High-strength Zr-based bulk amorphous alloys containing nanocrystalline and nanoquasicrystalline particles

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Abstract

It was recently found that the addition of special elements leading to the deviation from the three empirical rules for the achievement of high glass-forming ability causes new mixed structures consisting of the amorphous phase containing nanoscale compound or quasicrystal particles in Zr–Al–Ni–Cu–M (M = Ag, Pd, Au, Pt or Nb) bulk alloys prepared by the copper mold casting and squeeze casting methods. In addition, the mechanical strength and ductility of the nonequilibrium phase bulk alloys are significantly improved by the formation of the nanostructures as compared with the corresponding amorphous single phase alloys. The composition ranges, formation factors, preparation processes, unique microstructures and improved mechanical properties of the nanocrystalline and nanoquasicrystalline Zr-based bulk alloys are reviewed on the basis of our recent results reported over the last two years. The success of synthesizing the novel nonequilibrium, high-strength bulk alloys with good mechanical properties is significant for the future progress of basic science and engineering. © 2000 Published by Elsevier Science Ltd.

Keywords: Bulk nanostructure alloy; Nanoscale compound; Nanoscale quasicrystalline phase; Bulk amorphous alloy; Crystallization; Mechanical property; Localized deformation mode

1. Introduction

A supercooled liquid of ordinary metallic alloys is extremely unstable and transforms to a crystalline state within a short time of less than $10^{-4}$ s in the vicinity of nose temperature on the continuous cooling transformation (CCT) curve. Such an unstable supercooled liquid has resulted in a universal conclusion that all engineering bulk metallic alloys with a thickness above several millimeters are composed of crystalline phases. The universal conclusion had been maintained without any exceptions for the last several thousands years. However, during the last decade, some exceptions have been reported because of the discoveries of stabilized supercooled liquid alloys without crystallization even during cooling at slow rates below 100 K/s \cite{1,2}. As a result, bulk amorphous alloys have been prepared in a number of alloy systems such as Mg-\cite{3}, Ln(lanthanide)-\cite{4}, Zr-\cite{5,6}, Fe-\cite{7}, Pd–Cu-\cite{8}, Ti-\cite{9}, Ni-\cite{10} and Co-\cite{11} bases and have gained some applications due to their unique mechanical properties, chemical properties and good workability resulting from the amorphous structure. It has subsequently been found that the use of the stabilized liquid also gives rise to bulk amorphous alloys containing nanocrystalline \cite{12} and nanoquasicrystalline \cite{13} particles with good mechanical properties in the Zr-based alloy systems. Thus, the stabilized supercooled liquid is a very useful medium to synthesize bulk alloys with various nonequilibrium structures that had not been obtained in a bulk form up to date. The combination of the bulk sample form and the new nonequilibrium structures is expected to open up a new area in basic science and engineering—stabilized supercooled liquid alloys. This paper is intended to present the features of the nonequilibrium microstructures obtained by the stabilization of the supercooled liquid in Zr-based alloys as well as the characteristics obtained by the formation of the nanostructures. It is also intended to highlight the importance of stabilized supercooled liquids in the development of new engineering materials.

2. Nonequilibrium phases in Zr-based alloys

Fig. 1 summarizes the features of the microstructure and the mechanical properties of Zr-based bulk alloys with a
thickness above several millimeters in Zr–Al–Ni–Cu and Zr–Al–Ni–Cu–M (M = Ag, Pd, Au, Pt or Nb) systems developed by our groups over the last decade. The structure can be divided into four groups: an amorphous single phase; amorphous plus nanoscale compound particles; amorphous plus nanocrystalline particles; and amorphous plus β-Zr or α-Zr phases. The volume fractions of the nanoscale compound, the quasicrystal, the bcc β-Zr solid solution and the hcp α-Zr phase extend in a wide range from 20 to 90%.

It is noticed that the mixed amorphous alloys containing the nanoscale compound or the quasicrystalline particles always exhibit higher strength and larger elongation as compared with the corresponding amorphous single phase alloys. In particular, the bulk amorphous alloy containing 20–30% of compound particles with a size of about 5 nm exhibits a high flexural strength of 4400 MPa which is about 2.2 times higher than that of the amorphous single phase alloy. Here, we focus on the recent results on the nanocrystalline [12,14–17] and nanoquasicrystalline [13,18–22] Zr-based bulk amorphous alloys after a brief description on the bulk amorphous single phase alloy.

