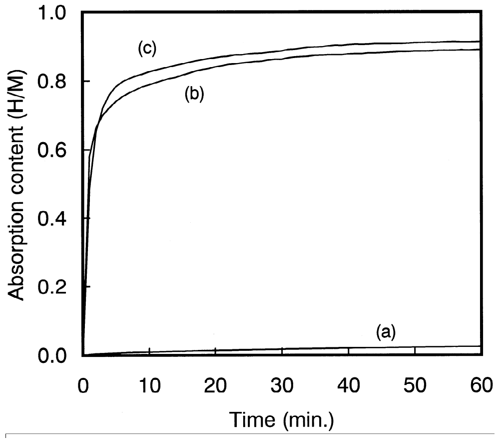

Fig. 3. Hydriding curves for (a) TiFe, (b)$TiFe_{0.95}Pd_{0.05}$ and (c) $TiFe_{0.9}Pd_{0.1}$ alloys at a hydrogen pressure of 3.5 MPa and temperature of 273 K.

Fig. 4 shows the PCT diagrams of TiFe, $TiFe_{0.95}Pd_{0.05}$, $TiFe_{0.9}Pd_{0.1}$ and $TiFe_{0.8}Pd_{0.2}$ alloys at 273 K.

Two plateau regions ascribed to the formation of the monohydride (β) and dihydride (γ) phases were obviously observed, though the hydrogen absorption capacities of the two phases were not significantly affected by partial substitution of Pd. The plateau pressure of the β-phase decreases with an increasing content of Pd, whereas that of

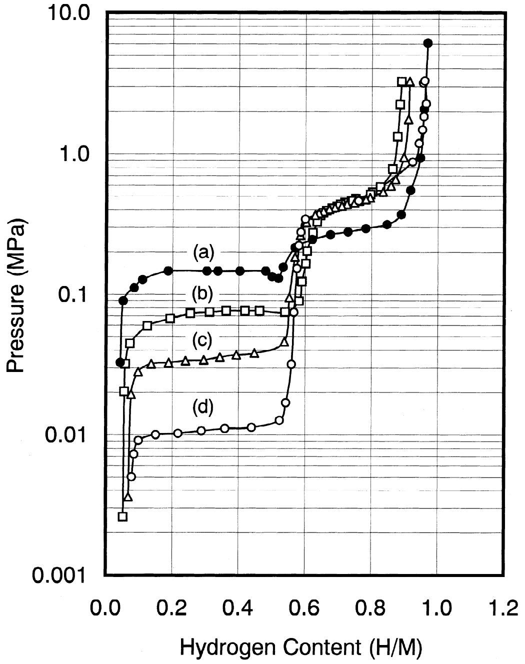

Fig. 4. PCT diagram in hydrogen desorption for (a) TiFe, (b) $TiFe_{0.9}Pd_{0.05}$, (c) $TiFe_{0.9}Pd_{0.1}$ and (d) $TiFe_{0.8}Pd_{0.2}$ alloys at 273 K.

the γ-phase is almost independent of the Pd content. It is considered that the expansion of the interstitial sites in the crystal lattices by partial substitution of Pd with a larger atomic radius than Fe contributes to the stabilization of only the monohydride.

4. Conclusion

Partial substitution by catalytically active Pd for the Fe is effective for lowering the activation temperature of intermetallic TiFe alloy. The substitution increases the lattice volume with maintaining the CsCl type crystal structure in the composition range from $TiFe_{0.95}Pd_{0.05}$ to $TiFe_{0.7}Pd_{0.3}$, and results in lowering the plateau pressures ascribed to formation of the monohydride in the PCT diagrams.

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