Glassy and icosahedral phases in rapidly solidified Ti–Zr–Hf–(Fe, Co or Ni) alloys

N. Chen a,*, D.V. Louzguine-Luzgin b, S. Ranganathan c, A. Inoue b

a Department of Materials Science, Graduate School, Tohoku University, Sendai 980-8577, Japan
b Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
c Department of Metallurgy, Indian Institute of Science, Bangalore 560012, India

Abstract

The icosahedral quasicrystalline, amorphous plus crystalline and glassy phases were formed in Ti_{40}Zr_{20}Hf_{20}(3d-LTM)_{20} alloys (3d-LTM=3d late transition metals Fe, Co and Ni). The icosahedral phase formed in the melt-spun Ti_{40}Zr_{20}Hf_{20}Fe_{20} alloy is metastable and the average size of the quasicrystalline icosahedral particles precipitated in the amorphous matrix is 5 nm. The metastable icosahedral phase transformed to a big-cubic fcc Hf_{2}Fe phase with the grain size of about 20 nm after annealing for 1.8 ks at 841 K. The glassy phase was formed in the melt-spun Ti_{40}Zr_{20}Hf_{20}Co_{20} alloy and no metastable phase was found to form during the transformation from glassy phase to a stable crystalline phase. Icosahedral phase formed in the melt-spun Ti_{40}Zr_{20}Hf_{20}Ni_{20} alloy transformed to a big-cubic fcc (Zr,Ti)_{2}Ni solid solution phase by a solid state reaction.

PACS: 61.43.Fs; 61.44.Br; 61.46.+w; 64.60.-i

1. Introduction

Since a thermodynamically stable icosahedral (I) phase with the composition near Ti_{41.5}Zr_{41.5}Ni_{17} was reported in Ti–Zr–Ni alloys in an as-solidified state as well as in an annealed state [1,2], extensive studies have been done [3–8]. From [6], an optimal quasicrystal-forming composition is found to be Ti_{40}Zr_{40}Ni_{20}. The formation of the I-phase was also extended to Zr-based Zr_{55}Cu_{30}Ti_{15}Ni_{10} alloy containing relatively low oxygen content (below 800 mass ppm) [9].

It is known that Hf is chemically similar to Zr and these two elements have the close values of the atomic radii of 0.159 and 0.160 nm, respectively [10]. Recently we have studied the effect of Hf addition substituting half quantity of Zr in the Ti_{40}Zr_{40}Ni_{20} alloy and successfully obtained the thermodynamically stable icosahedral phase in Ti_{40}Zr_{20}Hf_{20}Ni_{20} alloy [11]. In the present work we study the influence of the nearest similar 3d late transmission metals: Fe and Co substituting Ni in Ti_{40}Zr_{20}Hf_{20}Ni_{20} alloy on the formation of glassy and icosahedral phases.

2. Experimental procedure

Ingots of Ti_{40}Zr_{20}Hf_{20}(Fe, Co or Ni)_{20} alloys were prepared by arc-melting the mixtures of pure Ti, Zr, Hf, Fe, Co and Ni metals in a Ti-gettered argon atmosphere. The purity of Ti, Zr and Hf metals was over 99.7 mass% while the other metals had a 99.9 mass%
purity. From these alloy ingots, ribbon samples were prepared by rapid solidification of the melt on a single copper roller at a surface velocity of 40 m/s in an argon atmosphere. The structure of the samples was examined by X-ray diffractometry (XRD) with monochromatic CuKα radiation. The phase transformations were studied by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s and isothermal calorimetry. During isothermal calorimetry the samples were heated up to the testing temperature at the highest possible rate of 1.67 K/s. The microstructure was examined by transmission electron microscopy (TEM) using a JEM 2010 (JEOL) microscope operating at 200 kV. The samples for TEM were prepared by the ion milling technique.