3. Amorphous alloys

Fig. 2 shows the relation among the critical cooling rate ($R_c$), the maximum sample thickness ($t_{max}$) and the reduced glass transition temperature ($T_g/T_m$) for the main amorphous alloys reported up to date. It is well known that Fe-, Co- and Ni-based amorphous alloys have required high cooling rates above 10$^5$ K/s and the resulting sample thickness is usually less than about 50 µm [23,24]. As exceptional examples, Pd–Ni–P and Pt–Ni–P amorphous alloys have a lower critical cooling rate of about 10$^3$ K/s and the amorphous phase has been formed in the thickness range below several millimeters in the case of an ordinary unfluxed liquid [23]. Since 1988, various kinds of bulk amorphous alloys in Mg-, Ln-, Zr-, Ti-, Fe-, Pd–Cu-, Co- and Ni-based systems were developed [1,2]. The lowest $R_c$ is 0.10 K/s [25] and the largest $t_{max}$ approaches nearly 100 mm [26]. There is a clear tendency for the glass-forming ability to increase with increasing $T_g/T_m$. As examples, Fig. 3 shows the shape and outer appearance of bulk amorphous alloys in a cylindrical ingot with a diameter of 80 mm and a height of 85 mm for the Pd–Cu–Ni–P alloy and in a cylindrical rod with a diameter of 17 mm and a length of 600 or 120 mm for the Zr–Al–Ni–Cu alloy. Fig. 4 illustrates the CCT curves of the new bulk amorphous alloys with an $R_c$ of 1 K/s, together with the data of conventional crystalline alloys and ordinary amorphous alloys. The use of the bulk amorphous alloy can maintain a supercooled liquid state for a long time of up to about 10$^3$ s which is 6–7 orders longer than those for the ordinary amorphous alloys. The high stability enables us to analyze the structure, phase transformation and fundamental properties of the supercooled liquid, in addition to the formation of bulk
amorphous alloys. It is recognized that the new alloy systems lead to an opening up of new basic science and engineering fields in metallic materials.

Table 1 summarizes the typical bulk amorphous alloy systems reported up to date and the calendar years when each alloy system was reported in papers and patents [1,2]. The alloy systems can be divided into nonferrous and ferrous groups. It is recognized that the first alloy systems developed were nonferrous alloy systems, followed by ferrous alloy systems. It is particularly noticed that bulk amorphous alloys with diameters of several millimeters have recently been formed in Fe-, Co- and Ni-based alloy systems that are important for practical applications. When we look at the features of the bulk amorphous alloy systems, all these alloys satisfy three very simple empirical rules [1,2]: (1) multicomponent systems consisting of more than three elements; (2) significant difference in atomic size mismatch above 12% among the three main constituent elements; and (3) negative heats of mixing among their elements. It has subsequently been reported that the alloys with the three empirical rules can have a new liquid structure with highly dense random packed atomic configurations, new local atomic configurations and long-range homogeneous atomic configurations with attractive interactions [1,2,27]. The new liquid alloys crystallize through a single-stage crystallization process accompanying the simultaneous precipitation of more than three crystalline phases. That is, the bulk amorphous alloys shown in Table 1 cannot have a nanocrystalline structure after crystallization.

4. Bulk nanocrystalline alloys

If one wants to prepare a bulk nanocrystalline alloy by the process of the formation of a bulk amorphous alloy and then annealing, we must look for a new alloy system in which a
nanostructure is formed during crystallization. The previous data [28] indicate the following criteria for the formation of a nanocrystalline structure: (1) multistage crystallization processes; (2) high nucleation frequency; (3) low growth rate; and (4) enhancement of the thermal stability of the remaining amorphous phase caused by the redistribution of a solute element at the nanocrystal/amorphous interface. With the aim of satisfying the criteria for the formation of a nanocrystalline structure, the influence of additional elements (M) on the crystallized structure was examined for the Zr–Al–Cu–M alloys [12,14–17]. The additional (M) elements can be divided into three groups: (1) Pd, Pt and Au elements with much larger negative heats of mixing against Zr as compared with other atomic pairs; (2) Ti and Nb with nearly zero heat of mixing against Zr; and (3) Ag with a positive heat of mixing against Ni and Cu [29].

