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LETTER TO THE EDITOR

Icosahedral quasicrystalline phase formation in Zr-Al-Ni-Cu glassy alloys by addition of Nb, Ta and V elements

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Abstract
It is found that an icosahedral quasicrystalline phase is formed in the Zr-Al-Ni-Cu glassy alloy by addition of Nb, Ta or V elements. The icosahedral phase was confirmed as a primary precipitation phase in the melt-spun $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}X_5$ (X=Nb, Ta or V) glassy alloys with a two-stage crystallization process after the distinct glass transition. The onset temperature of the transformation from glass to icosahedral phase is 705 K for Nb, 710 K for Ta and 702 K for V at the heating rate of 0.67 Ks^{-1}. The size of the icosahedral particles is in the range of 10 to 50 nm. The second crystallization reaction results in the formation of Zr_2Cu + Zr_2Ni + Zr_3Al_2 phases through a sharp exothermic reaction. The formation of a nano scale icosahedral phase in the Zr-Al-Ni-Cu glassy alloy by addition of Nb, Ta or V, as well as noble metals, indicates that the increase of the nucleation rate contributes to the precipitation of the icosahedral phase, leading to the concept that the icosahedral short-range order exists in the glassy state in the Zr-Al-Ni-Cu alloy.

Since it was reported that an icosahedral quasicrystalline phase was formed in the Zr-Al-Ni-Cu [1] and Zr-Al-Ni-Cu-Ti [2] glassy alloys with high glass-forming ability, the formation mechanism of the icosahedral phase and the correlation between the quasicrystalline phase and the local structure [3] in Zr-based glassy alloys have attracted attention in relation to the aspects of the high stability of glassy state. However, a quasicrystalline phase in the Zr-based alloys is precipitated under the existence of oxygen impurity above 1700 ppm mass% [4] and the precipitation of the icosahedral phase strongly depends on the cooling rate and oxygen content in the sample preparation [5,6]. Very recently, the reproducible formation of the icosahedral phase as a primary precipitation phase from an amorphous state has been reported over a wide annealing temperature range in the Zr-Al-Ni-Cu-NM, Zr-Al-Ni-NM (NM=Ag, Pd, Au and Pt), Zr-Ni-M (M=Pd, Au and Pt), Zr-TM-Pd (TM=Fe, Co and Cu) and Zr-Pd glassy alloys [7–11]. These results give a unique opportunity to clarify the kinetics [12] and mechanism for

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the transformation from amorphous to icosahedral phase and the structural correlation between the amorphous and icosahedral phases. The authors have clarified that the noble metals play an important role in the increase of the nucleation rate and in the decrease of the grain growth rate [13]. These results strongly suggest that an icosahedral short-range order exists in the glassy state. However, little is known about the formation of an icosahedral phase in the Zr-based alloys containing other additional elements except noble metals. In this letter, we show that a nano scale icosahedral phase is formed in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}X_5$ (X=Nb, Ta or V) glassy alloys.

The melt-spun ribbon samples with a cross section of 0.03×1 mm^2 were produced from alloy ingots prepared by arc melting with high purity elements in an argon atmosphere. Thermal properties were measured by differential scanning calorimetry (DSC) at a heating rate of 0.67 Ks^{-1}. The structure of annealed samples was examined by x-ray diffractometry with Cu-Kα radiation and field-emission transmission electron microscopy (FE-TEM) with an accelerating voltage of 300 kV (JEOL JEM-3000F). The sample for TEM observation was prepared by the ion milling technique. ¶=SFigure+[b]1993601.eps19pcDSC curves of melt-spun $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}X_5$ (XNb, Ta and V) glassy alloys.

The oxygen content of the as-quenched ribbons is in the range of 400 to 900 ppm mass% analysed by the inductively coupled plasma spectroscopy, where the influence of oxygen impurity for the transformation behaviour can be ignored [4]. Figure 1 shows DSC curves of the melt-spun $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}X_5$ (X=Nb, Ta or V) glassy alloys. The glass transition is clearly observed for all alloys and the T_g is 650 K for the Nb alloy, 639 K for the Ta alloy and

