HYDROGEN ABSORPTION AND DESORPTION PROPERTIES OF AMORPHOUS TI-NI AND Hf-NI ALLOYS

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Summary

Hydrogen absorption and desorption properties of amorphous Ti-Ni and Hf-Ni alloys, prepared by the melt spinning technique, were investigated by X-ray diffraction and the volumetric method. These amorphous alloys absorb hydrogen in the amorphous state at low temperature and pressurecomposition-temperature curves of the hydrogenated amorphous alloys do not show pressure plateaux. Solution of hydrogen in the amorphous phase obeys Sieverts' law in the low hydrogen concentration region, but shows a positive deviation with increasing hydrogen concentration. Although the hydrogen absorption capacity of the amorphous alloys increases with inceasing titanium or hafnium content in the alloy, which is lower than that of the corresponding amorphous Zr-Ni alloys, approximately two hydrogen atoms are absorbed per titanium or hafnium atom. At higher temperatures, the amorphous Ti-Ni alloys crystallize to TiNi₃ + TiH₂, while the Hf-Ni alloys transform to HfH₂ + Hf₇Ni₁₀H_x, HfNiH₃ and Hf₂Ni₅ + Hf₇Ni₁₀H_x depending on the alloy composition.

1. Introduction

Amorphous alloys consisting of a combination of the stable-hydride forming early transition metals and late transition metals are expected to be good absorbers of hydrogen [1]. From this point of view, several investigations have been carried out to evaluate the hydrogen absorption characteristics of amorphous alloys [2-5]; however, many of them have been concerned with zirconium-based alloys such as Zr-Ni and Zr-Pd [3, 4, 6]. It has been reported that Ti-Ni and Hf-Ni alloys can also be

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produced in an amorphous state [7, 8]. In order to understand clearly the hydrogen absorption behaviour, it is useful to compare the situations observed in amorphous Ti–Ni, Zr–Ni and Hf–Ni alloys, because hydrogen absorption is considered to be controlled solely by the hydride-forming elements, titanium, zirconium and hafnium.

In the present work, the hydrogen absorption and desorption properties of amorphous Ti–Ni and Hf–Ni alloys have been investigated as a function of the titanium or hafnium content and are compared with those of amorphous Zr–Ni alloys reported earlier [5, 9].

2. Experimental details

Ti-Ni and Hf-Ni alloys were prepared from high purity metals (99.9% Ni, 99.6% Ti and 96% Hf) by arc melting under an argon atmosphere. Amorphous ribbons about 1 mm wide and 0.01 mm thick were produced under an argon atmosphere by the melt spinning method. All the samples were subjected to X-ray examination before and after hydrogenation using Cu K α radiation from an X-ray monochromator. Pressure-composition-temperature (P-C-T) relationships were determined by the conventional volumetric method. The experimental details have been described previously [10] and so they will not be repeated here. Briefly, the amorphous ribbons were polished with SiC grinding paper and were cut into pieces about 1 mm long. The samples were activated by pre-annealing at 473 K for 7.2 ks in a vacuum of 2×10^{-1} Pa. The samples were hydrided or dehydrided stepwise using hydrogen (purity, 99.99999%). The amount of hydrogen absorbed or desorbed by the sample was calculated from the decrease or increase in the hydrogen pressure in the closed system.

3. Results and discussion

3.1. Structure after hydrogen absorption

X-ray diffraction patterns of the as-quenched amorphous (a-) and hydrogenated a- $Hf_{67}Ni_{33}$ at different temperatures are shown in Fig. 1. The basic profile of the sample hydrogenated at 473 K is similar to that of the as-quenched one and characterized by a broad peak typically observed in many amorphous alloys. However, the hydrogenated sample shows a peak shift towards the lower angle side, indicating that hydrogen absorption has caused volume expansion in the sample. Weak peaks of hafnium hydride (HfH₂) appear superimposed over the amorphous peak at 573 K and they become stronger with increasing temperature. At a higher temperature of 773 K, the crystalline $Hf_7Ni_{10}H_x$ phase appears in addition to HfH_2 . At a still higher temperature of 873 K, the peaks of the pattern correspond to the hydrides HfH_2 and $Hf_7Ni_{10}H_x$, indicating that the amorphous phase decomposes into two crystalline phases.



