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Hydrogen absorption and desorption characteristics of ferro–titanium alloys

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Hydrogen absorption and desorption characteristics of commercially supplied ferro–titaniums with 41 to 51 at% Ti have been studied. The characteristics are similar to those of high purity FeTi although the ferro–titaniums include some impurities. The activation temperatures of the ferro–titaniums are slightly higher than that of the high purity FeTi. Plateaus in the hydrogen absorption and desorption curves are not obvious compared with those of high purity FeTi. It is concluded that the ferro–titaniums are good, low-cost hydrogen storage materials.

1. Introduction

The intermetallic compound iron–titanium has been developed as a hydrogen storage material [1] and attempts have been made to use it in hydrogen fuel cars and for storing energy in electric power stations, water pumps and reservoirs [2]. The compound forms a hydride, $FeTiH_2$ [1]. For this hydride to be commercially useful, the cost of materials must be lowered.

Ferro–titanium has been used to make special steels. The ferro–titanium usually contains some impurities. However, this material is expected to be used industrially as a hydrogen storage material in place of the high purity one. As a result the feasibility of ferro–titanium as a hydrogen storage material has been confirmed in this experiment.

Since large amounts of ferro–titanium have been fabricated to make special steels, the production techniques are well established. Ferro–titanium usually contains some impurities, for example, Al, Mn and Si. It is thought that these impurities affect the hydrogen storage capability of ferro–titanium. In this work, first the activation conditions necessary to make the alloys absorb hydrogen easily have been studied and the hydrogen storage abilities investigated.

2. Experimental procedure

Three ferro–titanium specimens with different compositions were used. Titanium contents of the specimens were 41, 46 and 51 wt%; the main impurities were Mn, Al, Si, Cu and C. The names and compositions of the specimens are shown in Table I. The specimens were spongy. The specimens were crushed to a powder with an average particle diameter of 10 μm. The powders were put in stainless steel specimen holders to examine their activation and hydrogen absorption behaviours. To evaluate the hydrogen absorption characteristics of the specimens the intermetallic compound FeTi was prepared using high purity iron and zone refined titanium.

The reactions between hydrogen and the alloys were examined by high pressure differential thermal analysis [3] (HDTA) under a hydrogen atmosphere. The absorption–desorption characteristics were determined by pressure–composition measurements. The hydrogen desorption rate from the hydride was obtained by measuring the amount of hydrogen flowing into a measuring cylinder from the specimen holder and the absorption rate was measured by pressure variations in the measuring system.

3. Results

3.1. Activation behaviour

The HDTA data for the high purity FeTi and the three ferro–titanium specimens are shown in Fig. 1. The hydrogen pressure was 10×10^5 Pa. The exothermal peak of the high purity FeTi was about 613 K, and the peaks of ferro–titanium specimens FT41, FT46 and FT51 were about 623, 648 and 653 K, respectively. These were all single peaks. After these peaks appeared, the

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TABLE I Chemical composition of ferro-titanium specimens (wt %)

Specimen number	Ti	Mn	Si	C	Al	Cu	P	S	Fe
FT41	41.8	0.19	0.03	0.05	0.08	0.03	0.01	0.01	Balance
FT46	46.3	0.21	0.02	0.05	0.09	0.03	0.01	0.01	Balance
FT51	51.8	0.18	0.03	0.05	0.08	0.05	0.01	0.01	Balance

specimens could absorb hydrogen easily. The exothermal peaks show the hydrogen absorption activation reaction of the specimens. The exothermal peak of specimen FT46, whose composition is close to that of the high purity FeTi, was about 35 K higher than that of the high purity FeTi. The activation temperature increased with increasing Ti content of the ferro–titanium specimens.

3.2. Pressure–composition isotherms of ferro–titanium

Pressure–composition isotherms of the ferro–titanium FT41 at 293 K are shown in Fig. 2. The equilibrium hydrogen absorption pressure of FT41 at 293 K was about 7.7×10^5 Pa. The hydrogen solubility at 10^5 Pa expressed as H/M (Fe + Ti) was about 0.03. After the hydride $Fe_{1.08}Ti_{0.92}H_{0.8}$ was formed, the equilibrium hydrogen absorption temperature increased rapidly, then the alloy formed the hydride $Fe_{1.08}Ti_{0.92}H_{1.2}$ at 45×10^5 Pa. When the hydrogen pressure was decreased after the hydride $Fe_{1.08}Ti_{0.92}H_{1.2}$ formed, the equilibrium hydrogen desorption pressure of the specimen decreased to about 3×10^5 Pa. However, the plateau of the curve was not obvious.

