High Strength and Good Ductility of Bulk Quasicrystalline Base Alloys in $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5-x}\text{Pd}_x$ System

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An icosahedral quasicrystalline phase was found to precipitate as a primary phase from the supercooled liquid in the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5-x}\text{Pd}_x$ ($x=5$ and 10 at%) amorphous alloys. No icosahedral phase is formed for the present $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy and hence the addition of Pd promotes the precipitation of the icosahedral phase. The volume fraction of the icosahedral phase increases with increasing Pd content and exceeds 90% for the 10%Pd alloy. The icosahedral phase changes to $\text{Zr}_2\text{Cu} + \text{Zr}_2\text{Ni} + \text{Zr}_2\text{Al}_3$ phases with further increasing annealing temperature. The icosahedral phase consists of fine grains with a size of about 35 nm and has a disordered (P-type) structure. Bulk amorphous alloys were produced in the diameter range up to 4 mm at 5%Pd and 2 mm at 10%Pd by copper mold casting. The icosahedral base alloys obtained by annealing the bulk amorphous phase exhibit improved mechanical properties. The Young's modulus, compressive yield strength, compressive fracture strength and fracture elongation including elastic elongation of the bulk 10%Pd alloy are 85 GPa, 1510 MPa, 1640 MPa and 2.2%, respectively, in the as-cast amorphous state and increase to 88 GPa, 1780 MPa, 1830 MPa and 3.1%, respectively, for the icosahedral base state obtained by annealing for 60 s at 705 K. The success of synthesizing the high-strength bulk alloys consisting mainly of icosahedral phase is promising for the future development of a new class of high-strength quasicrystalline material.

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I. Introduction

Since an icosahedral phase was found in a rapidly solidified $\text{Al}_{84}\text{Mn}_{16}$ alloy⁽¹⁾ and interpreted by the concept of a quasicrystal⁽²⁾, a large number of icosahedral quasicrystalline alloys have been synthesized in metastable and thermodynamically stable states. It is of importance to clarify formation mechanism and fundamental properties of new icosahedral alloys because the icosahedral atomic configuration which is different from the conventional crystalline and amorphous structures is expected to lead to a unique property. As typical alloy systems in which the icosahedral quasicrystals have been formed, one can list up Al-, Mg-, Zn-, Ga- and Ti-based systems⁽³⁾. More recently, it has been reported that the icosahedral phase is also formed in the Zr-Al-Ni-Cu⁽⁴⁾ and Zr-Al-Ti-Al-Ni⁽⁵⁾ alloys and its formation is dominated by the existence of an impurity oxygen element⁽⁶⁾⁽⁷⁾. The Zr-based alloy systems have a high glass-forming ability which enables the formation of bulk amorphous alloys by a copper mold casting method⁽⁸⁾⁻⁽¹⁰⁾. Consequently, it is particularly important to examine the formation of the icosahedral phase in the Zr-based alloy systems in the maintenance of high glass-forming ability. However, there have been no reproducible data on the formation of the icosahedral phase in the Zr-based alloy system and the absence of the reproducibility has been attributed to the difficulty of controlling an impu-

rity oxygen content⁽⁶⁾⁽⁷⁾.

Very recently, we have reported an evidence for the formation of an icosahedral phase in a wide annealing temperature range from the Zr-Al-Ni-Cu-Ag amorphous phase by the electron diffraction patterns⁽¹¹⁾⁽¹²⁾ and the precipitation behavior intentionally controlled by Ag content⁽¹³⁾. Considering that no icosahedral phase has been formed in the Zr-Al-Ni-Cu quaternary amorphous alloys prepared by our group⁽¹³⁾⁽¹⁴⁾, it has been presumed that the addition of Ag promotes the formation of the icosahedral phase in the Zr-Al-Ni-Cu system. The high glass-forming ability in the Zr-Al-TM (TM=transition metals) system has been pointed out to be obtained by the satisfaction of the three empirical rules in alloy components⁽⁸⁾⁻⁽¹⁰⁾, i.e., (1) multicomponent systems, (2) significant difference in atomic size ratios over 12%, and (3) negative heats of mixing. The satisfaction of the three empirical rules has been confirmed to result in the formation of a new liquid structure with the features of highly dense random packed atomic configurations, new local atomic configurations and long-range homogeneous atomic configurations⁽⁸⁾⁻⁽¹⁰⁾. The effectiveness of the Ag addition on the precipitation of the icosahedral phase has been thought⁽¹³⁾ to result from the generation of inhomogeneous icosahedral cluster regions caused by the deviation of the three empirical rules. Based on the formation mechanism of the icosahedral phase in the Zr-based alloys, we have subsequently searched for an effective element leading to the formation of the icosahedral phase.

