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Journal of Alloys and Compounds 253–254 (1997) 232–234

Journal of ALLOYS AND COMPOUNDS

Hydrogenation and phase structure of Ti–Fe–V alloys

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Abstract

Hydrogenation behavior and phase structures of some Ti–Fe–V ternary alloys were studied. Three different crystal structures, namely, a bcc, a CsCl-type and a C14 Laves phase structure were found. The atoms in the C14 Laves phase $TiFe_2$ could be partially substituted by vanadium atoms without changing its structure. It was found that the C14 Laves phase structure region was expanded nearly to the center of the Ti–Fe–V ternary phase diagram. Lattice parameters of the alloys increased almost in proportion with increasing average atomic size of the constituent elements. It was also found that hydrogen storage capacity at a constant pressure increased with increasing the degree of vanadium substitution. The pressure–composition (P–C) isotherms of the C14 Ti–Fe–V alloys strongly sloped and they had no flat plateau. The storage capacity of C14 Laves phase Ti–Fe–V alloy was optimized to be 1.0 at the chemical composition of $TiFeV_{0.7}$.

Keywords: Ti–Fe–V alloy; Laves phase; $TiFe_2$; P–C isotherms

1. Introduction

There are two intermetallic compounds in the Ti–Fe binary alloy system. One is TiFe, which has a CsCl type structure. The other is $TiFe_2$, which has a C14 Laves phase structure. Although the former reversibly absorbs and desorbs a large amount of hydrogen under ambient conditions, the latter is inactive to hydrogen [1]. In the Ti–Fe–V ternary alloy system, only Ti–V rich alloys [2,3] and Ti–Fe based ones [1,4] have been practically attractive materials, because of their high storage capacities.

However, hydrogenation behavior of many intermetallic compounds are highly modifiable in various ways. Actually, many kinds of hydrogen storage alloys were developed and their hydrogenation characteristics were optimized by metallurgical methods. Considering the affinities of constituent elements to hydrogen, the intermetallic compound, $TiFe_2$, may have potential to form a hydride.

In the present work, we attempted to modify the hydrogenation characteristics of $TiFe_2$ by partial substitution with vanadium. The relation among lattice parameters, chemical compositions and P–C isotherms were investigated.

2. Experimental

The alloy ingots were prepared by arc melting of high-purity metals. Each ingot was melted and solidified in an water-cooled copper crucible under an argon atmosphere. The as-cast ingots were then pulverized into powders with an average particle size smaller than 100 μm. Lattice structures of the alloys were studied by X-ray powder diffraction, using Cu Kα radiation with a carbon monochromator. Lattice parameters were determined by the least square method (LSM), using the diffraction angles, 2θ, of several peaks in the profile.

The initial hydrogenation (activation process) of these alloys is not so easy as compared with rare earth based alloys. The reason is thought to be attributed to a kind of blocking effect of surface oxides. In order to remove the oxides, the alloy particles were etched by a dilute aqueous HF solution. Immediately after the HF treatment, the particles were coated by a small amount of copper by a chemical plating method [5], in order to suppress re-formation of oxides.

The alloys were activated by keeping them under a 3.0 MPa hydrogen atmosphere, at 523 K for 3 h. After a complete activation, pressure–composition (P–C) isotherms of hydrogenation were determined by an automated Sieverts' type apparatus.

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0925-8388/97/$17.00
PII S0925-8388(96)03028-9

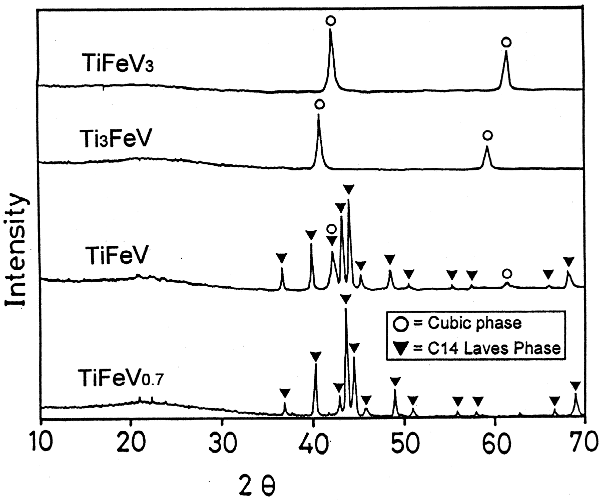

Fig. 1. X-Ray diffraction profiles. Target=Cu, 40 kV/150 mA.

3. Results and discussion

3.1. Crystal structures

The crystal structure of the ternary alloy system was found to be rather simple. The typical X-ray diffraction profiles obtained are shown in Fig. 1. The structures found in the present work were, a C14 Laves phase structure, a cubic (α-iron type) structure, another cubic (CsCl type) structure and mixtures of two of the three alloys. The resulting ternary phase diagram is shown in Fig. 2.

The alloys with the α-iron structure were thought to be Ti-substituted Fe–V solid solutions. Similarly, the CsCl-type alloys were thought to be V-substituted TiFe alloys, and the C14 alloy were to be V-substituted $TiFe_2$ alloys. In the Fe–V binary system, another phase which is known as σ-phase exists, however, it did not appear in the alloys studied in the present work.