Pressure–composition isotherms of the ferro–titanium FT46 and the high purity FeTi at 293 K are shown in Fig. 3. Since these two specimens have almost the same composition, these isotherms can be compared with each other. Here, the previously reported discontinuity [1] in the hydrogen desorption isotherm plateau was not observed in the pressure–composition isotherm of the high purity FeTi. The plateaus of the isotherms of FT46 are not as abvious as those of the high purity FeTi. That is, the equilibrium hydrogen desorption pressure of FT46 did not show a clear plateau and increased gradually in the hydrogen pressure range of about 2×10^5 to 8×10^5 Pa. After the hydride $FeTiH_{1.25}$ was formed, the equilibrium hydrogen adsorption pressure of FT46 increased rapidly, and the hydrogen content in the specimen saturated. Here, the specimen formed the hydride $FeTiH_{1.83}$. The hydrogen desorption pressure of FT46 was about 2.8×10^5 Pa around $H/M = 1$.

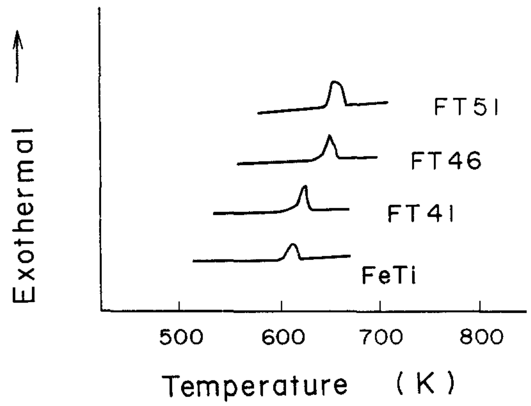

Figure 1 HDTA curves of ferro–titanium and FeTi specimens.

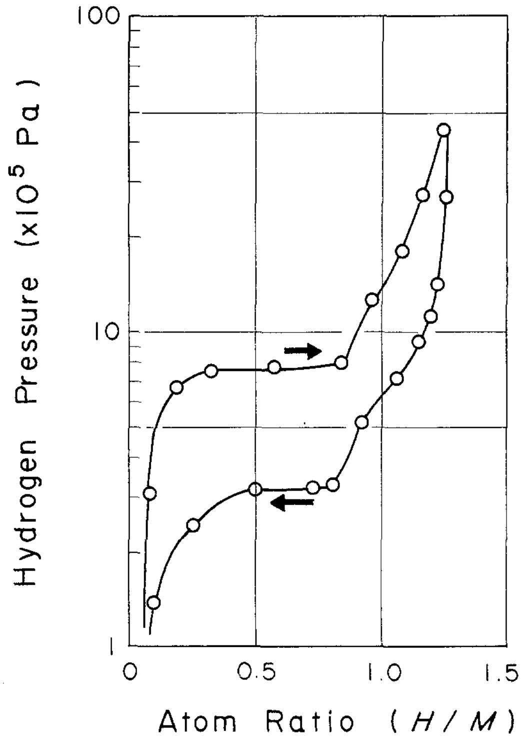

Figure 2 Pressure–composition isotherms of ferro–titanium specimen FT41 at 293 K; absorption (→) and desorption (←).

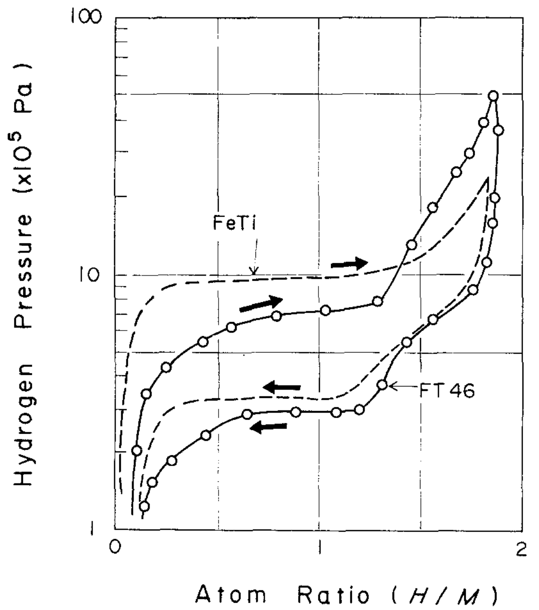

Figure 3 Pressure–composition isotherms of ferro–titanium specimen FT46 at 293 K; absorption (→) and desorption (←).