Fig. 5 shows the DSC curves of (a) Zr60Al10Cu30 and (b) Zr60Al10Cu20Pd10 amorphous alloys. The crystallization mode changes from a single stage to two stages in the maintenance of the supercooled liquid region by the addition of Pd and the extra exothermic peak appears in the higher temperature side. The X-ray diffraction pattern of the Pd-containing alloy subjected to annealing in the supercooled liquid region, followed by water quenching consists of a broad peak due to the remaining amorphous phase and low intensity peaks due to the precipitation of the Zr2Cu phase. The low intensity peaks of the precipitates indicate the possibility of forming a nanocrystalline structure in the residual existence of the amorphous phase. On the other hand, the Zr–Al–Cu amorphous alloy crystallizes completely by the same annealing treatment and the crystalline peaks of Zr2Cu and Zr2Al phases have high intensities. In order to confirm the formation of the nanocrystalline structure in the Pd-containing alloy, a bright-field TEM image and the selected-area electron diffraction pattern are shown in Fig. 6. It is seen that the alloy has a mixed structure consisting of fine Zr2Cu compound particles with a size of less than 10 nm embedded in the remaining amorphous phase. On the other hand, the Zr2Cu and Zr2Al phases in the Zr–Al–Cu alloy have coarse grains with a size of about 450 nm. The contrasting result between the two alloys clearly indicates the importance of the remaining amorphous phase for the formation of the nanocrystalline structure.

### Table 1
Typical bulk amorphous alloy systems reported up to date

| Nonferrous alloy system | Year |
|------------------------|------|
| Mg–Ln–M (Ln = lanthanide metal, M = Ni, Cu, Zn) | 1988 |
| Ln–Al–TM (TM = VI–VIII group transition metals) | 1989 |
| Ln–Ga–TM | 1989 |
| Zr–Al–TM | 1990 |
| Ti–Zr–TM | 1993 |
| Zr–Ti–TM–Be | 1993 |
| Zr–(Ti,Nb,Pd)–Al–TM | 1995 |
| Pd–Cu–Ni–P | 1996 |
| Pd–Ni–Pd–P | 1996 |
| Pd–Cu–B–Si | 1997 |
| Ti–Ni–Cu–Sn | 1998 |

| Ferrous alloy system | Year |
|---------------------|------|
| Fe–(Al,Ga)–(P,C,B,Si,Ge) | 1995 |
| Fe–(Nb,Mo)–(Al,Ga)–(P,B,Si) | 1995 |
| Co–(Al,Ga)–(P,B,Si) | 1996 |
| Fe–(Zr,Hf,Nb)–B | 1996 |
| Co–(Zr,Hf,Nb)–B | 1996 |
| Ni–(Zr,Hf,Nb)–B | 1996 |
| Fe–Co–Ln–B | 1998 |

Fig. 5. DSC curves of melt-spun (a) Zr60Al10Cu30 and (b) Zr60Al10Cu20Pd10 amorphous alloy annealed for 1.8 ks at 726 K.

Fig. 6. Bright-field TEM image and selected-area electron diffraction pattern of a melt-spun Zr60Al10Cu20Pd10 amorphous alloy annealed for 1.8 ks at 726 K.
We further examined the redistribution behavior of the solute elements between the Zr$_2$Cu and the remaining amorphous phase in the nanocrystallized structure of the Zr–Al–Cu–Pd alloy by using the nanobeam EDX spectroscopy technique. As summarized in Fig. 7, no distinct difference in Cu and Pd concentrations is seen, but the Al element is significantly enriched into the remaining amorphous phase. The nanocrystalline Zr$_2$Cu compound can be expressed as

![Fig. 7. High-resolution TEM image, nanobeam diffraction patterns and analytical compositions of the nanocrystalline particle and the residual amorphous phase in a Zr$_{60}$Al$_{10}$Cu$_{20}$Pd$_{10}$ amorphous alloy annealed for 1.2 ks at 726 K. (b) and (d): nanocrystalline particle. (c) and (e): residual amorphous phase.](image)
the chemical formula of Zr$_2$(Cu,Pd). The atom-probe FIM result [30] also indicates the absence of redistribution for Cu and Pd as well as the significant enrichment of Al into the remaining amorphous phase. It is therefore said that the residual existence of the amorphous phase is attributed to an increase in the thermal stability caused by the enrichment of Al.