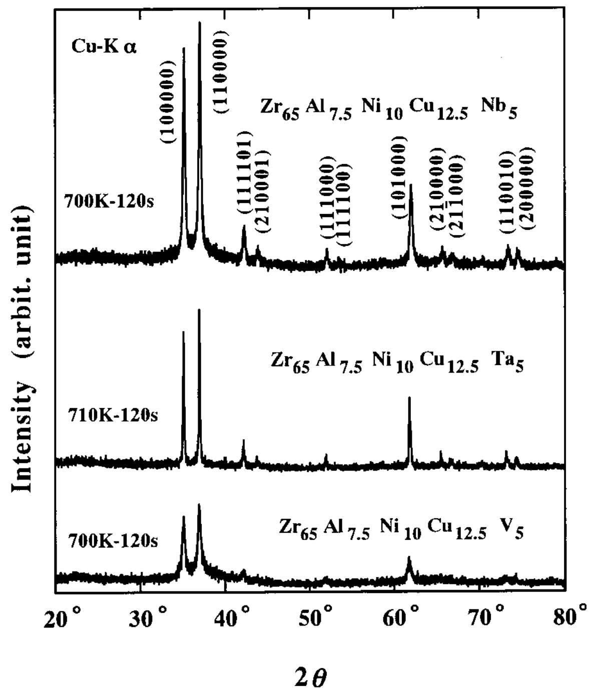

Figure 1. X-ray diffraction patterns of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}X_5$ (X=Nb, Ta and V) glassy alloys annealed for 120 s at 700 K and 710 K.

637 K for the V alloy. The crystallization proceeds through two exothermic reactions for all alloys. The onset temperature, T_x of the first exothermic peak is 705 K for the Nb-containing alloy, 710 K for the Ta alloy and 702 K for the V alloy. The sharp second exothermic reaction is also observed in the Nb and Ta alloys. The temperature interval between two exothermic peaks is approximately 60 K. However, in the V alloy, the second exothermic reaction consists of two exothermic peaks. The temperature interval between the first exothermic peak and the higher peak of the second reaction is approximately 40 K. Thus, the crystallization behaviour with a two-stage reaction is similar to that of $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}M_5$ (M=Ag, Pd, Au and Pt) glassy alloys [7]. Figure 2 shows x-ray diffraction patterns of the samples annealed for 120 s at 700 K and 710 K, which were subjected to the transformation due to the first exothermic peak. Several peaks can be observed in addition to a halo peak in the Nb and V alloys. In the Ta alloy, a halo peak is not observed except for some sharp diffraction peaks. All the sharp diffraction peaks can be identified as the icosahedral phase in the Nb, Ta and V alloys. In figure 3 we show the bright-field TEM image (a) and nano beam electron diffraction patterns (b)–(d) of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Nb_5$ glassy alloy annealed for 120 s at 700 K. Very fine particles in the diameter range from 10 to 50 nm are seen over the whole area. The precipitates have a nearly spherical morphology and are homogeneously distributed. A similar structure consisting of fine grains is also obtained for the alloys containing Ta or V. The nano beam electron diffraction patterns with a beam diameter of 2.4 nm clearly denote the three kinds of electron diffraction patterns revealing the five-, three- and two-fold symmetries, which can be identified as the icosahedral structure. Since no diffraction patterns reflected from any other crystalline phases are observed, the structure of the annealed sample consists of a single icosahedral phase. Figure 4 shows the nano beam electron diffraction patterns taken from the precipitated particles in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ta_5$ (a)–(c) annealed for 120 s at 710 K and $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}V_5$ (d)–(f) annealed for 120 s at 700 K. The three kinds of electron diffraction patterns of each alloy revealing the five-, three- and two-fold symmetries, are also identified as the icosahedral structure. The patterns corresponding to the other crystalline phases are not confirmed in both alloys. Thus, it is clarified that the single icosahedral phase is formed in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}X_5$ (X=Nb, Ta or V) alloy systems. It is concluded that the first exothermic peak in the DSC curves is recognized as the transformation from glass to icosahedral phase.

In order to examine the thermal stability of the icosahedral phase, we carried out the annealing at higher temperatures. Figure 5 shows x-ray diffraction patterns of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}X_5$ (X=Nb, Ta or V) alloys annealed for 60 s at 873 K corresponding to the temperature above the second exothermic peak. The diffraction peaks are identified as $Zr_2Cu + Zr_2Ni + Zr_3Al_2$ for all alloys. Neither residual existence of icosahedral phase nor broad peak due to the amorphous phase is recognized in all the alloys. We conclude that the second exothermic peak results from the transition from the icosahedral to the crystalline phases. The icosahedral phase is a metastable phase which appears as a primary precipitation phase in the two-stage crystallization process, being similar to those of the noble metal-containing alloys.

