Hydrogen Storage Characteristics of FeTi Containing Zirconium

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The effect of Zr addition to FeTi on the initial hydriding process, the pressure-composition isotherms and the microstructure was investigated. The partial substitution of Zr (1 − 15 at%) for Fe, Ti or both enhanced the activation of FeTi and it hydrided at 303 K after a short incubation time without any heat treatment. All the alloys were composed of FeTi and other two phases. The FeTi phase contained almost no Zr and the changes in the plateau pressure caused by the addition of Zr were not pronounced. The other two phases contained rather large amounts of Zr and the compositions of these phases can be approximately represented by (Ti1−yZry)2Fe and (Fe1−wZrw)2Ti, respectively. The former phase readily reacted with hydrogen and the latter phase did not react with hydrogen. The results obtained in this study show that the presence of the (Ti1−yZry)2Fe phase in the alloy plays a crucial role in shortening the incubation time, but decreases the hydrogen storage capacity of the alloy because the hydride of (Ti1−yZry)2Fe phase is too stable to decompose at the temperature and pressure used in this study.

An FeTi alloy with good performance was obtained by the dispersion of small amounts of the (Ti1−yZry)2Fe phase as fine particles in the alloy. That is, the rapidly cooled Fe0.98TiZr0.02 alloy, which is estimated to contain about 5 mol% (Ti1−yZry)2Fe phase in the alloy, was activated after a short incubation time at room temperature with its hydrogen storage capacity as large as the undoped FeTi alloy.

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I. Introduction

It is well known that the intermetallic compound FeTi is a promising material for the storage and purification of hydrogen. However, the most significant problem of FeTi is that it is rather difficult to activate and the activation requires an involved process. It must be subjected to high temperature (~673 K) annealing in vacuum or in hydrogen, or to a high hydrogen pressure (~4.0 MPa) for a long period(1)(2).

It has been proposed(3)-(5) that partial substitution of transition elements for Fe in FeTi promotes the activation of FeTi during the initial hydriding. However, the mechanism by which activation is improved has not been fully elucidated.

In our previous studies(6)-(8), it was proposed that the presence of a second phase in the FeTi alloy played a crucial role in shortening the incubation time for initial hydriding of the alloy. That is, the second phase and/or the interface between the FeTi phase and second phase act as entrance sites for the hydrogen to diffuse into the alloy and/or active sites for hydriding.

In order to obtain an FeTi alloy with better performance and to obtain a better fundamental understanding of the role of the additional element in promoting activation, the effect of Zr addition on the hydriding process, the hydrogen storage characteristics and the microstructure of the FeTi alloy was investigated in this study.

II. Experimental Procedure

FeTi alloys, in which Zr was partially substituted for Fe, Ti or both (i.e. Fe1−x, TiZr3x, FeTi1−yZry and Fe1−(x/2)Ti1−(x/2)Zr3x) were pre-
pared from a commercially pure ingot of Fe(99.9%), sponge Ti (99.5%) and Zr(99.9%) by nonconsumable arc-melting on a water-cooled copper hearth in an argon atmosphere. The argon atmosphere was purified by melting a zirconium button and allowing it to react with residual oxygen and nitrogen. After initial melting, the ingots were reversed several times to achieve homogeneity. Each ingot was then mechanically pulverized to −40 to +60 mesh size in air. After pulverization, the alloy powders were immediately loaded in the reaction tube which was sealed, evacuated and then filled with hydrogen to 4.0 MPa. The transverse sections of specimens were cut and polished by standard metallographic techniques and the compositions of the phases in the alloys were determined by energy dispersive X-ray analysis (EDX).

The hydriding rate and pressure-composition isotherms were measured using a Sieverts’ apparatus. All the measurements were carried out using the volumetric method. The pressure change was continuously monitored to determine the hydriding rate during the initial hydriding process.

III. Results and Discussion

Figure 1 shows the amount of hydrogen absorbed versus time during the initial hydriding (activation) process at 303 K for Fe$_{1-x}$TiZ$_x$ (x: 0.1, 0.2 and 0.3) alloys. This figure also contains the results (dotted lines) for Fe$_{1-x}$TiM$_x$ (x: 0.1, 0.2 and 0.3) alloys for comparison. As can be seen from this figure, all the alloys were hydrided at 303 K after some incubation time without any heat treatment. The incubation time was very short when compared to that for the alloys with Mn and became shorter with increasing Zr content (1.3 × 10$^2$ s for x=0.1, 35 s for x=0.2, 12 s for x=0.3). Furthermore, the amount of hydrogen absorbed during the initial hydriding increased significantly with increasing Zr content. It should be pointed out that the initial hydriding process was divided into two stages (I and II) at H/M=0.7 for x=0.3, H/M=0.55 for x=0.2 and H/M=0.20 for x=0.1 as shown by the arrow marks, that is, the hydriding rate in stage I was very fast but it became rather slower in stage II.