hedral phase in the crystallization process of the Zr–Al–Ni–Cu base amorphous alloys and found that the addition of Pd, Au and Pt elements as well as Ag is effective for the formation of the icosahedral phase from the amorphous phase⁽¹⁵⁾. This paper is intended to present the formation of the icosahedral phase during crystallization in the amorphous Zr–Al–Ni–Cu–Pd alloys and the changes in the mechanical strength and ductility of the Zr-based bulk amorphous alloys by the precipitation of the icosahedral phase and to investigate the reason for the effectiveness of Pd addition on the precipitation of the icosahedral phase from the supercooled liquid in the Zr-based amorphous alloys.

II. Experimental Procedure

Multicomponent alloys with compositions of $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5-x}\text{Pd}_x$ ($x=0, 5$ and 10 at%) were examined in the present study. Their alloy ingots were prepared by arc melting the mixtures of pure metals with purities of 99.8 mass%Zr including impurities of 320 mass ppmO, 211 mass ppmFe, 44 mass ppmHf and 35 mass ppmCr, 99.99 mass%Al, 99.9 mass%Ni, 99.99 mass%Cu and 99.9 mass%Pd in an argon atmosphere. The Zr metal was prepared by arc melting Zr sponge of 99.8 mass% purity. Bulk amorphous alloys in a cylindrical form with different diameters below 7 mm were produced by a copper mold casting method. Amorphous alloy ribbons with a cross section of 0.03×1 mm² were also produced by a melt spinning method in an argon atmosphere. Thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. Amorphous, icosahedral and crystalline phases were examined by X-ray diffraction, ordinary transmission electron microscopy (TEM) and high-resolution TEM linked with nanobeam electron diffraction technique. The nanobeam diameter was approximately 2.4 nm. Mechanical properties were measured at an initial strain rate of $3.4 \times 10^{-4} \text{ s}^{-1}$ with an Instron testing machine. The gauge dimension of compressive testing specimens was 2 mm in diameter and 4 mm in height. The fracture surface was examined by scanning electron microscopy.

III. Results

Figure 1 shows the DSC curves of the melt-spun $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5-x}\text{Pd}_x$ ($x=0, 5$ and 10 at%) amorphous alloys. The 0%Pd alloy crystallizes through a single exothermic reaction. It has been previously reported that the single exothermic reaction is due to the simultaneous precipitation of Zr_2Cu , Zr_2Ni , Zr_2Al_3 and ZrNi phases⁽¹³⁾⁽¹⁴⁾. However, the addition of 5 and 10 at%Pd changes the crystallization process from the single stage to two stages and the peak intensity of the first exothermic peak increases with increasing Pd content. Although the additional exothermic peak is seen at the lower temperature side, a rather large supercooled liquid region exceeding 50 K is maintained even for the 10%Pd alloy.

Fig. 1 DSC curves of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$, $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{12.5}\text{Pd}_5$ and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{7.5}\text{Pd}_{10}$ amorphous alloys.

Fig. 2 X-ray diffraction patterns of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{12.5}\text{Pd}_5$ and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{7.5}\text{Pd}_{10}$ alloys annealed for 60 s at 705 K.

In order to clarify the precipitation phase due to the first-stage exothermic reaction, X-ray diffraction patterns of the 5%Pd and 10%Pd alloys annealed for 60 s at 705 K just above the first exothermic reaction are shown in **Fig. 2**. Although a low-intensity broad peak due to the residual existence of an amorphous phase is recognized, all the other diffraction peaks are identified as an icosahedral phase. It is clearly concluded that the first exothermic peak is due to the precipitation of an icosahedral phase from the supercooled liquid region. Furthermore, we have confirmed that the broad peak of the amorphous phase for the 10%Pd alloy almost completely disappears after annealing at the temperatures between the first and the second exothermic peaks. The first exothermic peak for the 10%Pd-alloy is concluded to result from the transition of amorphous to the mostly single icosahedral phase. In addition, this result indicates that the volume fraction of the icosahedral phase in the 10%Pd alloy subjected to annealing can be estimated by measuring the annealing-induced change in the heat of

Fig. 3 Bright-field TEM image (a) and selected-area electron diffraction pattern (b) and its identified result (c) of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{7.5}\text{Pd}_{10}$ alloy annealed for 60 s at 705 K.

