Initial crystallization processes of Zr-Cu-Rh metallic glasses



2001 J. Phys.: Condens. Matter 13 L803

(http://iopscience.iop.org/0953-8984/13/35/102)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) L803–L809 PII: S0953-8984(01)22957-9

**LETTER TO THE EDITOR**

# Initial crystallization processes of Zr–Cu–Rh metallic glasses

**Chunfei Li[1,3], Limin Wang[1] and Akihisa Inoue[2]**

[1] Inoue Superliquid Glass Project, ERATO, JST, Sendai 982-0807, Japan
[2] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

E-mail: li@sendai.jst.go.jp

Received 22 March 2001
Published 16 August 2001
Online at stacks.iop.org/JPhysCM/13/L803

**Abstract**
$Zr_{70}Cu_{30}$ and $Zr_{70}Cu_{20}Rh_{10}$ glassy alloys were prepared by a single-roller melt-spinning method and their crystallization processes were studied by differential scanning calorimetry, x-ray diffraction and transmission electron microscopy. For the $Zr_{70}Cu_{30}$ alloy, the glassy state crystallizes through a single exothermic reaction due to the precipitation of the stable $Zr_2Cu$ crystalline phase. For the $Zr_{70}Cu_{20}Rh_{10}$ alloy, metastable icosahedral quasicrystalline and FCC-$Zr_2Rh$ phases precipitate from the glassy matrix in the initial crystallization process, followed by the phase transformation to $Zr_2Cu$ and ZrRh crystalline phases upon further annealing. These results illustrate that the partial substitution of Cu by Rh in the $Zr_{70}Cu_{30}$ glassy alloy is effective in promoting the precipitation of the metastable icosahedral quasicrystalline phase. To explain these experimental results, the existence of icosahedron-like atomic clusters in the $Zr_{70}Cu_{20}Rh_{10}$ glassy alloy is suggested.

## 1. Introduction

The Zr–Al–Ni–Cu alloy system is an attractive combination to researchers engaged in the studies of glassy alloys owing to its high glass-forming ability [1, 2], which is defined as the critical cooling rate required to avoid the formation of any detectable crystalline/quasicrystalline phases. The high-glass forming ability is evidenced by the successful preparation of cylindrical bulk glassy alloys with diameters up to 30 mm. $Zr_{55}Al_{10}Ni_5Cu_{30}$ [2] and $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ [1] are the typical two compositions for the preparation of bulk glassy alloys. A large supercooled liquid region $\Delta T_x$, which is defined as the temperature span between the glass transition temperature $T_g$ and the crystallization temperature $T_x$, is observed in the differential scanning calorimetry (DSC) curves of the

[3] Corresponding author: Inoue Superliquid Glass Project, Yagiyamaminami 2-1-1, Taihaku-ku, Sendai 982-0807, Japan.

metallic glasses. The existence of the supercooled liquid state at temperatures below $T_x$ is expected to enable the warm-working of the bulk glassy alloy to a desired shape, which is important for practical application. In order to examine the reason for the high stability of the supercooled liquid, the crystallization processes of a number of Zr-based metallic glasses have been studied [3–7]. It has been reported that the addition of noble metal M (M = Pd, Pt, Au or Ag) to the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy causes a change in the crystallization mode from the single step one to the double step one [6, 7]. The low temperature exothermic reaction corresponds to the precipitation of a metastable icosahedral quasicrystalline phase (I-phase) from the glassy matrix. Furthermore, the partial dispersion of nanoscale I-phase particles in $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}M_5$ metallic glasses leads to good mechanical properties [7, 8]. For these reasons, the formation of the I-phase in M-containing Zr-based alloys has attracted great attention.

To determine the dominant elements in the precipitation of the I-phase, the possibility of the I-phase formation in ternary Zr-based glassy alloys has also been examined. Reports on the precipitation of the I-phase have been limited to Pd-, Pt- or Au-containing ternary metallic glasses [9, 10]. This paper is intended to report the precipitation of the I-phase in $Zr_{70}Cu_{20}Rh_{10}$ metallic glass, which contains no Pd, Pt or Au elements. The reasons for the precipitation of the I-phase is discussed by comparing the crystallization process of $Zr_{70}Cu_{20}Rh_{10}$ metallic glass with that of $Zr_{70}Cu_{30}$.