Very surprisingly, the nanocrystallized alloys maintained a good bending ductility, which is the same as that for the as-quenched amorphous alloy. Fig. 8 shows the tensile fracture strength ($\sigma_f$), Vickers hardness ($H_V$) and Young’s modulus ($E$) as a function of the volume fraction ($V_f$) of the Zr$_2$(Cu,Pd) phase for the Zr$_{60}$Al$_{10}$Cu$_{20}$Pd$_{10}$ amorphous alloy. All the properties increase almost linearly over the whole $V_f$ range up to 75% and the increasing ratios to those for the amorphous single phase are 18, 20 and 19%, respectively. With further increasing annealing treatment, the sample becomes brittle by the disappearance of the remaining amorphous phase, accompanying a significant decrease in $\sigma_f$ and $\epsilon_f$. The similar linear increase in $\sigma_f$, $H_V$ and $E$ in the wide $V_f$ range of up to about 75% $V_f$ is also recognized for a Zr$_{60}$Al$_{10}$Cu$_{22}$Au$_8$ amorphous alloy. The increasing ratios of their properties are also evaluated to be approximately 20%. Furthermore, the nanocrystallized alloys containing the Zr$_2$(Cu,Pd) phase of 75% can be cold rolled up to a reduction ratio of about 40% in thickness. A number of deformation markings were introduced on the surface of the cold-rolled alloy, but no appreciable crack was observed.

![Fig. 8. Changes in tensile fracture strength ($\sigma_f$), Vickers hardness ($H_V$) and Young’s modulus ($E$) with volume fraction ($V_f$) of Zr$_2$(Cu,Pd) compound for Zr$_{60}$Al$_{10}$Cu$_{20}$Pd$_{10}$ and Zr$_{60}$Al$_{10}$Cu$_{22}$Au$_8$ amorphous alloys annealed at different conditions.](image1)

![Fig. 9. Changes in $\sigma_f$, $E$ and $\epsilon_f$ with $V_f$ for bulk amorphous Zr$_{60}$Al$_{10}$Cu$_{20}$Pd$_{10}$ and Zr$_{60}$Al$_{10}$Cu$_{15}$Pd$_{10}$Fe$_5$ alloys annealed at different conditions.](image2)
The Zr-based alloys had high glass-forming ability leading to the formation of bulk amorphous alloys in the diameter range of up to 5 mm even in the dissolution state of Pd, Au or Pt by copper mold casting. Consequently, the use of these alloys enabled us to measure the change in the mechanical properties of the bulk amorphous rods by the precipitation of the nanoscale compound. Fig. 9 shows the $\sigma_f$, $E$ and $\epsilon_f$ as a function of $V_f$ for Zr$_{10}$Al$_{10}$Cu$_{20}$Pd$_{10}$ and Zr$_{10}$Al$_{10}$Cu$_{15}$Pd$_{10}$Fe$_{5}$ bulk amorphous rods with a diameter of 4 mm in the as-cast state. It is seen that all the properties increase almost linearly in the limited $V_f$ range of up to 30–40%. The fracture of the bulk alloys with improved mechanical properties takes place along the maximum shear plane and the fracture surface consists mainly of a well-developed vein pattern, as shown in Fig. 10. With further increasing $V_f$, the fracture mode changes into a perpendicular type. These features in the deformation and fracture modes are just the same as those for the bulk amorphous single phase alloys with good ductility. The above-described data were obtained in the tensile deformation mode. When we use the compressive deformation mode, the continuous decrease in flow stress is clearly observed for the nanocrystalline bulk amorphous alloys. Fig. 11 shows the compressive stress–elongation curve of the Zr$_{10}$Al$_{10}$Cu$_{20}$Pd$_{10}$ bulk amorphous rod with $V_f$ of about 20%. One can see a much larger elongation accompanying a continuous decrease in flow stress that cannot be obtained for the amorphous single phase alloy. The continuous decrease in flow stress has been confirmed to occur by the continuous decrease in the cross section caused by the progress of shear sliding along the maximum shear plane. This deformation mode is confirmed from the evidence that a distinct deformation step is

![Fig. 10. Tensile fracture mode and fracture surface of Zr$_{10}$Al$_{10}$Cu$_{20}$Pd$_{10}$ amorphous alloys with different $V_f$ of Zr$_2$(Cu,Pd).](image)