The pressure–composition isotherms of FT51 at 293 K are shown in Fig. 4. The hydrogen absorption and desorption pressures of FT51 were about 8.5 x 10^5 and 3.5 x 10^5 Pa, respectively, around $H/M = 1$. The plateaus of the curve were more obvious than those of FT46. The ferro–titanium formed the hydride $Fe_{0.9}Ti_{1.1}H_{2.2}$ at 293 K under about 10^7 Pa hydrogen pressure.

The enthalpy changes in hydride formation at a composition of $H/M = 1$ obtained from the temperature dependence of hydride formation pressures are −0.31 eV for FT46 and −0.24 eV for the high purity FeTi. The enthalpy change of the ferro–titanium specimen are larger than that of the high purity FeTi.

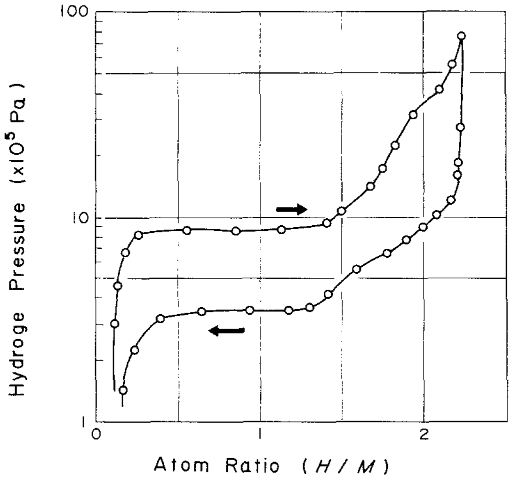

Figure 4 Pressure–composition isotherms of ferro–titanium specimen FT51 at 293 K; absorption (→) and desorption (←).

On the other hand, the enthalpy changes of hydride dissociation for FT41, FT46, FT51 and the high purity FeTi at a composition of $H/M =$ 0.4 were 0.33, 0.31, 0.30 and 0.25 eV, respectively. In this case, the enthalpy changes of the ferro–titaniums were larger than that of the high purity FeTi and decreased with increasing Ti content in the alloy.

3.3. Hydrogen desorption rate

The relative hydrogen desorption rates at 293 K, when hydrogen from hydrides was released into 10^5 Pa atmosphere from a composition of $MH_{0.8}$, are shown in Fig. 5. The desorption rate of the high purity FeTi was the best and the rate decreased in the order FT51, FT46 to FT41. The apparent activation energies for hydrogen desorption obtained from the temperature dependencies of the initial hydroden desorption rates are 0.33 eV for FT41, 0.38 eV for FT46, 0.40 eV for FT51 and 0.26 eV for the high purity FeTi.

3.4. Hydrogen absorption rate

The relative hydrogen absorption rates of the specimens when 3 x 10^6 Pa hydrogen pressure was applied at 293 K, are shown in Fig. 6. The rates were in the order FeTi, FT46, FT51 to FT46. The rate of high purity FeTi was the highest. The apparent activation energies for hydrogen absorption obtained from the temperature dependencies

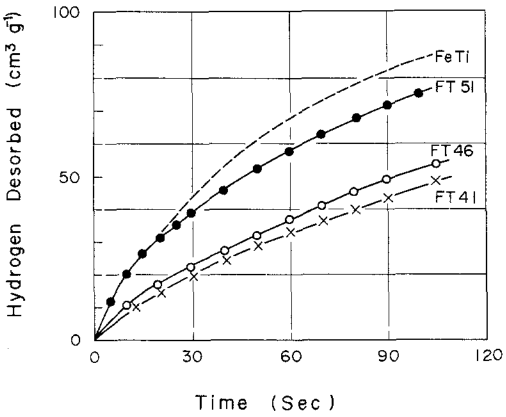

Figure 5 Hydrogen desorption rates of ferro–titanium and FeTi specimens at 293 K.