## 2. Experimental procedure

Alloy ingots were prepared by arc-melting a mixture of pure metals. From the alloy ingots, ribbons with a cross-section of approximately $0.03 \times 1$ mm$^2$ were prepared by a single roller melt-spinning method in an argon atmosphere. The melt-spun ribbons were annealed in the DSC cell to examine the initial precipitates or in an evacuated silica tube to verify the stable crystalline phases. The structure was examined by x-ray diffraction (XRD) and the thermal stability was investigated by DSC at a heating rate of 0.67 K s$^{-1}$. The microstructure was examined using a transmission electron microscope (TEM) JEM-3000F, operated at 300 kV. The diameter of the electron beam was focused to 1.0 nm in the nanobeam diffraction.

## 3. Results and discussion

DSC curves of the melt-spun ribbons are shown in figure 1. For the $Zr_{70}Cu_{30}$ alloy, the glassy state changes to a supercooled liquid state accompanying an endothermic reaction marked with $T_g$. The supercooled liquid region is followed by a single exothermic reaction. For the $Zr_{70}Cu_{20}Rh_{10}$ glassy alloy, the supercooled liquid region is followed by two exothermic reactions.

XRD patterns of the $Zr_{70}Cu_{30}$ alloy are shown in figure 2. The halo-ring indicates that the melt-spun ribbon is in a glassy state. XRD patterns of the alloy annealed under the conditions of 642 K–0.5 min and 642 K–60 min indicate that the crystallization proceeds through the direct precipitation of the stable $Zr_2Cu$ crystalline phase from the glassy matrix. The XRD pattern of the $Zr_{70}Cu_{20}Rh_{10}$ ribbon annealed for 0.5 min at 683 K is shown in figure 3. The diffraction peaks are identified as I- and FCC-$Zr_2Rh$ [11] phases, which was verified by TEM observation to be illustrated later. Further annealing at the same temperature leads to the phase transformation to stable $Zr_2Cu$ and ZrRh crystalline phases, indicating that the initial I- and FCC-$Zr_2Rh$ phases are in a metastable state.

To verify the above indexing result in the XRD patterns and to examine the morphology of

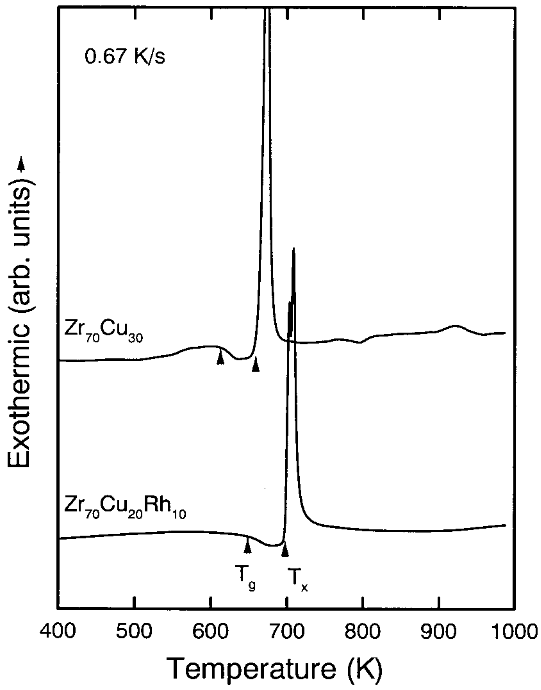


**Figure 1.** DSC curves of the melt-spun $Zr_{70}Cu_{30}$ and $Zr_{70}Cu_{20}Rh_{10}$ ribbons.

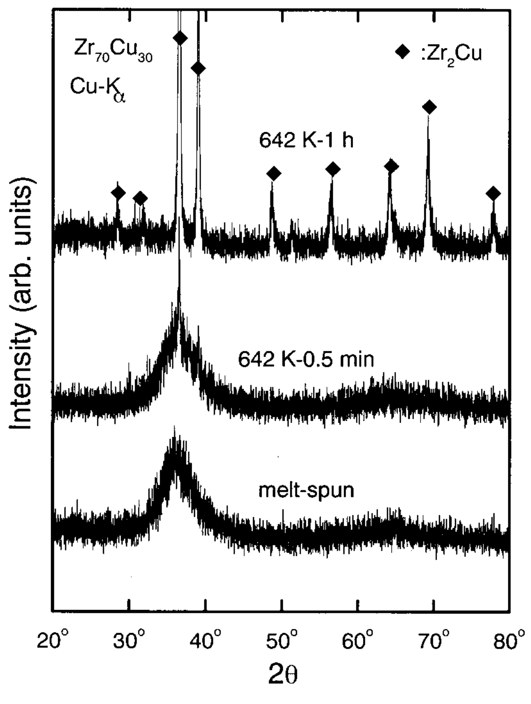


**Figure 2.** XRD patterns of the melt-spun and annealed $Zr_{70}Cu_{30}$ ribbon. Annealing was performed in the DSC cell (642 K–0.5 min) or in an evacuated silica tube (642 K–1 h).