3. Experimental results

Fig. 1 shows X-ray diffraction patterns of the melt-spun Ti₄₀Zr₂₀Hf₂₀(Fe, Co or Ni)₂₀ alloys. The nanoscale icosahedral particles primarily precipitated in the amorphous matrix of the melt-spun Ti₄₀Zr₂₀Hf₂₀Fe₂₀ alloy upon cooling while a single I-phase was formed in the melt-spun Ti₄₀Zr₂₀Hf₂₀Ni₂₀ alloy. A glassy single phase was obtained in the melt-spun Ti₄₀Zr₂₀Hf₂₀Co₂₀ alloy.

It is interesting to find that the broad halo of the melt-spun Ti₄₀Zr₂₀Hf₂₀Fe₂₀ alloy is somewhat shifted from that of the glassy Ti₄₀Zr₂₀Hf₂₀Co₂₀ alloy. This is connected with precipitation of the I-phase within the glassy matrix. However, the location of the (101000) peak in Ti₄₀Zr₂₀Hf₂₀Fe₂₀ alloy is also different from that in the XRD pattern of the Ti₄₀Zr₂₀Hf₂₀Ni₂₀ alloy although the three late transition metals have similar atomic radii values of 1.24 nm for Fe and 1.25 nm for Co and Ni.

Fig. 2 shows DSC curves of the melt-spun Ti₄₀Zr₂₀Hf₂₀(Fe, Co or Ni)₂₀ alloys. There are two exothermic peaks in the DSC curve of the melt-spun Ti₄₀Zr₂₀Hf₂₀Fe₂₀ alloy caused by the phase transformations on heating. The first exothermic peak is related to the precipitation of a big-cubic fcc cF₉₆ Hf₂Fe phase with a lattice constant of a = 1.205 nm (Fig. 3).

The structure of Ti₄₀Zr₂₀Hf₂₀Fe₂₀ alloy in as-solidified state and annealed for 1.8 ks at 841 K is shown in Fig. 4(1(a)) and (2(a)), respectively. The average size of the quasicrystalline particles dispersed in the amorphous matrix in the as-melt-spun Ti₄₀Zr₂₀Hf₂₀Fe₂₀ alloy is 5 nm while the average size of the metastable big-cubic cF₉₆ Hf₂Fe phase precipitated by the first exothermic peak is 20 nm.

---

**Fig. 1.** XRD patterns of the melt-spun Ti₄₀Zr₂₀Hf₂₀(Fe, Co or Ni)₂₀ alloys.

**Fig. 2.** DSC curves of the melt-spun Ti₄₀Zr₂₀Hf₂₀(Fe, Co or Ni)₂₀ alloys.

**Fig. 3.** XRD patterns of the Ti₄₀Zr₂₀Hf₂₀Fe₂₀ alloy in the (a) as-solidified state and (b) annealed for 1.8 Ks at 841 K.
This phase has a cluster structure close to that in the I-phase [12–15] which is reflected in the very close location of the strong XRD peaks for these two phases as shown in Fig. 3. The DSC trace of the melt-spun Ti_{40}Zr_{20}Hf_{20}Co_{20} alloy shows an increase in $C_p$ at the glass transition temperature ($T_g$) and a single exothermic peak due to subsequent devitrification starting at $T_x$ indicating that no metastable phase was formed during the transformation from glassy phase to stable crystalline phase.

From the DSC curve of the melt-spun Ti_{40}Zr_{20}Hf_{20}Ni_{20} alloy at the first heating pass the I-phase is stable below 1000 K. Concerning the phase transformation related to an endothermic peak in the DSC curve it has been reported that I-phase forms by peritectoid reaction from Laves phase + αTi/Zr phase or by a solid-state transformation from Laves phase [1–3,16,17]. In the present study Fig. 5 shows the transformation happens between I-phase and big-cubic fcc C96 (Zr,Ti)$_2$Ni solid solution phase. During the cooling of the sample to room temperature at a slow cooling rate under an argon atmosphere partially (Zr,Ti)$_2$Ni phase transformed to I-phase again. It is therefore concluded that the reaction between I-phase and (Zr,Ti)$_2$Ni phase should be reversible. The reason why that (Zr,Ti)$_2$Ni phase cannot transform to I-phase completely can be considered as non-sufficiently large driving force for I-phase nucleation due to the small enthalpy difference (4.68 J/g) between I-phase and (Zr,Ti)$_2$Ni phase as shown in the DSC curve. In the second heating and third heating curves the endothermic peak shifted to the lower temperature (see Fig. 2). The reason can be identified that smaller quantity I-phase than initial state makes the transformation happen at a smaller driving force.