We have reported the effect of the addition of noble metals such as Ag, Pd, Au and Pt on the precipitation behaviour of the icosahedral phase in the Zr-based glassy alloys [13]. The nucleation rate increases significantly from 10^{16} to 10^{20} $m^{-3}\,s^{-1}$ and the grain growth rate decreases from approximately 10^{-8} to 10^{-9} ms^{-1} by addition of 10 at.% Ag or Pd in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.5}M_{10}$ (M=Ag or Pd). Therefore, it is concluded that the role of noble metals is an increase of the nucleation rate and a decrease of the grain growth rate. For this conclusion, it is suggested that the icosahedral short-range order exists in the as-quenched glassy state [3,14,15] and the precipitation of the icosahedral phase is enhanced by the increase of the nucleation rate. Therefore, we can point to the possibility of forming the icosahedral

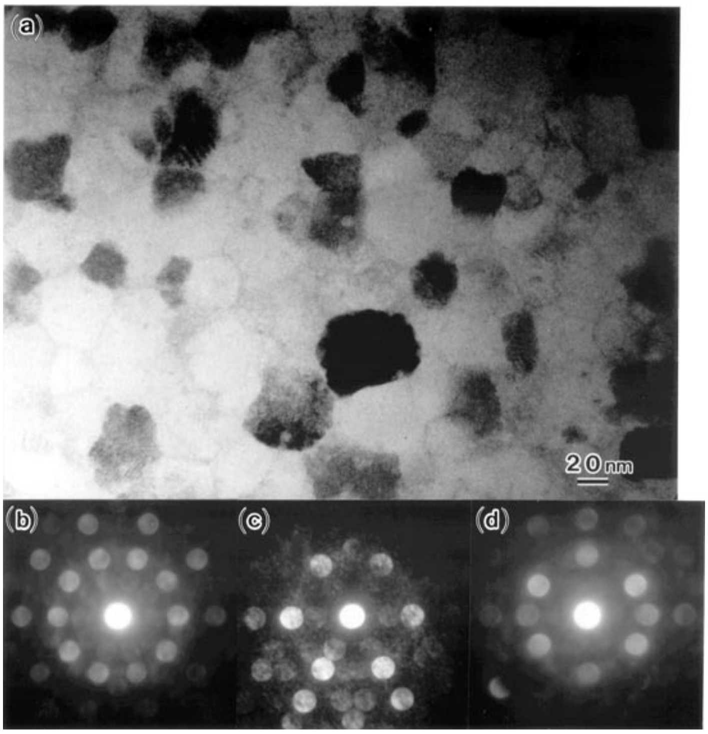

Figure 2. Bright-field TEM image (a) and nano beam electron diffraction patterns (b)–(d) of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Nb_5$ glassy alloy annealed for 120 s at 700 K. The beam diameter for nano beam diffraction is approximately 2.4 nm.

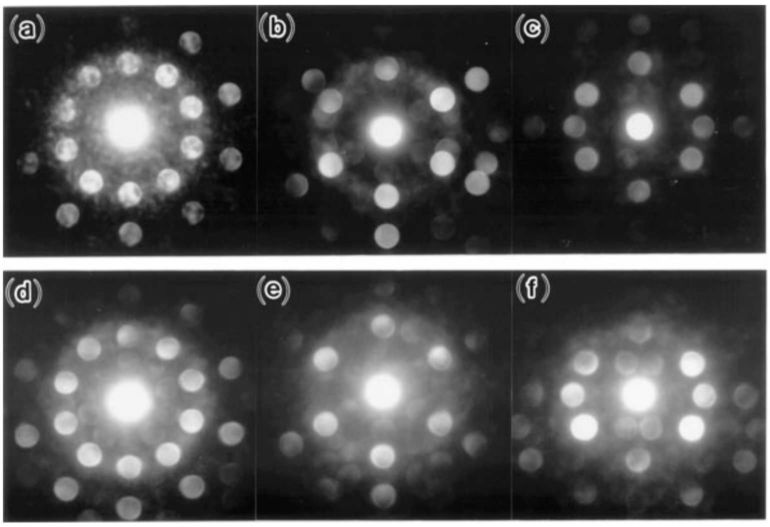

Figure 3. Nano beam electron diffraction patterns of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}X_5$ (X=Ta (a)–(c) and V (d)–(f)) glassy alloys annealed for 120 s at 710 K for Ta containing alloy and 700 K for V containing alloy. The beam diameter for nano beam diffraction is approximately 2.4 nm.