Fig. 4 Nanobeam electron diffraction patterns revealing the five-, three- and two-fold symmetries for the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{7.5}\text{Pd}_{10}$ alloy annealed for 60 s at 705 K.

the first exothermic reaction. **Figure 3** shows the bright-field TEM image, selected-area electron diffraction pattern and its identified result of the 10%Pd alloy annealed for 60 s at 705 K. The alloy consists of very fine grains with an average size of about 35 nm, but it is difficult to

obtain a clear evidence on the residual existence of amorphous phase in the TEM image. The electron diffraction pattern taken from the selected area with a diameter of 1 μm consists of a number of reflection rings, in addition to a halo ring due to the remaining amor-

Fig. 5 X-ray diffraction patterns of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{12.5}\text{Pd}_5$ and $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{7.5}\text{Pd}_{10}$ alloys annealed for 60 s at 873 K.

Fig. 6 Compressive stress-elongation curves of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{7.5}\text{Pd}_{10}$ alloy in as-cast and annealed (705 K, 60 s) states.

Fig. 7 Compressive fracture surface of the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{7.5}\text{Pd}_{10}$ alloy. (a) and (b); as-cast state, (c) and (d); annealed state for 60 s at 705 K.

phous phase. As shown in Fig. 3(c), the reflection rings are identified to be an icosahedral phase, indicating that the fine grains have an icosahedral structure and each grain has random orientations. With the aim of

confirming the structure of the icosahedral phase, *i.e.*, a disordered P-type or an ordered F-type icosahedral phase, the nanobeam electron diffraction patterns of the icosahedral particles are shown in Fig. 4. These diffrac-

tion patterns reveal the five-, three- and two-fold symmetries. No extra reflection spots corresponding to an ordered icosahedral phase is seen, indicating that the icosahedral phase has a disordered P-type structure.

Figure 5 shows the X-ray diffraction patterns of the 5%Pd and 10%Pd alloys annealed for 60 s at 873 K above the second exothermic peak. The diffraction peaks are identified as Zr_2Cu , Zr_2Ni and Zr_2Al_3 phases and no icosahedral phase is seen. The crystallization of the 5%Pd and 10%Pd alloys takes place through the process of amorphous $\rightarrow$ amorphous + icosahedral $\rightarrow$ mostly single icosahedral $\rightarrow \text{Zr}_2\text{Cu} + \text{Zr}_2\text{Ni} + \text{Zr}_2\text{Al}_3$. The icosahedral phase is a metastable phase which precipitates from the supercooled liquid. Based on the DSC data shown in Fig. 1, we evaluated the volume fraction of the icosahedral phase from the change in the heat of the first exothermic peak due to the precipitation of the icosahedral phase. The volume fraction thus obtained increases with increasing Pd content and exceeds 90% for the 10%Pd alloy.