Fig. 1. X-ray diffraction patterns of the amorphous $Hf_{67}Ni_{33}$ alloy hydrogenated for 86.4 ks at a hydrogen pressure of 5 MPa at various temperatures (Ψ , HfH_2 ; \blacksquare , $Hf_7Ni_{10}H_x$).

Fig. 2. Structures of the amorphous Hf–Ni alloys hydrogenated at various temperatures in hydrogen at a pressure of 5 MPa.

The phase fields for the various structures of the amorphous Hf–Ni alloys are collectively shown in Fig. 2 as a function of the hydrogenation temperature. From this figure, we can see that all the alloys absorb hydrogen in the amorphous state at low temperatures. In the nickel-rich alloys, however, the amorphous state is retained to high temperatures. The HfNiH₃ phase appears along with the amorphous phase at 673 K and it is observed homogeneously only above 783 K in $Hf_{50}Ni_{50}$, while Hf_2Ni_5 and $Hf_7Ni_{10}H_x$ are formed at 873 K in $Hf_{36}Ni_{64}$.

Figure 3 shows X-ray diffraction patterns of the hydrogenated a- $Ti_{67}Ni_{33}$ alloy. This alloy also absorbs hydrogen in the amorphous state up to 473 K and crystallizes to $TiNi_3 + TiH_2$ at 673 K.

The phase fields for the amorphous Ti–Ni alloys are shown in Fig. 4 as a function of the hydrogenation temperature. Similiarly to the Hf–Ni alloys, the nickel-rich Ti–Ni alloys absorb hydrogen in the amorphous state up to a higher temperature compared with the nickel-poor alloys. It is interesting to notice that the same crystalline phases, $TiNi_3$ and TiH_2 , are observed in both the alloys at higher temperatures.

Table 1 shows the structures of the amorphous Ti-Ni, Zr-Ni [9] and Hf-Ni alloys crystallized either in a hydrogen atmosphere or in vacuum (shown in parentheses). The structural changes in amorphous Ti-Ni and Zr-Ni



Fig. 3. X-ray diffraction patterns of the amorphous $Ti_{67}Ni_{33}$ alloy hydrogenated for 86.4 ks at a pressure of 5 MPa at various temperatures (\mathbf{v} , TiH₂; \mathbf{I} , TiNi₃).

Fig. 4. Structures of the amorphous Ti–Ni alloys after hydrogenation in hydrogen at a pressure of 5 MPa.

TABLE 1

Structures after crystallization in either a hydrogen atmosphere (or vacuum)

Ti ₄₀ Ni ₆₀		Ti ₆₇ Ni ₃₃
TiNi ₃ + TiH ₂ (TiNi ₃ + TiNi)		TiNi ₃ + TiH ₂ (Ti ₂ Ni)
Zr ₃₇ Ni ₆₃	$Zr_{50}Ni_{50}$	Zr ₆₇ Ni ₃₃
$\begin{array}{l} \mathrm{Zr_2Ni_7} + \mathrm{ZrH_2} \\ (\mathrm{Zr_2Ni_5} + \mathrm{Zr_7Ni_{10}}) \end{array}$	$Zr_2Ni_7 + ZrH_2$ (ZrNi)	$Zr_2Ni_7 + ZrH_2$ (Zr_2Ni)
Hf ₃₆ Ni ₆₄	<i>Hf</i> 50 <i>Ni</i> 50	<i>Hf</i> ₆₇ <i>Ni</i> ₃₃
$\begin{array}{l} \mathrm{Hf_{2}Ni_{5}}+\mathrm{Hf_{7}Ni_{10}H_{x}}\\ \mathrm{(Hf_{2}Ni_{5}}+\mathrm{Hf_{7}Ni_{10})} \end{array}$	HfNiH ₃ (HfNi)	$\begin{array}{l} Hf_7 Ni_{10}H_x + HfH_2 \\ (Hf_2 Ni) \end{array}$