Figure 2 shows the amount of hydrogen absorbed versus time during the initial hydriding process at 303 K for Fe$_{1-(x/2)}$Ti$_{1-(x/2)}$Z$_x$ (x: 0.1, 0.2 and 0.3) alloys. All the alloys were hydrided at 303 K after some incubation time. The incubation times for these alloys (1.8 × 10$^2$ s for x=0.1, 40 s for x=0.2, 20 s for x=0.3) were a little longer and the amounts of hydrogen absorbed were smaller than that for the Fe$_{1-x}$TiZ$_x$ alloys (Fig. 1). The change in the initial hydriding rate (arrow marks) was also observed on each curve, but the H/M values at which the rate changed (H/M=0.59 for x=0.3, 0.47 for x=0.2, 0.20 for x=0.1) were lower than those for the Fe$_{1-x}$TiZ$_x$ alloys.

Figure 3 shows the amount of hydrogen absorbed during the initial hydriding process at 303 K for the FeTi$_{1-x}$Z$_x$ (x: 0.1, 0.2 and 0.3) alloys. The incubation times were longer (2.0 × 10$^2$ s for x=0.1, 45 s for x=0.2, 30 s for x=0.3) and the amounts of hydrogen absorbed were smaller than those for the alloys shown in Figs. 1 and 2. The H/M values at which the rate changed (H/M: 0.5 for x=0.3, 0.43 for x=0.2, 0.2 for x=0.1) were also lower than those for the alloys previously mentioned. The amounts of hydrogen absorbed during the initial hydriding process were larger and the incubation times for the initial hydriding
were shorter in the order of \( \text{Fe}_{1-x} \text{TiZr}_x \), \( \text{Fe}_{1-(x/2)} \text{Ti}_{1-(x/2)} \text{Zr}_x \), and \( \text{FeTi}_{1-x} \text{Zr}_x \) alloys. These alloys had the same Zr content \((x)\). It should be noted that the incubation times for the initial hydriding of the alloys with Zr were much shorter than those for the previously reported\(^8\) alloys containing Mn. Furthermore, the amounts of hydrogen absorbed and the hydriding rates during the initial hydriding process of the alloys with Zr were markedly different from those of the alloys with Mn\(^8\).

Figures 4(a)(b)(c), 5(a)(b)(c) and 6(a)(b)(c) show the pressure-composition isotherms (PCT curves) at 303 K of \( \text{Fe}_{1-x} \text{TiZr}_x \), \( \text{Fe}_{1-(x/2)} \text{Ti}_{1-(x/2)} \text{Zr}_x \), \( \text{FeTi}_{1-x} \text{Zr}_x \) alloys \((0.1 \leq x \leq 0.3)\), respectively. The hydrogen storage capacity of these alloys markedly decreased with increasing Zr content in spite of the fact that the amount of hydrogen absorbed during the initial hydriding process increased with increasing Zr content (Figs. 1–3). Furthermore, when the hydrogen storage capacity of the undoped FeTi alloy at 4.0 MPa and 303 K was assumed to be about \( H/M = 0.90 \)\(^1\), the decrease in the hydrogen storage capacities caused by the addition of Zr approximately corresponded to the \( H/M \) values at which the initial hydriding rate changed (arrow marks in Figs. 1–3). These results strongly suggest that two types of hydrides were formed during the initial hydriding process and one of them was too stable to decompose during the treatment for 3.6 ks in vacuum at 303 K, after which treatment PCT measurements were carried out. It was seen from the PCT curves that the changes in the plateau pressure caused by the addition of Zr \((0.1 \leq x \leq 0.3)\) were far smaller than those caused by the addition of Mn\(^8\). This suggests that the addition of Zr did not change.
markedly the composition of the FeTi phase as the addition of Mn did(8).

In order to elucidate the cause of the large differences in the hydriding process (Figs. 1–3) and the PCT curves (Figs. 4–6), microstructural observations of the alloys and an analysis of the phases in the alloys were done using SEM and EPMA. As typical examples, Fig. 7(a), (b) and (c) show the SEM photographs of a cross-section of the arc-melted Fe0.9TiZr0.1, Fe0.95Ti0.95Zr0.1 and FeTi0.9Zr0.1, respectively. All the alloys consisted of three phases. The compositions of these phases were determined by EDX and plotted in Fig. 8. It was found that the FeTi phase contained almost no Zr, while the second phases contained rather a large amount of Zr and the compositions of the second phases can approximately be represented by (Ti1−yZry)2Fe and (Fe1−wZrw)2Ti. The (Ti1−yZry)2Fe phase reacted readily with hydrogen and its hydride did not decompose in vacuum at 303 K, while the (Fe1−wZrw)2Ti did not react with hydrogen. It can be considered from this result that the (Ti1−yZry)2Fe phase reacted with hydrogen in stage I during the initial hydriding process at first and then the reaction of FeTi phase with hydrogen followed.