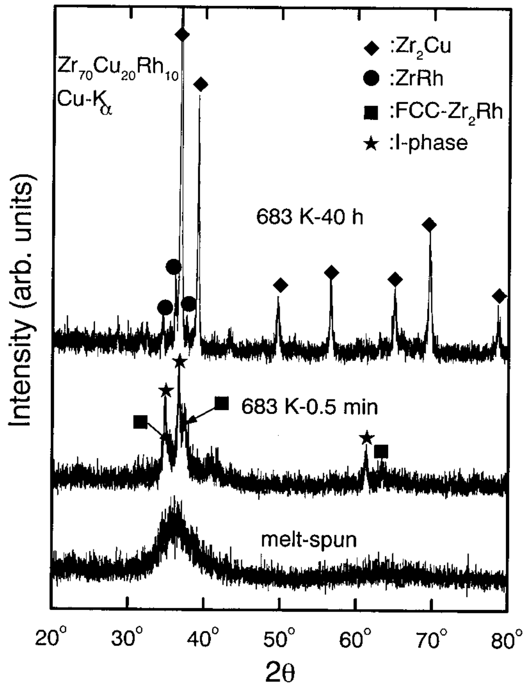


**Figure 3.** XRD patterns of the melt-spun and annealed $Zr_{70}Cu_{20}Rh_{10}$ ribbon. Annealing was performed in the DSC cell (683 K–0.5 min) or in an evacuated silica tube (683 K–40 h).

the annealed specimen, the $Zr_{70}Cu_{20}Rh_{10}$ ribbon annealed for 0.5 min at 683 K was examined by TEM. The bright-field TEM image shown in figure 4 reveals that the size of the precipitated particle ranges from 20 to 40 nm in diameter. Figures 5(a), 5(b) and 5(c) show the nanobeam electron diffraction patterns corresponding to the five-, three- and twofold symmetries of the I-phase, respectively. Figure 5(d) is the nanobeam electron diffraction pattern of FCC-$Zr_2Rh$ taken with the incident electron beam parallel to the [1 1 1] orientation.

It is well known that the centre site of the icosahedron in an I-phase can be occupied by an atom or can remain empty [12]. The atomic radius of the atom occupying the centre site should be approximately 5% smaller than that occupying the vertex. The Ti-based I-phase belongs to the center-site-occupied type [13]. Noticing the fact that Zr and Ti are located in the same 4A group in the periodic table, the icosahedral centre sites of the present I-phase are presumed to be occupied by atoms. The vertices should be occupied mainly by Zr atoms because of the alloy composition. Considering the atomic radii of Zr (0.162 nm), Cu (0.128 nm) and Rh (0.134 nm), it is suggested that the centre site of the icosahedron is occupied by an Rh atom.

The precipitation of an I-phase was found in all the 4A elements (Ti, Zr and Hf) based glassy alloys, e.g., $Ti_{60}Zr_{15}Ni1_{15}Cu_{10}$ [14], $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ [6] and $Hf_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ [15]. The formation of the I-phase in the 4A-element-based alloys is closely related to the $Ti_2Ni$-type compounds [11], which are represented by $A_2B$ hereafter. The A component includes Sc, Ti and Hf. The B component includes Ni, Rh, Pd and Pt. $Ti_2Ni$, $Hf_2Rh$, $Sc_2Pd$ and $Hf_2Pt$ are the representative of these compounds. Although there are no stable $Ti_2Ni$-type $A_2B$ compounds with the A sites occupied by Zr atoms, a metastable $Zr_2Ni$ compound of $Ti_2Ni$ type was reported in the initial crystallization processes of Zr–Ni metallic glassy alloys [16].