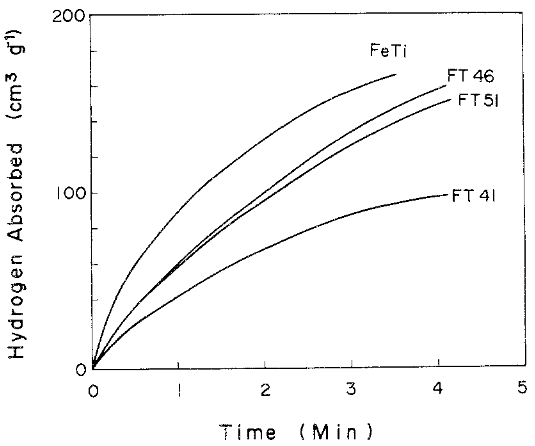

Figure 6 Hydrogen absorption rates for ferro–titanium and FeTi specimens at 293 K.

of the initial hydrogen absorption rates are − 0.34 eV for FT41, − 0.36 eV for FT46, − 0.40 eV for FT51 and − 0.26 eV for the high purity FeTi.

4. Discussion

4.1. Activation process

The activation temperature of ferro–titanium specimen FT46 under 10×10^5 Pa hydrogen atmosphere was higher than that of the high purity FeTi. It is assumed that this is an impurity effect.

The activation reaction is thought to be a hydrogen reductive reaction of oxide films, contaminants and absorbants on the specimen surface. These interrupt the reaction between the alloy and the hydrogen molecule.

The difference is considered to be caused by the impurities Mn, Al and Si in the ferro–titanium. That is, although the oxygen atoms bond to Fe and Ti atoms in the manner Fe–O–Ti on the crystal surface, the addition of impurities changes the Fe–O–Ti bond to Fe(*M*)–O–Ti(*M*), where *M* refers to impurity elements. The impurity atoms Mn, Al and Si can substitute for Fe and Ti at the lattice points. Supposing that the impurity atoms occupy Fe positions and if the Fe–O bond dominates the difficulty of the activation reaction, the impurities increase the activation temperature of the ferro–titanium because the oxide formation free energy of the impurities are larger than that of iron. The reason that the activation temperature of specimen FT41 was lower than that of FT46 is presumably because the Ti content is less than that of FT46. Similarly, the temperature of FT51 increased with Ti content.

The activation temperatures of the three ferro–titaniums FT41, 46 and 51 are slightly higher than that of the high purity FeTi. However, they can be utilized as hydrogen storage materials in place of the high purity one.

4.2. Absorption–desorption characteristics

On the plateau in the desorption isotherm of the hydride dissociation of high purity FeTi, the discontinuity [1] was not observed in the present work. Since the dissociative reaction is endothermic, a super-cooling effect was often observed in the transition region from the higher hydride to the lower hydride formation. For this reason, the discontinuity was observed only when the measuring system was not held in equilibrium (isotherm). It is therefore assumed that the discontinuity is due to the supercooling effect.

The lower hydrides are $Fe_{1.08}Ti_{0.92}H_{0.8}$ for FT41, $FeTiH_{1.25}$ for FT46 and $Fe_{0.9}Ti_{1.1}H_{1.45}$ for FT51. The hydrogen absorbed by these alloys is proportional to the Ti content of the alloys. On the other hand, the higher hydrides are $Fe_{1.08}Ti_{0.92}H_{1.2}$ for FT41, $FeTiH_{1.85}$ for FT46 and $Fe_{0.9}Ti_{1.1}H_{2.2}$ for FT51. These hydrogen absorptions are also proportional to the Ti content of the alloys.

5. Conclusion

Hydrogen absorption and desorption characteristics of commercially supplied ferro–titanium are similar to the characteristics of high purity FeTi. In the range of this experiment, the hydrogen storaged in the ferro–titaniums increased with increasing Ti content. The ferro–titaniums FT46 and FT51 have industrially useful characteristics, but it is thought that FT41 can not be practically used because of its low hydrogen storage ability compared to high purity FeTi. It is concluded that the ferro–titaniums are good, low-cost hydrogen storage materials.

References

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