It is important to point out that bulk amorphous alloys in the Zr–Al–Ni–Cu–Pd system are produced by copper mold casting and the critical maximum thickness is larger than 7 mm for the 0%Pd alloy, about 4 mm for the 5%Pd alloy and 2 mm for the 10%Pd alloy. The bulk alloys consisting mainly of nanoscale icosahedral phase are also produced by annealing the Pd-containing bulk amorphous alloys in the wide temperature range around the first exothermic peak. Figure 6 shows the compressive stress-strain curves of the bulk amorphous $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{7.5}\text{Pd}_{10}$ alloy with a diameter of 2 mm in the as-cast and annealed (705 K, 60 s) states. The Young's modulus (E), compressive yield strength ($\sigma_{c,y}$), compressive fracture strength ($\sigma_{c,f}$) and compressive fracture elongation ($\varepsilon_{c,f}$) are 85 GPa, 1510 MPa, 1640 MPa and 2.2%, respectively, for the amorphous alloy and increase to 88 GPa, 1780 MPa, 1830 MPa and 3.1%, respectively, for the icosahedral base alloy obtained by annealing at 705 K. It is noticed that the mechanical properties for the bulk Zr-based alloys are distinctly improved by the precipitation of the icosahedral base phase. It is further seen that the increase in elongation occurs accompanying the generation of serrated flow. Figure 7 shows the compressive fracture surface appearance of the 10%Pd alloy in the as-cast amorphous and annealed (705 K, 60 s) icosahedral base states. The fracture takes place along the maximum shear plane which is declined by about 50 degrees to the direction of compressive load for both the state alloys and a well-developed vein pattern is seen over the whole fracture surface. There is no distinct difference in the fracture mode between the amorphous and the icosahedral base alloys. The fracture mode indicates that the icosahedral base alloy also keeps good ductility.

IV. Discussion

1. High mechanical strength and good ductility for the icosahedral base alloys

It is well known that the icosahedral alloys themselves with stoichiometric compositions have high hardness and are extremely brittle⁽¹⁶⁾. Consequently, the improved mechanical properties combined with good ductile nature for the icosahedral base alloys are attributed to the maintenance of high strength and good ductility for the small amount of intergranular amorphous phase. The increase in the mechanical strength is due to the combination of the following three factors; (1) nanoscale particle size effect. The fine icosahedral phase can act as an effective resistance medium against the shear deformation of the amorphous matrix, (2) low interfacial energy effect. The amorphous/icosahedral interface has highly packed atomic configurations without excess vacancy because of the lower interfacial energy as compared with the solid/solid interfacial energy. (3) quasiperiodic structure effect. The icosahedral particles have a three-dimensional quasiperiodic atomic configuration in which the movement of dislocations is difficult. Furthermore, the increase in fracture elongation seems to result from the localization of deformation into the intergranular amorphous phase. The localization generates the multi-axis-stress condition and the work softening due to an increase in temperature in the intergranular amorphous phase. These two factors are favorable for the increase in ductility. The generation of the serration in the stress-strain curve for the icosahedral base alloy also suggests that the preferential plastic deformation in the intergranular amorphous phase occurs via the repeating mechanism of local sliding in a limited distance in the intergranular amorphous region, followed by an instantaneous stop caused by the resistance of the nanoscale icosahedral particles. In addition, the coefficient of thermal expansion for the amorphous phase⁽¹⁷⁾ is much larger than that for the icosahedral phase⁽¹⁸⁾. During the cooling from the annealing temperature, a compressive stress field is generated in the intergranular amorphous phase, leading to the increases in the strength and elongation of the icosahedral base alloys.

2. Formation of the icosahedral base structure

We discuss the reason for the precipitation of the icosahedral phase as an intermediate metastable phase in the crystallization process of the Zr–Al–Ni–Cu amorphous alloys containing Ag⁽¹¹⁾ or Pd element. Considering the absence of an icosahedral phase in the crystallization process of the Zr–Al–Ni–Cu alloys without Ag or Pd element prepared by our group⁽¹³⁾⁽¹⁴⁾, the addition of the Ag or Pd element is concluded to promote the formation of the icosahedral phase. As shown in Fig. 1, the addition of the Pd element changes the crystallization mode from the single stage to the two stages. It has been reported that the quaternary $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ alloy

