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Hydrogen absorption properties of amorphous and crystalline alloys in the pseudobinary ZrCo–TiNi system

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Abstract

The single phase amorphous alloys were prepared by rapid quenching of the pseudobinary $(ZrCo)_{100-x}$ $(TiNi)_x$ alloys. The amorphous a-$(ZrCo)_{70}(NiTi)_{30}$ alloy crystallized into the ordered B2 compound, while the others did into the disordered bcc alloys. The *PCT* curve of the crystalline compounds showed a plateau pressure, while that of the amorphous one did not. Nearly the same amount of hydrogen was absorbed in the amorphous and crystalline phases. Both the amorphous and crystalline alloys showed the maximum hydrogen absorption capacity of 1.6 (H/M) at the composition of $x=30$, i.e. at the composition where the alloys crystallized into the B2 structure. The present work indicates that the ordered (B2) alloy absorbs much more hydrogen rather than the corresponding disordered (bcc) ones.
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Keywords: Intermetallics; Amorphous; Hydrogen absorption; *PCT* curves

1. Introduction

Amorphous alloys consisting of an early transition metal and a late one are expected to absorb a large amount of hydrogen. Actually, it has been demonstrated that amorphous alloys such as Ti–Cu [1] Zr–Ni [2] and so on [3] absorb a fairly large amount of hydrogen. However, it is still uncertain which state of alloys (amorphous or crystalline) absorbs much hydrogen. Furthermore, it is interesting to find whether ordered compounds absorb much more hydrogen rather than the corresponding disordered bcc alloys. In the present work, the hydrogen absorbing properties of amorphous and crystalline alloys with the compositions $(ZrCo)_{100-x}(TiNi)_x$ were investigated. The hydrogen absorption capacity of B2 ordered compounds was compared with that of bcc disordered alloys.

2. Experimental

Pseudobinary $(ZrCo)_{100-x}(TiNi)_x$ compounds were prepared by arc melting and subsequently rapidly quenched by a single roller melt spinning technique in an argon atmosphere. Structures of the as quenched and heat treated samples were identified with the Rigaku X-ray diffractometer (XRD) using the CuKα radiation. Thermal stability and the crystallization behaviors of the amorphous alloys were examined at a heating rate of 40 K/min by the differential scanning calorimeter (DSC) under argon atmosphere. The *PCT* curves of the amorphous and crystalline alloys were measured using the high pressure Sieverts apparatus.

3. Results and discussion

Fig. 1 shows XRD patterns of rapidly quenched $(ZrCo)_{100-x}(TiNi)_x$ alloys. The XRD pattern for $x=0$ (ZrCo) is mainly indexed on the basis of the bcc phase. The XRD pattern for $x=100$ (TiNi) shows a broad maximum overlapped with the Bragg peaks of the bcc structure, which consists of both amorphous and crystalline phases. On the other hand, XRD patterns for $10 \leq x \leq 95$ show only a broad maximum characteristic of an amorphous phase. The DSC curves of such samples show an exothermic peak of crystallization. Furthermore, a bright field image of TEM for these samples is featureless and the corresponding electron diffraction patterns show a halo. From XRD, DSC and TEM, the rapidly quenched

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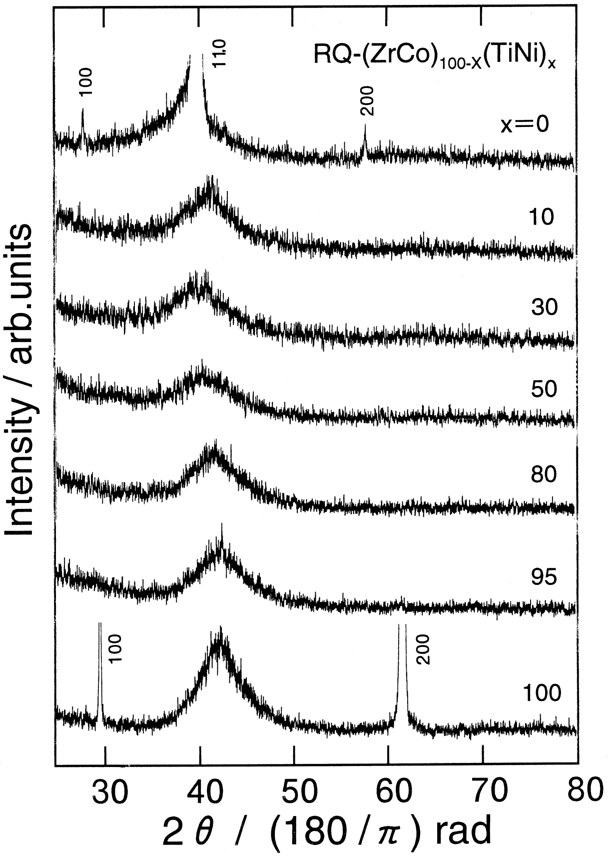