alloys are similar and can be expressed as follows with respect to increasing hydrogenation temperature: hydrogen absorbed amorphous phase $[Am(H)] \rightarrow Am'(H) + Ti(or Zr)H_2 \rightarrow TiNi_3(or Zr_2Ni_7) + Ti(or Zr)H_2$, *i.e.* one kind of hydride $TiH_2(ZrH_2)$ and an intermetallic compound $TiNi_3(Zr_2Ni_7)$ are formed. In these alloys, the hydride phase is easily and preferentially formed, which results in a lowering of the Ti(Zr) concentration in the amorphous matrix phase. When the Ti(Zr) concentration in the matrix decreases to $\text{TiNi}_3(\text{Zr}_2\text{Ni}_7)$ the matrix phase crystallizes, because the amorphous phase of that composition is unstable as can be judged from the fact that the amorphous phase is not obtained at that composition by liquid quenching. Thus, since the crystallization process of the amorphous Ti-Ni and Zr-Ni alloys in a hydrogen atmosphere is considered to be controlled by the formation of hydrides, the same crystalline phases are obtained at high temperature. In contrast, several kinds of hydrides, HfH_2 , $\text{Hf}_7\text{Ni}_{10}\text{H}_x$ or HfNiH_3 are formed in the Hf-Ni system. It is worth noting that the formation of the HfH_2 phase is suppressed in amorphous $\text{Hf}_{50}\text{Ni}_{50}$ and $\text{Hf}_{36}\text{Ni}_{64}$ and the reasons for this are not known at present. Further investigations are necessary to understand this behaviour.

3.2. P-C-T relationships

Figure 5 shows the P-C-T curves for amorphous and crystalline Hf-Ni alloys at 473 K, where the equilibrium hydrogen pressure is plotted against hydrogen concentration, expressed as the hydrogen to metal atomic ratio (H/M). The hydrogen pressure is found to increase gradually with hydrogen concentration in the amorphous state, *i.e.* the P-C-T curves for the amorphous Hf-Ni alloys do not show pressure plateaux and the capacity for dissolving hydrogen increases with hafnium concentration in the alloy. There is a significant difference between the P-C-T curves of $a-Hf_{50}Ni_{50}$ and c-HfNi. While the hydrogen pressure increases continuously with hydrogen concentration in the amorphous state, a pressure plateau appears in the crystalline state. This plateau may be due to the coexistence of two hydrides, *viz*. HfNiH and HfNiH₃, similarly to the case of c-ZrNi [11]. From the absence of pressure plateaux, it is suggested that no hydride with a specific structure forms in the amorphous Hf-Ni alloys, but a solid solution of hydrogen is formed.



Fig. 5. P-C-T curves of amorphous (•) and crystalline ($^{\circ}$) Hf-Ni alloys at 473 K: 1, Hf₃₆Ni₆₄; 2, Hf₅₀Ni₅₀; 3, Hf₆₇Ni₃₃.

Generally, Sieverts' law for ideal hydrogen solution can be applied for a single homogeneous system at low concentration. Sieverts' law can be expressed as

$$X_{\rm H} = K_{\rm H} (P_{\rm H_2})^{1/2} \tag{1}$$

where $X_{\rm H}$ is the atomic fraction of hydrogen, $P_{\rm H}$, the equilibrium hydrogen pressure and $K_{\rm H}$ the Sieverts' law coefficient. Figure 6 shows a plot of the square root of the pressure versus hydrogen concentration for amorphous Hf-Ni alloys. These results show that Sieverts' law is obeyed in the relatively low hydrogen concentration region. The isotherm for a-Hf₆₇Ni₃₃ in the low hydrogen pressure region was estimated as the broken line similar to the other alloys, because its pressure was too low for accurate measurement. A positive deviation from Sieverts' law is observed as the hydrogen content increases. The deviation begins at about $0.1X_{\rm H}$, $0.25X_{\rm H}$ and $0.45X_{\rm H}$ for a-Hf $_{36}$ Ni $_{64}$, a-Hf $_{50}$ Ni $_{50}$ and a-Hf $_{67}$ Ni $_{33}$ respectively. Similar positive deviations have been reported in the P-C-T curves of the amorphous Zr-Ni alloys [4, 5] and some intermetallic compounds [12]. This, however, is not the general behaviour, since most of the pure metal-hydrogen and disordered alloy-hydrogen systems reported in the literature show a negative deviation from Sieverts' law. The positive deviation observed in the present alloys, indicating an apparent H-H repulsive interaction, may correspond to the change in the local environment around the hydrogen atom. Recently, the coordination number of metal atoms around deuterium atoms in amorphous Zr-Ni alloys has been measured as a function of deuterium concentration by neutron diffraction [13]. According to that experiment, deuterium atoms are trapped in 4Zr tetrahedral sites in the low deuterium concentration region and with further absorption the 3Zr + 1Ni and 2Zr + 2Ni sites are occupied. The transition from 4Zr to 3Zr + Ni site occupation occurs at



Fig. 6. P-C-T curves of the amorphous Hf-Ni alloys expressed by the Sieverts' relation. Fig. 7. P-C-T curves for the a-Ti₄₀Ni₆₀ (\bullet), a-Zr₃₇Ni₆₃ (\blacksquare) and a-Hf₃₆Ni₆₄ (\blacktriangle) alloys at 473 K.