It was reported previously(8) that the presence of the second phase played a crucial role in promoting the initial hydriding. That is, even if the second phase does not react with hydrogen, the interfaces between the FeTi phase and second phase would act as entrance sites for hydrogen to diffuse into the alloy and/or act as active sites for the hydriding. Furthermore, if second phase reacts readily with hydrogen, even the presence of a small amount of second phase will significantly promote hydriding during the initial hydriding process. The concentration of phases in the alloys were then measured from microstructural
observation and plotted against Zr addition in Fig. 9. This figure clearly shows that the fraction of the FeTi phase rapidly decreased with increasing Zr addition \((x)\) value in all alloy types. On the contrary, the fractions of the second phases markedly increased with increasing \(x\). Decreases in the hydrogen storage capacity with increasing \(x\) correspond well to the decreases in the fraction of FeTi phase with increasing \(x\). The predominant second phase in the Fe\(_{1-x}\)Ti\(_{z}\) alloys is \((\text{Ti}_{1-y}\text{Zr}_y)_2\text{Fe}\) which reacted readily with hydrogen and the incubation time for the initial hydriding was the shortest, while the predominant second phase in the Fe\(_{1-x}\)Zr\(_{x}\) alloy is \((\text{Fe}_{1-w}\text{Zr}_w)_2\text{Ti}\) did not react with hydrogen and had the longest incubation time. That is, the incubation time becomes shorter in the order Fe\(_{1-x}\)Ti\(_{z}\), Fe\(_{1-(x/2)}\text{Ti}_{1-(x/2)}\text{Zr}_x\) and Fe\(_{1-x}\)Zr\(_x\). The amount of \((\text{Ti}_{1-y}\text{Zr}_y)_2\text{Fe}\) phase in the alloy are large and the \(H/M\) value becomes higher in the same order as previously stated. This result shows that the presence of the \((\text{Ti}_{1-y}\text{Zr}_y)_2\text{Fe}\) phase plays an important role in shortening the incubation time for the initial hydriding.

As already stated, it was found that the presence of the \((\text{Ti}_{1-y}\text{Zr}_y)_2\text{Fe}\) phase is very effective in shortening the incubation time and in accelerating the initial hydriding rate, but it decreased the hydrogen storage capacity of the alloys. From these results, it can be considered that the dispersion of small amounts of \((\text{Ti}_{1-y}\text{Zr}_y)_2\text{Fe}\) phase into the alloy as fine particles will shorten the incubation time without decreasing the hydrogen storage capacity of the alloy.

To confirm this, the initial hydriding characteristics and the pressure-composition
isotherms were measured for the Fe$_{0.98}$TiZr$_{0.02}$ alloy, whose (Ti$_{1-y}$Zr$_{y}$)$_2$Fe content was expected to be approximately 5 mol% from Fig. 9(a). In order to clarify the effect of the size of the (Ti$_{1-y}$Zr$_{y}$)$_2$Fe phase on the initial hydriding characteristics and the hydrogen storage characteristics, the Fe$_{0.98}$TiZr$_{0.02}$ alloy was prepared in three different ways as follows. (a) In order to disperse the (Ti$_{1-y}$Zr$_{y}$)$_2$Fe phase as fine particles in the alloy, small buttons (about 1 g) of the alloy were arc-melted individually on the water-cooled copper hearth to rapidly cool them. They were then annealed at 1123 K for 3.6 ks to relieve stress. (b) The arc-melted buttons (a) were annealed at 1123 K for a prolonged period (172.8 ks) to enlarge the size of the (Ti$_{1-y}$Zr$_{y}$)$_2$Fe particles. (c) The annealed buttons from procedure (b) were melted in the same way as in (a) to confirm their reproducibility. Figure 10(a), (b) and (c) show the SEM photographs of the cross-sections of alloys (a), (b) and (c), respectively. As can be seen from these photographs, the particles of the (Ti$_{1-y}$Zr$_{y}$)$_2$Fe phase are much finer in alloys (a) and (c) than those in alloys (b) whose (Ti$_{1-y}$Zr$_{y}$)$_2$Fe phase is agglomerated to relatively large particles.