Fig. 1. X-ray diffraction patterns of rapidly quenched $(ZrCo)_{100-x}(TiNi)_x$ alloys.

$(ZrCo)_{100-x}(TiNi)_x$ are concluded to be amorphous for $10 \leq x \leq 95$. Such formation of the amorphous alloys from bcc type alloys is a first finding to our knowledge, because amorphous alloys are usually obtained by rapid quenching of the metals with the low symmetry or multiphase alloys with the low melting point.

Fig. 2 shows the enthalpy change ($-\Delta H_x$), determined from the area of crystallization exothermic peak in the DSC curve, and the apparent activation energy (E_a), determined by the peak shift method of Kissinger [4], for crystallization of a-$(ZrCo)_{100-x}(TiNi)_x$ alloys as a function of x. Both ΔH_x and E_a show an irregular, but similar composition dependence. It is worth noticing that the composition dependence for them shows a peculiar point at $x=30$, i.e. they take minimum values at this composition. This experimental result suggests that the crystallization behavior of this amorphous alloy is slightly different from the others.

Fig. 3 shows XRD patterns of c-$(ZrCo)_{100-x}(TiNi)_x$ alloys prepared by heating over 50 K of the crystallization temperature of the amorphous alloys. The XRD patterns for $x=0$, 30 and 100 are indexed on the basis of the ordered B2 structure, while the others are indexed on the basis of the disordered bcc alloy. By comparing Figs. 2 and 3, it is suggested that the peculiar crystallization behavior for $x=30$ (Fig. 2) closely relate to the formation of the B2 phase.

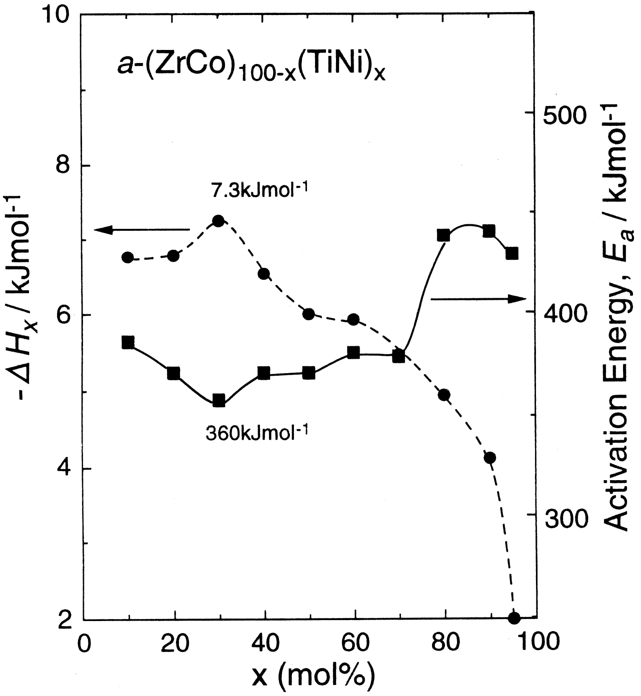

Fig. 2. Enthalpy change ΔH and the apparent activation energy E_a for crystallization of a-$(ZrCo)_{100-x}(TiNi)_x$ alloys.