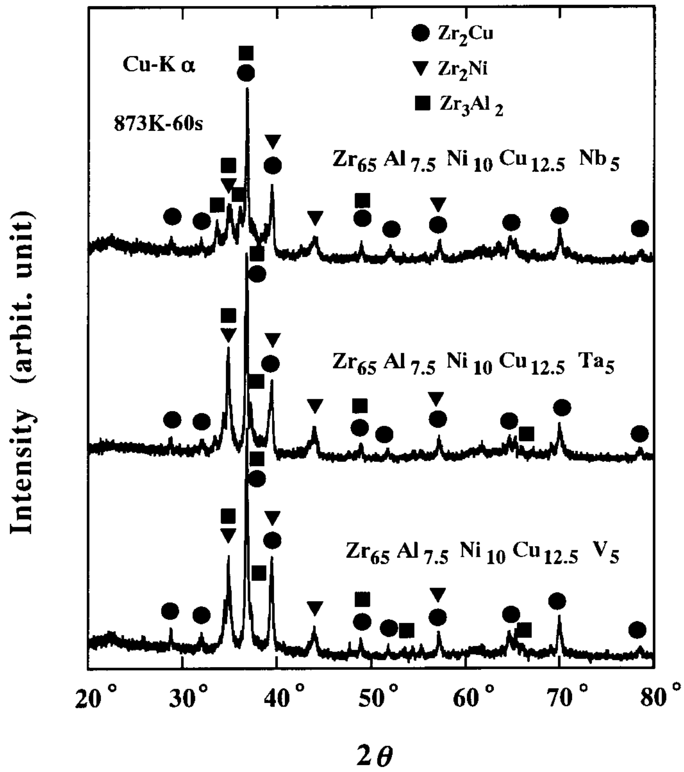

Figure 4. X-ray diffraction patterns of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}X_5$ (X=Nb, Ta and V) glassy alloys annealed for 60 s at 873 K.

phase by the addition of other elements which has the effect of increasing the nucleation rate. The noble metals have a strong chemical affinity with Zr and a weak affinity with Ni or Cu [16]. It is realized that the addition of noble metals obstruct the three empirical rules for the high glass forming ability [17]. Since the Nb, Ta and V have a weak or positive chemical affinity with Zr or Cu and have a relatively strong affinity with Ni [16], by adding them we can expect the similar effect of increasing the nucleation rate. In the present study, it is concluded that the increase of the nucleation rate is attributed to the icosahedral phase formation in the Zr-Al-Ni-Cu glassy alloy by addition of Nb, Ta and V. These discoveries strongly imply the existence of icosahedral short-range order in the glassy state. We suggest that the icosahedral short-range order stabilizes the glassy state by restraint of long-range atomic rearrangements to form a crystalline phase [7].

In conclusion, the transformation from glass to icosahedral phase is found in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}X_5$ (X=Nb, Ta or V) glassy alloys. A single icosahedral phase is formed after annealing for 120 s at 700 K and 710 K. The icosahedral particles have a nearly spherical morphology with a diameter range of 10 to 50 nm. Since the addition of Nb, Ta or V elements play a significant role in an increase of the nucleation rate, the present discovery strongly supports the possibility of the existence of the icosahedral short-range order in the glassy state, leading to the restraint of crystallization reaction. This study also suggests that the icosahedral short-range order stabilizes the glassy state by the restraint of long-range atomic rearrangements to form the crystalline phase.

References

[1] Köster U, Meinhardt J, Roos S and Liebertz H 1996 *Appl. Phys. Lett.* **69** 179
[2] Xing L Q, Eckert J, Löser W and Schultz L 1999 *Appl. Phys. Lett.* **74** 664
[3] Xing L Q, Hufnagel T C, Eckert J, Löser W and Schultz L 2000 *Appl. Phys. Lett.* **77** 1970
[4] Murty B S, Ping D H, Hono K and Inoue A 2000 *Appl. Phys. Lett.* **76** 55
[5] Eckert J, Mattern N, Zinkevitch M and Seidel M 1998 *Mater. Trans. JIM.* **39** 623
[6] Köster U, Meinhardt J, Roos S and Rüdiger A 1996 *Mater. Sci. Forum* **225–227** 311
[7] Inoue A, Zhang T, Saida J, Matsushita M, Chen M W and Sakurai T 1999 *Mater. Trans. JIM.* **40** 1181
[8] Inoue A, Saida J, Matsushita M and Sakurai T 2000 *Mater. Trans. JIM.* **41** 362
[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] Saida J, Matsushita M, Li C and Inoue A 2001 *Philos. Mag. Lett.* **81** 39
[12] Saida J, Matsushita M, Zhang T, Inoue A, Chen M W and Sakurai T 1999 *Appl. Phys. Lett.* **75** 3497
[13] Saida J, Matsushita M, Li C and Inoue A 2000 *Philos. Mag. Lett.* **80** 737
[14] Shen Y, Poon S J and Shiflet G J 1986 *Phy. Rev.* B **34** 3516
[15] Matsubara E, Waseda Y, Tsai A P, Inoue A and Masumoto T 1990 *J. Mater. Sci.* **25** 2507
[16] de Boer F R, Boom R, Mattens W C M, Miedema A R and Niessen A K 1988 *Cohesion in Metals* (Amsterdam: North-Holland) p 361
[17] Inoue A 2000 *Acta Mater.* **48** 279