![Fig. 11. Compressive stress and elongation curves of: (a) Zr$_{55}$Al$_{10}$Ni$_{5}$Cu$_{30}$ amorphous alloy with 0% $V_f$; (b) Zr$_{60}$Al$_{10}$Cu$_{20}$Pd$_{10}$ amorphous alloy with 0% $V_f$; and (c) Zr$_{60}$Al$_{10}$Cu$_{20}$Pd$_{10}$ nanocrystalline alloy with 20% $V_f$.](image)
frequently observed for the sample subjected to the compressive deformation test. Based on the above-described experimental data, the deformation and fracture mode of the nanoscale mixed phase alloy is schematically illustrated in Fig. 12. The deformation and fracture occur in the intergranular amorphous phase region along the maximum shear plane. In the mechanism, the remaining amorphous phase must have good ductility. The high ductility is presumably because of the introduction of a high density of free volumes by annealing in the supercooled liquid region, followed by water quenching. Furthermore, the amorphous/\( \text{Zr}_2(\text{Cu}, \text{Pd}) \) interface has a highly dense packed atomic configuration because of a much lower liquid/solid interface energy [31] as compared with the solid/solid interface energy.

5. Mechanism for the formation of the nanostructure

As described above, the addition of Pd or Au to the Zr–Al–Cu amorphous alloys causes a drastic decrease in the particle size of the primary precipitation phase from about 450 to less than 10 nm. With the aim of clarifying the mechanism for the significant difference in the particle size, we made the kinetic analysis on the precipitation behavior of the \( \text{Zr}_2(\text{Cu}, \text{Pd}) \) phase on the basis of an exothermic peak due to the precipitation of the compound phase on the DSC curves which were measured during isothermal treatment at various temperatures. The data were analyzed in the framework of the Johnson–Mehl–Avrami (J–M–A) relation [32]. In the J–M–A analysis of the data at the transformation ratios between 0.2 and 0.8, a good linear relation was recognized for the Zr–Al–Cu, Zr–Al–Cu–Pd and Zr–Al–Cu–Au alloys. The Avrami exponent (\( n \)-value) lies in the range of 3.0–3.5 for the three alloys. Considering the morphology of the primary precipitates, the Zr–Al–Cu amorphous alloy crystallizes by a polymorphic mode with decreasing nucleation rate, while the Pd- and Au-containing alloys can have a diffusion-controlled growth mode in which all precipitates can grow from small dimensions with increasing nucleation rate [33,34]. The activation
energy for the precipitation of the compound was also determined by the Arrhenius and Kissinger analytical methods. The activation energies increase significantly from about 2 eV for the Zr–Al–Cu alloy to 3.7 eV for the Pd- and Au-containing alloys, indicating the difficulty of the progress of crystallization by the addition of Pd or Au. Based on the experimental kinetic data, the formation process of nanocrystalline Zr2(Cu,Pd) particles embedded in an amorphous matrix is schematically illustrated in Fig. 13. The addition of Pd with a much larger negative heat of mixing against Zr generates a high density of Zr–Pd rich clusters which can act as preferential nucleation sites of the Zr2(Cu,Pd) compound. The compound particles can have a very slow growth rate because of the necessity of the enrichment of Al into the remaining amorphous phase. It is thus interpreted that the addition of Pd to the Zr-based alloy.

![DSC curves of Zr60Al10Cu20Pd10 amorphous alloys prepared by melt spinning at different ejection temperatures of liquid.](image)

![Changes in various thermal properties with liquid temperature for Zr60Al10Cu20Pd10 amorphous alloys.](image)
satisfies the criteria for the formation of a nanocrystalline structure, i.e. multistage crystallization process, high nucleation frequency, slow growth rate, and the increase in thermal stability of the remaining amorphous phase caused by the enrichment of Al.

6. Influence of liquid temperature on the thermal stability of amorphous alloys

In order to confirm the existence of the Zr–Pd rich clusters in liquid, we examined the change in the thermal stability of the Zr_{60}Al_{10}Cu_{20}Pd_{10} and Zr_{60}Al_{10}Cu_{30} amorphous alloys with ejection temperature of the liquid phase. Fig. 14 shows the DSC curves of the Pd-containing amorphous alloys prepared from different liquid temperatures. It is clearly seen that the exothermic peaks due to crystallization shift systematically to a higher temperature side. The properties of \( T_c, T_x, T_{p1}, T_{p3}, T_{s3}, \Delta T_c \) and \( \Delta T_3 \) associated with the thermal stability of the amorphous alloy are plotted as a function of liquid temperature in Fig. 15. The definition of each symbol is given in the figure. All the thermal properties