Fig. 4 shows XRD patterns of c-$(ZrCo)_{100-x}(TiNi)_x$ hydrogenated at 473 K for 86 ks at 5 MPa H_2. The XRD pattern of the sample for $x=0$ (ZrCo) is indexed on the basis of $ZrCoH_3$ with the CrB structure, while that for $x=100$ (TiNi) is indexed on the basis of TiNiH. On the other hand, the XRD pattern of the sample for $x=30$ is indexed on the basis of the B2 structure, and the other pseudobinary alloys are indexed on the basis of the bcc structure. Therefore, it is concluded that these bcc type pseudobinary alloys absorb hydrogen keeping their original crystal structure.

Fig. 5 shows structures of a-$(ZrCo)_{100-x}(TiNi)_x$ alloys after hydrogenation at 5 MPa H_2 for 86 ks as a function of temperature. The open circles indicate the alloys which absorb hydrogen keeping the amorphous state. The amorphous alloys absorb hydrogen below the critical temperature, i.e. the crystallization temperature T_x which increases with the amount of x. For $x=30$ and 50, the amorphous alloys absorb hydrogen below T_x, and decomposes into ZrH_2 + the amorphous phase with increasing temperature. However, for $x=70$, no formation of TiH_2 was detected above T_x. Thus the crystallization behaviors of the pseudobinary amorphous alloys are complex and depend strongly on the alloy composition. The minimum of the crystallization temperature is 650 K for $x=30$. Then, the hydrogen absorption properties of the amorphous alloys were investigated at 473 K so that no crystallization occurs during long-term hydrogenation.

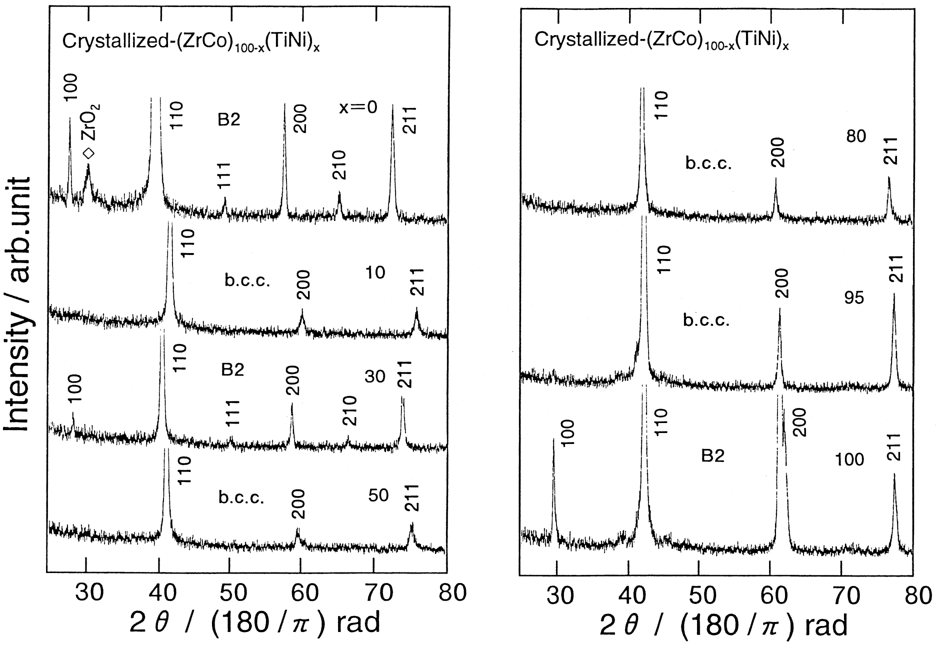

Fig. 3. X-ray diffraction patterns of annealed $(ZrCo)_{100-x}(TiNi)_x$ alloys.