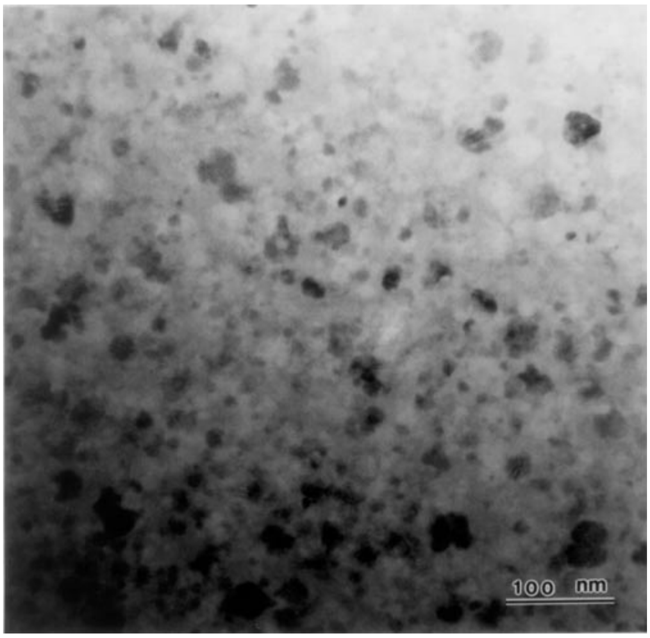


**Figure 4.** Bright-field TEM image of the $Zr_{70}Cu_{20}Rh_{10}$ ribbon annealed for 0.5 min at 683 K in the DSC cell. The precipitated particle size ranges from 20 to 40 nm.

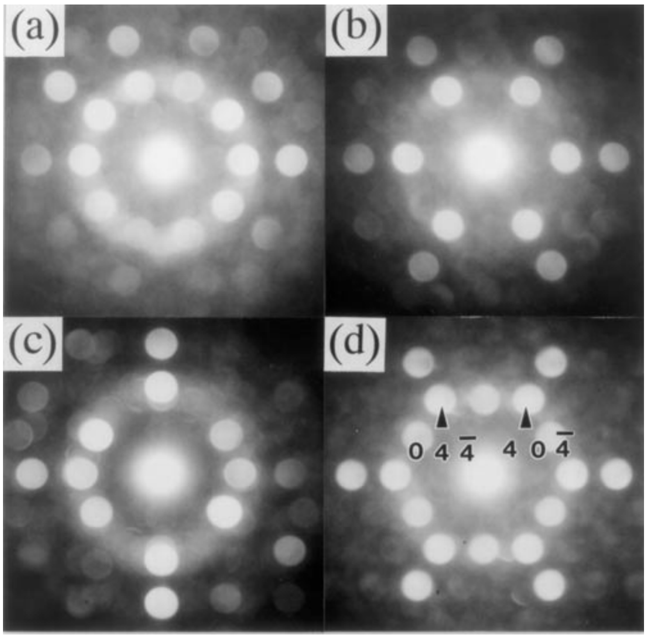


**Figure 5.** Nanobeam electron diffraction patterns of the $Zr_{70}Cu_{20}Rh_{10}$ ribbon annealed for 0.5 min at 683 K. (a), (b) and (c) correspond to the five-, three- and twofold symmetries of the I-phase, respectively. (d) is the electron diffraction pattern of FCC-$Zr_2Rh$ taken with the incident electron beam parallel to the [1 1 1] orientation.

Furthermore, Zr can form stable $Ti_2Ni$-type compounds with Pd, Rh and Pt in the existence of oxygen and with Zn in the existence of nitrogen [11]. The local atomic configuration of the $A_2B$ compound consists of an icosahedron, in which the centre site is occupied by one B atom and the vertices are occupied by nine A atoms and three B atoms [17]. The threefold symmetry axis of the icosahedron in the $Ti_2Ni$-type compound is approximately parallel to the [1 1 1] orientation. This explains the resemblance of the FCC-$Zr_2Rh$ diffraction pattern (figure 5(d)) to that of the I-phase with threefold symmetry (figure 5(b)). It is noted that the existence of the above-mentioned Ni, Pd or Pt is necessary for the precipitation of an I-phase in 4A-element-based metallic glasses, e.g., Ni in $Ti_{60}Zr_{15}Ni_{15}Cu_{10}$ [14], Pd in $Zr_{70}Cu_{10}Pd_{10}$ [10] and Pt in $Hf_{70}Cu_{20}Pt_{10}$ [18]. The present experimental results demonstrate that the addition of Rh to the Zr–Cu glassy alloy is effective in promoting the formation of an I-phase. Based on these experimental results, it is suggested that icosahedron-like atomic clusters, the atomic configuration of which is similar to that in the $Ti_2Ni$-type crystalline phases, exist in the glassy states. This speculation is also supported by an analysis of chemical affinities and atomic radii. Taking the present $Zr_{70}Cu_{20}Rh_{10}$ glassy alloy as an example, the heats of mixing for Zr–Cu, Zr–Rh and Cu–Rh atomic pairs are -23, -72 and -2 kJ $mol^{-1}$, respectively [19]. The atomic binding between the Zr–Rh atomic pair is much stronger than those of Zr – Cu and Cu–Rh, implying that the Rh atom is intended to be surrounded by as many as possible Zr atoms in the melt. The formation of an icosahedron-like atomic cluster, in which the centre site is occupied by an Rh atom and the vertices are occupied mainly by Zr atoms, satisfies the above-mentioned requirement. This speculation is also supported by the analysis of geometrical factors, which is mentioned above. Some of the icosahedron-like atomic clusters in the melt may be quenched to the glassy state and serve as the seeds for the precipitation of the metastable I- and FCC-$Zr_2Rh$ phases in the initial crystallization process.