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Fig. 16. (a) High-resolution TEM image and nanobeam electron diffraction pattern taken from the small region with a diameter of 2.4 nm for a bulk amorphous Zr_{55}Al_{10}Ni_{5}Cu_{29}Nb_{1} alloy prepared by squeeze casting. (b) Trace of fringe contrast regions in (a).
except \( T_g \) increase significantly with increasing liquid temperature, indicating that the amorphous alloys with higher thermal stability are obtained in the case of higher liquid temperature. This change is interpreted in the assumption that the density of clusters decreases with increasing liquid temperature by the dissolution into liquid and a more homogenized amorphous phase is formed from the liquid with reduced density of clusters. Here, it is important to describe that no appreciable change in \( T_g \), \( T_x \) and \( \Delta T_x \) with liquid temperature is seen for the Zr–Al–Cu amorphous alloys, because of easy formation of the homogenized liquid in the absence of Pd.

7. Nanocrystalline alloys prepared by the cooling rate-controlled process

In the specialized liquid containing nanoscale clusters, the use of the cooling rate-controlled process is expected to produce a much finer mixed structure consisting of amorphous and nanocrystalline phases. In addition, the resulting amorphous phase can include a higher density of free volumes as well as a residual compressive stress field around nanocrystalline particles and result in the formation of a bulk nanocrystalline alloy with better mechanical properties. Fig. 16(a) shows a high-resolution TEM image of a Zr\(_{55}\)Al\(_{10}\)Ni\(_{5}\)Cu\(_{29}\)Nb\(_{1}\) bulk alloy sheet with a thickness of 4 mm prepared by squeeze casting. It is seen that a number of fringe contrast regions are homogeneously dispersed in the amorphous matrix. The fringe contrast regions taken at different reflection conditions are traced in Fig. 16(b), indicating that the fringe contrast regions have an average size of about 5 nm and the volume fraction is estimated to be about 20%. Fig. 17 shows the flexural stress–deflection curves of the nanocrystalline amorphous alloy, together with the data of the amorphous single phase alloy. The nanocrystalline alloy exhibits a very high flexural strength of 4400 MPa which is about 2.2 times higher than that for the amorphous single phase alloy. Furthermore, the nanocrystalline alloy did not fracture during the three-point bending test. The good ductility for the nanocrystalline alloy is also supported from the generation of a number of deformation markings on the lateral surface of the bending specimen, which is in contrast to the absence of deformation markings for the amorphous single phase. Table 2 summarizes the mechanisms for high strength and good ductility for the bulk nanocrystalline alloy. The mechanisms can be classified into two different types by the difference in the focusing phases, i.e. the nanoparticle and the remaining amorphous matrix. The nanoparticle has a perfect crystal structure with ideal high strength and can act as an effective resistant medium against shear deformation of the amorphous matrix. In addition, the nanoparticle/amorphous interface has a highly dense packed atomic configuration because of a low interface energy [31]. On the other hand, the amorphous matrix includes a high density of free volumes, residual compressive stress field and multiple axis stress field and has a localized deformation mode. The localization of deformation into the remaining amorphous phase enhances the deformability owing to the softening caused by the increase in temperature in the localized region. The combination of these factors is presumed to result in the extremely high strength and good ductility for the nanoscale mixed phase alloy.

8. Nanoquasicrystalline alloys

By the use of the mechanisms for the high strength and good ductility for the nanocrystalline alloys, it is expected to develop a completely different type of mixed phase bulk

![Fig. 17. Flexural stress and deflection curve of the nanocrystalline Zr\(_{55}\)Al\(_{10}\)Ni\(_{5}\)Cu\(_{29}\)Nb\(_{1}\) amorphous alloy. The data of the amorphous Zr\(_{55}\)Al\(_{10}\)Ni\(_{5}\)Cu\(_{30}\) amorphous alloy are also shown for comparison.](image)