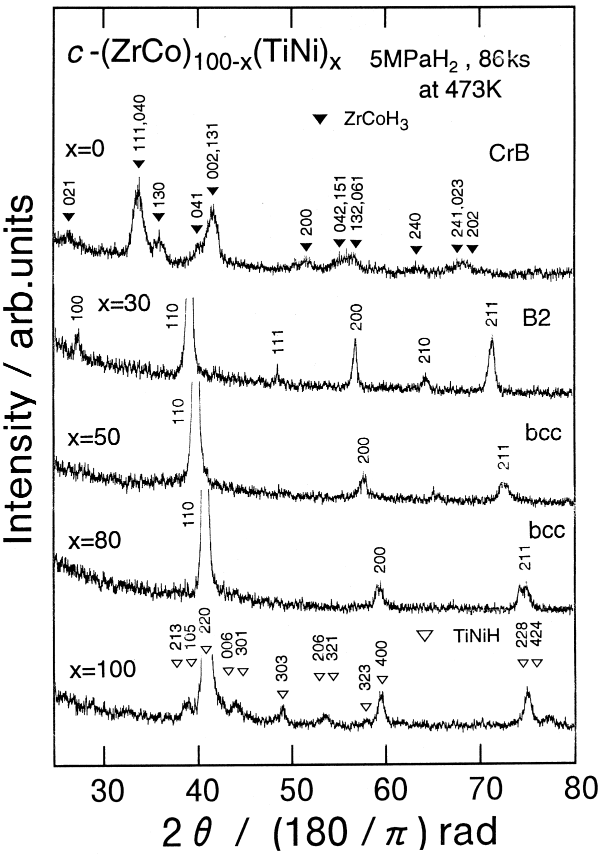

Fig. 4. X-ray diffraction patterns of c-$(ZrCo)_{100-x}(TiNi)_x$ alloys hydrogenated at 473 K for 86 ks.

Fig. 6 shows the typical *PCT* curves of a- and c-$(ZrCo)_{70}(TiNi)_{30}$ alloys at 473 K. The hydrogen pressure increases with increasing hydrogen content (H/M) for the amorphous alloys indicating the formation of the solid solution alloy. On the other hand, the *PCT* curves of the crystalline phase shows the pressure plateau below 1.0 (H/M) indicating the formation of metal hydride.

Fig. 7 shows the maximum amount of hydrogen absorbed at 5 MPa H_2 and at 573 K in the c- and a-$(ZrCo)_{100-x}(TiNi)_x$ alloys as a function of composition. Both c- and a-alloy absorb nearly same amount of hydrogen for $20 \leq x \leq 80$. It is worth noticing that maximum amount of hydrogen, i.e. 1.6 (H/M) hydrogen is absorbed in the c- and a-alloys for $x = 30$. As mentioned above, $(ZrCo)_{70}(TiNi)_{30}$ has the B2 structure. Therefore, the ordered alloy absorbs much amount of hydrogen in comparison with the disordered bcc phase. The reason why the ordered B2 alloy absorbs much hydrogen is still uncertain and may be clarified by examining hydrogen occupation sites in both states of alloys by neutron diffraction.

4. Summary and conclusions

The single phase amorphous alloys were prepared by rapid quenching of the pseudobinary $(ZrCo)_{100-x}(TiNi)_x$ alloys in the range of $x = 10$–95 mol%. The amorphous a-$(ZrCo)_{70}(NiTi)_{30}$ alloy crystallized into the ordered B2 compound, while the others did into the disordered bcc alloys. The crystalline c-$(ZrCo)_{70}(NiTi)_{30}$ absorbed hydrogen keeping the B2 structure, while the others absorbed

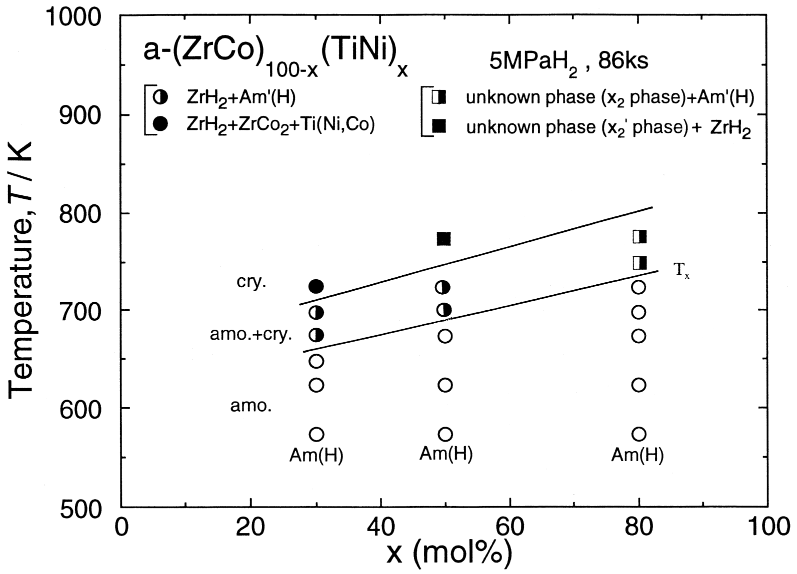

Fig. 5. Structures of *a*-$(ZrCo)_{100-x}(TiNi)_x$ alloys after hydrogenation for 86 ks at several temperatures.