## 4. Summary

The substitution of 10 at.% Cu by Rh in the $Zr_{70}Cu_{30}$ metallic glass causes a change in the crystallization mode from the single step one to the double step one. The single step crystallization of the $Zr_{70}Cu_{30}$ metallic glass corresponds to the direct precipitation of stable $Zr_2Cu$ crystalline phase from the glassy matrix. The low temperature exothermic reaction of the $Zr_{70}Cu_{20}Rh_{10}$ metallic glass corresponds to the precipitation of I- and FCC-$Zr_2Rh$ phases, which transform to other stable crystalline phases upon further annealing. It is suggested that the addition of Rh to the $Zr_{70}Cu_{30}$ glassy alloy introduces icosahedron-like atomic clusters to the glassy state, which serve as the seeds for the precipitation of metastable I- and FCC-$Zr_2Rh$ phases in the initial crystallization process.

## References


[1] Inoue A, Zhang T, Nishiyama N, Ohba K and Masumoto T 1993 *Mater. Trans. JIM* **34** 1234
[2] Inoue A and Zhang T 1996 *Mater. Trans. JIM* **37** 185
[3] Eckert J, Mattern N, Zinkevitch M and Seidel M 1998 *Mater. Trans. JIM* **39** 623
[4] Gebert A, Eckert J and Schultz L 1998 *Acta Mater.* **46** 5475
[5] Mattern N, Eckert J, Seidel M, Kühn U, Doyle S and Bächer I 1997 *Mater. Sci. Eng.* A **226–228** 468
[6] Chen M W, Zhang T, Inoue A, Sakai A and Sakurai A 1999 *Appl. Phys. Lett.* **75** 1697
[7] Inoue A, Zhang T, Saida J, Matsushita M, Chen M W and Sakurai T 1999 *Mater. Trans. JIM* **40** 1181
[8] Inoue A, Zhang T, Saida J, Matsushita M, Chen M W and Sakurai T 1999 *Mater. Trans. JIM* **40** 1137
[9] Saida J, Matsushita M, Li C and Inoue A 2000 *Appl. Phys. Lett.* **76** 3558
[10] Matsushita M, Saida J, Li C and Inoue A 2000 *J. Mater. Res.* **15** 1280
[11] Nevitt M V 1967 *Intermetallic Compounds* ed J H Westbrook (New York: Wiley) pp 217–229

[12] Takeuchi S and Edakawa K 1997 *Crystalline, Quasicrystalline and Amorphous Solid* (Tokyo: Uchitaroukakuho) pp 87–116 (in Japanese)
[13] Dong C, Hei Z K, Wang L B, Song Q H, Wu Y K and Kuo K H 1986 *Scr. Metall.* **20** 1155
[14] Wang L, Li C and Inoue A *Mater. Trans. JIM* at press
[15] Li C, Matsushita M, Saida J and Inoue A 2000 *Appl. Phys. Lett.* **77** 528
[16] Altounian Z, Batalla E, Strom-Olsen J O and Walter J L 1987 *J. Appl. Phys.* **61** 149
[17] Yang Q B 1988 *Phil. Mag. Lett.* **57** 171
[18] Li C and Inoue A *J. Mater. Sci. Lett.* at press
[19] De Boer F R, Boom R, Mattens W C M, Miedema A R and Niessen A K 1989 *Cohesion in Metals* (Amsterdam: Elsevier) pp 718–9