crystallizes through the single exothermic reaction due to the simultaneous precipitation of four crystalline phases of Zr_2Cu , Zr_2Ni , Zr_2Al_3 and ZrNi phases⁽¹³⁾⁽¹⁴⁾. The previous structure data obtained by the anomalous X-ray scattering method⁽¹⁹⁾⁽²⁰⁾ and density measurement⁽²¹⁾ indicate that the quaternary amorphous alloy has a unique disordered structure with highly dense random packed atomic configurations, new local atomic configurations and long-range homogeneous atomic configurations. The structural features of the quaternary amorphous alloy have not been obtained for other metallic amorphous alloys which require high cooling rates over 10^4 K/s for glass formation. It has been pointed out that the formation of the unique amorphous structure is a universal phenomenon for the multicomponent alloy systems having the following features in alloy components^{(8)–(10)}, *i.e.*, (1) multicomponent alloy systems consisting of more than three elements, (2) significant atomic size ratios over 12% among the main three elements, and (3) negative heats of mixing among their elements. The features of the disordered atomic configurations are also interpreted in the assumption that the amorphous alloys include a number of icosahedral atomic configurations on a short-range scale which are different from the ordinary icosahedral structure with long-range icosahedral atomic configuration. In addition, it has been presented that the new type of liquid structure in the quaternary amorphous alloy have low atomic mobility of the constituent elements and high thermal stability against crystallization^{(8)–(10)}. The decomposition reaction of the supercooled liquid in the Zr-Al-Ni-Cu alloy without Pd element begins to occur at the higher temperature and leads to the simultaneous precipitation of the four crystalline phases after the enhancement of atomic mobility. On the other hand, the addition of the Pd element, which deviates from the three empirical rules for stabilization of supercooled liquid, generates short-range scale inhomogeneous regions in the long-range homogeneous atomic configurations including short-range icosahedral atomic configurations. The generation of the inhomogeneous atomic configuration regions seems to enable the precipitation of the icosahedral phase as a primary metastable phase in an isolated particle form before the direct transition from the supercooled liquid to crystalline phases. The clarification in the short- and medium-range atomic configurations of the Pd-containing amorphous alloys is expected to shed light on the mechanism for the precipitation of the icosahedral quasicrystalline phase for the Zr-based amorphous alloys containing Ag or Pd element. In any event, it is important to find the Zr-based bulk amorphous alloys in which the icosahedral quasicrystalline phase can be steadily formed at an intermediate stage in the crystallization process. By extending the concept of the present alloy design, we can expect to obtain other bulk amorphous alloys with good mechanical properties containing a high volume fraction of icosahedral phase.

V. Summary

We examined the influence of Pd element on the glass-forming ability, crystallization behavior and mechanical properties for the $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5-x}\text{Pd}_x$ ($x=0, 5$ and 10 at%) amorphous alloys in the melt-spun ribbon and cast bulk forms. The results obtained are summarized as follows.

(1) Although the Zr-Al-Ni-Cu amorphous alloy crystallizes through a single exothermic reaction due to the simultaneous precipitation of Zr_2Cu , Zr_2Ni , Zr_2Al_3 and ZrNi phases, the addition of 5 to 10%Pd changes the crystallization mode to two-stage reactions in the maintenance of the supercooled liquid region. The peak intensity of the first exothermic reaction increases with increasing Pd content.

(2) The first exothermic reaction is due to the precipitation of an icosahedral phase. The icosahedral phase in the 5%Pd and 10%Pd alloys annealed for 60 s at 705 K has fine grains with grain sizes of 35 to 40 nm. The highest volume fraction exceeds 90% for the 10%Pd alloy. The second exothermic reaction results from the structural change from icosahedral to $\text{Zr}_2\text{Cu} + \text{Zr}_2\text{Ni} + \text{Zr}_2\text{Al}_3$ phases. The icosahedral phase is a metastable phase and the addition of Pd is essential for the precipitation of the icosahedral phase in the Zr-Al-Ni-Cu amorphous alloy.

(3) The bulk amorphous alloys were also produced in a thickness range up to about 4 mm for the 5%Pd alloy and 2 mm for the 10%Pd alloy by the copper mold casting method. The E , $\sigma_{c,y}$, $\sigma_{c,f}$ and $\varepsilon_{c,f}$ are 85 GPa, 1570 MPa, 1640 MPa and 2.2%, respectively, for the bulk amorphous alloy and increase to 88 GPa, 1780 MPa, 1830 MPa and 3.1%, respectively, for the icosahedral base alloy obtained by annealing for 60 s at 705 K. The improvement of the mechanical properties is presumed to result from the combination of the following factors, *i.e.*, (1) nanoscale particle size effect, (2) low interface energy effect, (3) quasiperiodic structure effect, (4) localized deformation effect, and (5) residual compressive stress effect.

The formation of the bulk icosahedral base alloys with improved mechanical properties in the Zr-based alloy systems indicates the possibility of practical use as a new quasicrystalline base material with high mechanical strength and good ductility.

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