Fig. 8. P-C-T curves for the a- $Zr_{50}Ni_{50}$ (\blacksquare) and a-Hf₅₀Ni₅₀ (\blacktriangle) alloys at 473 K.

Fig. 9. P-C-T curves for the a-Ti₆₇Ni₃₃ (\bullet), a-Zr₆₇Ni₃₃ (\blacksquare) and a-Hf₆₇Ni₃₃ (\blacktriangle) alloys at 473 K.

the hydrogen concentration corresponding to the deviation from the Sieverts' law. Consequently, it has been concluded that this deviation is related to the changes in the local environmental structure around hydrogen atoms [5, 13]. Similarly, the positive deviation observed in the amorphous Hf-Ni alloys may correspond to the changes in the local environmental structure around hydrogen atoms. This assumption will be confirmed if the coordination number of metal atoms around deuterium atoms is examined as a function of the deuterium concentration.

The P-C-T curves of the amorphous Ti-Ni and Hf-Ni alloys are compared with those of the amorphous Zr-Ni ones [5] as shown in Figs. 7 - 9. No pressure plateau has been observed in any alloy. The hydrogen contents at a certain hydrogen pressure for both amorphous Ti-Ni and Hf-Ni alloys are lower than that for the amorphous Zr-Ni alloys. This will be discussed again later.

3.3. Hydrogen absorption capacity

Hydrogen absorption capacity $M_{\rm H}$, defined as the maximum hydrogen content, is plotted against hydride-forming metal content in Fig. 10 for all the amorphous alloys and crystalline Hf-Ni alloys. It is seen that the $M_{\rm H}$ values of the crystalline Hf-Ni alloys show an irregular variation with the constituents of the alloys and the crystal structures. However, the $M_{\rm H}$ values of the amorphous alloys increase with increasing titanium, zirconium or hafnium content and are close to the line connecting the origin and the point (H/M) = 2, although the deviation from the line is large for the nickelrich alloys. This result indicates that the number of hydrogen atoms per titanium, zirconium or hafnium atom is approximately two, almost independent of alloy type or composition. However, it is well known that titanium, zirconium and hafnium form dihydrides TiH₂, ZrH₂ and HfH₂



Fig. 10. Compositional dependence of the hydrogen absorption capacity $M_{\rm H}$ of the amorphous Ti–Ni (•), Zr–Ni (•) and Hf–Ni (\bigstar) alloys and of the crystalline Hf–Ni (\bigtriangleup) alloys at 473 K and a hydrogen pressure of 5 MPa.

respectively, *i.e.* these metals have the ability to bind two hydrogen atoms. Consequently, it is suggested that the hydrogen absorption capacity of the amorphous alloys is determined mainly by the number of hydrogen atoms that can be bound by the hydride-forming metal in the alloy.

It is also interesting to notice that the $M_{\rm H}$ values of the amorphous Ti-Ni and Hf-Ni alloys are always lower than those of the corresponding Zr-Ni alloys. In these amorphous alloys, the lower the equilibrium hydrogen pressure $P_{\rm H_2}$ at a certain hydrogen content, the larger is the $M_{\rm H}$ value, because hydrogen pressure increases monotonically with hydrogen concentration. Hence the amorphous Zr-Ni-H system is so stable that the amorphous Zr-Ni alloys absorb much hydrogen compared with the corresponding amorphous Ti-Ni and Hf-Ni alloys. In contrast, ZrH₂ is the most stable hydride among these, because the enthalpy of formation of the binary hydride ZrH₂ (-67 kJ (mol H)⁻¹). From this, it can be concluded that amorphous alloys containing metals having a low enthalpy of formation of the binary hydride can absorb a large quantity of hydrogen.

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