hydrogen in the bcc state. The crystallization temperature of the amorphous phase increased with increasing the amount of *x*. The *PCT* curve of the crystalline alloys showed the plateau pressure, while that of the amorphous one did not. Nearly same amount of hydrogen was absorbed in the amorphous and crystalline phase. Both the amorphous and crystalline alloys showed the maximum hydrogen absorption capacity of 1.6 (H/M) at the composition of $x=30$, i.e. where the alloy crystallized the B2 structure. The present work showed that that ordered (B2) alloy could absorb much hydrogen rather than the corresponding disordered (bcc) ones.

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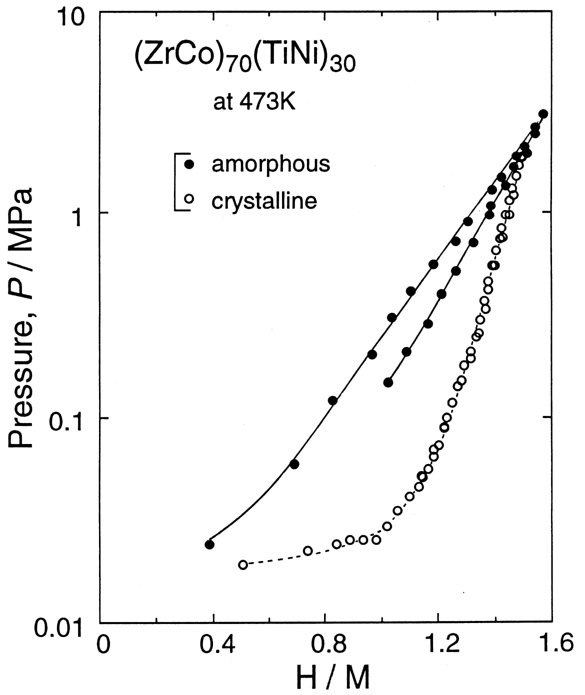

Fig. 6. Typical *PCT* curves of amorphous and crystalline $(ZrCo)_{70}(TiNi)_{30}$ alloys at 473 K.

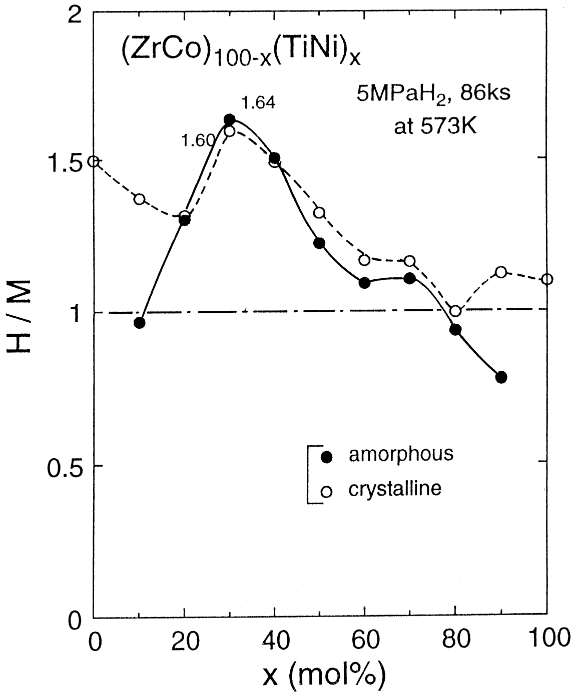

Fig. 7. Maximum hydrogen contents absorbed in amorphous and crystalline $(ZrCo)_{100-x}(TiNi)_x$ alloys at 5 MPa H_2 and at 573 K.

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