4. Discussion

In the melt-spun Ti_{40}Zr_{20}Hf_{20}Fe_{20} alloy, the transformation from amorphous + nanoscale I-phase to residual amorphous + 'big-cubic' Hf$_2$Fe phase obeys the following kinetic law [18] for the volume fraction ($x$) transformed as a function of time ($t$)

$$X(t) = 1 - \exp[-kt^n].$$  \hfill (1)

Fig. 6(b) shows the linear Avrami plot $\ln[-\ln(1 - x)]$ versus $\ln(t)$. From the Avrami exponent $n$ value of 2.3 obtained from the least squares fitting of the Avrami plot which is close to 2.5, it may be said that the transformation from amorphous + I-phase to residual amorphous + big-cubic Hf$_2$Fe phase is a diffusion-controlled type at nearly constant nucleation rate.

It is reported that the addition of Cu to the Ti–Zr–Ni system leads to a significant improvement in amorphous- and I-phase-forming abilities [19–23]. However the I-phase formed directly at rapid solidification or precipitated upon annealing in Ti–Zr–Ni–Cu alloys was metastable and transformed to the stable crystalline phases during heating to high temperature [24,9].
The present work the substitution of half Zr by Hf in the quasicrystal-forming composition Ti$_{40}$Zr$_{40}$Ni$_{20}$ alloy [6] which is near the composition of the stable I-phase Ti$_{41.5}$Zr$_{41.5}$Ni$_{17}$ [1] does not affect significantly the precipitation of an I-phase. As a result the I-phase formed in the melt-spun Ti$_{40}$Zr$_{20}$Hf$_{20}$Ni$_{20}$ alloy also has a high stability. The chemical similarity of Hf and Zr elements with close values of atomic radii of 0.159 and 0.160 nm, respectively, can be taken into consideration. The substitution of Ni by Fe and Co in the melt-spun Ti$_{40}$Zr$_{20}$Hf$_{20}$Ni$_{20}$ alloy causes an improvement in the glass-forming ability and Co is the most effective element to enable the formation of a single glassy phase. On the other hand, Ni is the most optimum element for the formation of I-phase in the rapidly solidified Ti–Zr–Hf–(Fe, Co or Ni) alloys. It is possible that higher Ti content is required for stabilization of the I-phase in Fe- and Co-bearing alloys [7].

5. Summary

(1) Among the rapidly solidified Ti–Zr–Hf–(Fe, Co or Ni) alloys a stable single I-phase was obtained only in the melt-spun Ti$_{40}$Zr$_{20}$Hf$_{20}$Ni$_{20}$ alloy, which indicates that Ni is the most effective element for the formation of I-phase while the addition of Co leads to a significant improvement in the glass-forming ability.

(2) A mixture of amorphous plus nanoscale metastable I-phase with an average size of 5 nm was formed in the melt-spun Ti$_{40}$Zr$_{20}$Hf$_{20}$Fe$_{20}$ alloy. The amorphous phase in this alloy crystallizes through a double-stage exothermic reaction, the first peak of which corresponds to the precipitation of a big-cubic fcc Hf$_2$Fe phase with a grain size of about 20 nm.

(3) The phase transformation (amorphous + nano I-phase → residual amorphous + ‘big-cubic’ fcc Hf$_2$Fe related to the first exothermic peak in the DSC curve of the melt-spun Ti$_{40}$Zr$_{20}$Hf$_{20}$Fe$_{20}$ alloy may correspond to a peritectic-type transformation involving nucleation and diffusion-controlled growth of Hf$_2$Fe phase at nearly constant nucleation rate.

Acknowledgements

The authors thank the useful discussion from Dr Hasegawa and Dr Bian.

References