Figure 11 shows the amount of hydrogen absorbed versus time during the initial hydriding process at 303 K for alloys (a), (b) and (c). This figure clearly shows that decreasing the size of the (Ti$_{1-y}$Zr$_{y}$)$_2$Fe particles markedly shortens the incubation time, that is, the incubation time for the alloys (a) and (c) are about $4 \times 10^2$ s, while that for alloy (b) is about $6 \times 10^3$ s.

Figure 12(a), (b) and (c) show the PCT curves for the alloys (a), (b) and (c) at 303 K, respectively. Although the flatness of the plateau region of alloy (b), annealed for 172.8 ks, is more apparent than those of the alloys (a) and (c), the hydrogen storage capacities of all the alloys are almost the same and are nearly equal to that of the undoped FeTi alloy. The incubation times of these alloys, (a), (b) and (c), were longer than those of the alloys with higher Zr contents (Figs. 1-3), but it is apparent that the initial hydriding was significantly improved by the dispersion of a small amount of the (Ti$_{1-y}$Zr$_{y}$)$_2$Fe phase compared to the initial hydriding process of the undoped FeTi alloy. That is, the undoped FeTi alloy does not show activation at 303 K and in 4.0 MPa hydrogen and usually needs heat-treatment in vacuum at 673 K for 3.6 ks and then exposure in 4.0 MPa hydrogen.

It can be concluded from these results that the dispersion of small amounts of (Ti$_{1-y}$Zr$_{y}$)$_2$Fe phase as fine particles in the FeTi alloy significantly accelerates the initial hydriding without decreasing the hydrogen storage capacity of the alloy.
The effect of partial substitution of Zr for Fe, Ti, or both in FeTi, i.e. \( \text{FeTi}_{1-x}\text{Zr}_x \) and \( \text{FeTi}_{1-(x/2)}\text{Ti}_{1-(x/2)}\text{Zr}_x \), on the hydriding rates during the initial hydriding process, pressure-composition isotherms and microstructures of the alloys were investigated.

The following results were obtained.

1. The partial substitution of Zr for Fe, Ti, or both in FeTi enhanced the activation of FeTi and it hydrided at room temperature after a short incubation time without any heat treatment. However, the hydrogen storage capacity decreased markedly with increasing Zr addition. The effect of Zr addition in shortening the incubation time was more pronounced than that of Mn.

2. All the alloys were composed of FeTi and other two phases. The FeTi phase contained almost no Zr and the changes in the plateau pressure caused by the addition of Zr were not pronounced comparing to those

IV. Conclusions

The effect of partial substitution of Zr for Fe, Ti or both in FeTi, i.e. \( \text{FeTi}_{1-x}\text{Zr}_x \), on the hydriding rates during the initial hydriding process, pressure-composition isotherms and microstructures of the alloys were investigated.

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2. All the alloys were composed of FeTi and other two phases. The FeTi phase contained almost no Zr and the changes in the plateau pressure caused by the addition of Zr were not pronounced comparing to those.
caused by the addition of Mn. The second phases, on the other hand, contained rather large amounts of Zr and the compositions of these phases can approximately be represented by \((\text{Ti}_{1-y}\text{Zr}_y)_2\text{Fe}\) and \((\text{Fe}_{1-w}\text{Zr}_w)_2\text{Ti}\), respectively. The \((\text{Ti}_{1-y}\text{Zr}_y)_2\text{Fe}\) phase readily reacted with hydrogen, while the \((\text{Fe}_{1-w}\text{Zr}_w)_2\text{Ti}\) phase did not react with hydrogen.

(3) It was found that the higher the amounts of \((\text{Ti}_{1-y}\text{Zr}_y)_2\text{Fe}\) phase in the alloy, the shorter the incubation time and the faster the initial hydriding rate. The effect of Zr addition on shortening of the incubation time at the same Zr content was more pronounced in the order of \(\text{Fe}_{1-x}\text{TiZr}_x\), \(\text{Fe}_{1-(x/2)}\text{Ti}_{1-(x/2)}\text{Zr}_x\) and \(\text{FeTi}_{1-x}\text{Zr}_x\) alloys, because the concentration of the \((\text{Ti}_{1-y}\text{Zr}_y)_2\text{Fe}\) phase increases in the same order.

(4) The FeTi alloy with the dispersion of small amounts of \((\text{Ti}_{1-y}\text{Zr}_y)_2\text{Fe}\) phase as fine particles, \(\text{Fe}_{0.96}\text{TiZr}_{0.02}\), was activated at 303 K after an incubation time of \(4 \times 10^2\) s without any activation treatment. The hydrogen storage capacity of this alloy was nearly equal to that of the undoped FeTi, which requires an activation treatment at 673 K and in 4.0 MPa hydrogen.

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