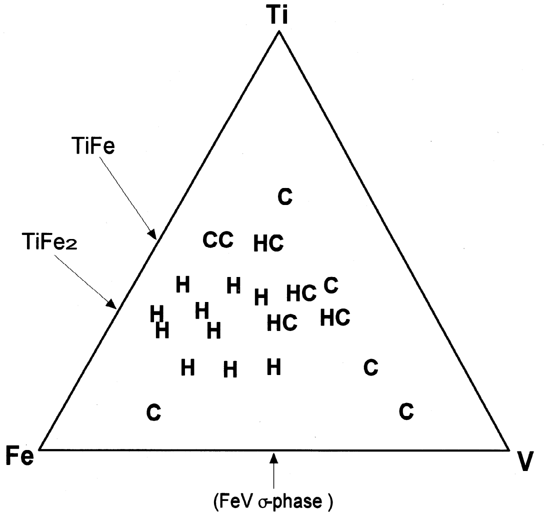

Fig. 2. Phase diagram of Ti–Fe–V ternary alloy system. The symbols mean: CC, two cubic phase (α-V/Fe type+CsCl type); C, cubic (α-V/Fe type); HC, hexagonal+cubic; H, hexagonal (=C14 Laves phase).

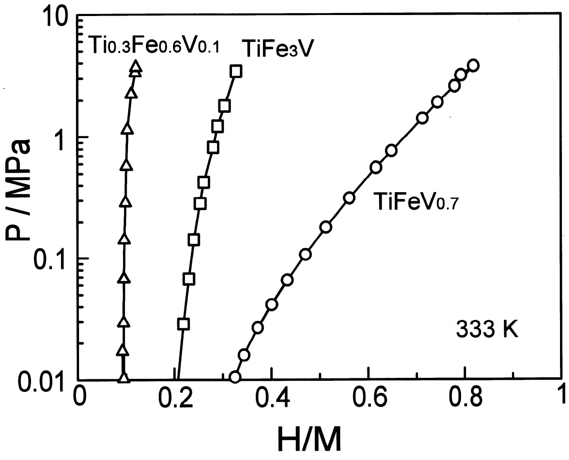

Fig. 3. P–C isotherms (desorption parts) of Ti–Fe–V alloys with C14 Laves phase structure.

3.2. Hydrogenation

The typical pressure–composition (P–C) isotherms at 333 K for 3 Laves phase alloys are shown in Fig. 3. Hydrogen dissociation pressure decreased with increasing the amount of vanadium substitution. Fig. 4 shows P–C isotherms of the alloy $TiFeV_{0.7}$. Some cubic alloys in this ternary system (in the Fe-poor region) have been reported to have flat plateaus [3], however, the isotherms of these Laves phase alloys strongly sloped and did not have flat plateaus. This means that the hydrides of these C14 Laves phase alloys are of a solid solution type, similar to the case of amorphous materials. The energy of the hydrogen site in the hydride was thought to have a large deviation. The steep tangent in the isotherm at 333 K suggests that the storage capacity of this alloy saturates at $H/M=1.0$.

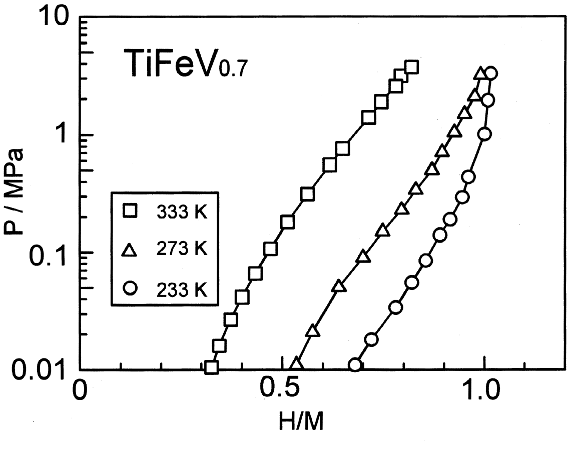

Fig. 4. P–C isotherms of $TiFeV_{0.7}$ alloy.

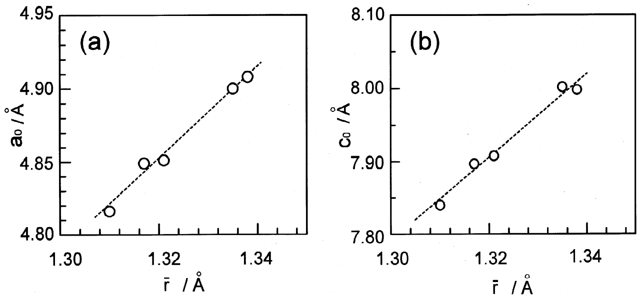

Fig. 5. Lattice parameters vs. average atomic size ($\bar{r}$) plots. (a) a_0 vs. $\bar{r}$; (b) c_0 vs. $\bar{r}$. Average atomic size $\bar{r}$ is calculated by the following equation:

$$\bar{r} = \sum_{x=\mathrm{Fe,Ti,V}} c_x \cdot r_x,$$

c_x = atomic fraction of each element, r_x = atomic radius, $r_{\mathrm{Fe}} = 1.24$ Å, $r_{\mathrm{Ti}} = 1.45$ Å and $r_{\mathrm{V}} = 1.31$ Å.

3.3. Lattice parameters

The lattice volume of the C14 Laves phase increased with increasing average atomic size of the alloy. Fig. 5(a) and Fig. 5(b) show the lattice parameters vs. average-atomic-size plots for 5 alloys with C14 Laves phase structures. These figures suggests that Vegard's Law is well satisfied, similar to the case of Ti–Zr based multi-component alloys [6].

The elemental substitution in $TiFe_2$ by vanadium is thought to have two effects. The first one enhances the cell volume and, consequently, expands the accommodation site of hydrogen in its hydrides. The second one increases the affinity of the alloy to hydrogen. Both of these effects are expected to increase hydrogen storage capacity of the alloy, by lowering the equilibrium pressure of hydrogen.

4. Conclusion

Hydrogen absorption capacity of C14 Laves phase $TiFe_2$ was enhanced by partial substitution by vanadium. Its absorption capacity H/M was optimized to be 1.0, at the chemical composition of $TiFeV_{0.7}$, at 333 K.

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