| Table 2 Mechanisms for high strength and good ductility for the bulk amorphous Zr-based alloys containing nanocrystalline particles |
|---|
| (I) Nanocrystalline particle effect |
| (1) Perfect crystal effect (ideal high strength) |
| (2) Nanoscale effect (suppression of shear deformation in glassy matrix) |
| (3) Low interfacial energy effect (highly dense packing at the interface) |
| (II) Metallic glassy phase effect |
| (1) Insensitive effect to structural relaxation (large allowance to crystalline phase) |
| (2) Compressive residual stress effect (difference in thermal expansion coefficient) |
| (3) Multi-axis stress effect (increase in deformability) |
| (4) Localized deformation effect (work softening due to an increase in temperature) |
alloy with good mechanical properties. More recently, we have found [13,18–22] that the addition of Ag, Pd, Au or Pt to the Zr–Al–Ni–Cu amorphous alloys also changes the crystallization mode from a single stage to two stages and the first exothermic reaction is due to the precipitation of an icosahedral phase with nanoscale grain size. As an example, Fig. 18 shows the DSC curves of the Zr65Al7.5Ni10Cu17.52xPdx (x = 0, 5 and 10 at%) amorphous alloys. It is clearly seen that the crystallization changes from a single stage to two stages and the increase in Pd content causes a decrease in the first exothermic peak temperature and an increase in the second peak temperature as well as an increase in the glass transition temperature in the main-

tenance of the rather large supercooled liquid region. Fig. 19 shows a bright-field TEM image (a) and selected-area electron diffraction pattern (b) of the Zr65Al17.5Ni10Cu2.5Pd10 amorphous alloy annealed for 60 s at 705 K, together with the identified result of the diffraction pattern. All the reflection rings can be indexed as an icosahedral phase and hence the grains with a size of about 30 nm are concluded to have an icosahedral structure. In addition, from the residual existence of the broad halo-like ring, one can notice the residual existence of a small amount of amorphous phase. The TEM image contrast also suggests that the remaining amorphous phase surrounds the nanoscale icosahedral particles and each icosahedral particle is in an isolated state. Furthermore, we examined the absence of a crystalline phase in the mixed structure shown in Fig. 19(a) by using the nanobeam electron diffraction technique. Fig. 20 shows the nanobeam electron diffraction patterns taken from the small regions with a size of about 2.4 nm. All the diffraction patterns can be identified as the icosahedral phase and no crystalline diffraction pattern due to a crystalline phase is recognized from the sample shown in Fig. 19. It is therefore concluded that the first exothermic reaction is due to the precipitation of the icosahedral grains with a size of about 30 nm. It has also been confirmed that the alloy heated to the temperature well above the second exothermic peak has a mixed crystalline structure of Zr4Al3, Zr2Cu, Zr2Al and Zr2Ni phases and the second exothermic peak results from the transition from the icosahedral phase to the crystalline mixtures.

We further measured the mechanical properties of the icosahedral-based bulk alloys in comparison with those for the bulk amorphous single phase alloy. Fig. 21 shows the compressive stress–elongation curves of the as-cast amorphous single phase alloy and the mostly single icosahedral phase alloy in a bulk form of 2 mm in diameter and 4 mm in height. Young’s modulus, compressive fracture

Fig. 18. DSC curves of melt-spun Zr65Al17.5Ni10Cu17.52xPdx (x = 0, 5 and 10 at%) amorphous alloys.

Fig. 19. Bright-field TEM image and selected-area electron diffraction pattern of the Zr65Al17.5Ni10Cu2.5Pd10 amorphous alloy annealed for 60 s at 705 K. The indexed result of the reflection rings is also shown for reference.
strength, total fracture elongation including elastic elongation and plastic elongation are 85 GPa, 1640 MPa, 2.2% and 0.2%, respectively, for the amorphous single phase alloy and 88 GPa, 1830 MPa, 3.1% and 1.2%, respectively, for the quasicrystalline-based alloy. It is noticed that all the properties including plastic elongation are improved for the icosahedral-based alloy. The fracture of the icosahedral-based alloys also takes place along the maximum shear plane, which is declined by about 54° to the direction of applied compressive load and the fracture surface consists of a well-developed vein pattern. The shear-type fracture mode is just the same as that for the amorphous single phase alloy. However, the spacing among the veins is considerably smaller for the icosahedral-based alloy and the diameter of the vein itself appears to increase slightly. This change indicates that the increase in temperature during the final adiabatic fracture becomes more significant for the icosahedral-based alloy. Based on these experimental data, a schematic illustration of the deformation and fracture mode for the icosahedral-based alloy is shown in Fig. 22. As is the case for the nanocrystalline alloys consisting of nanoscale particles surrounded by an amorphous phase, the fracture of the icosahedral-based alloy also takes place in the intergranular amorphous phase region along the maximum shear plane. The limitation of the propagation route of the final fracture crack into the intergranular amorphous phase region is consistent with the well-developed vein pattern on the fracture surface of the icosahedral-based alloy. The simultaneous improvement of mechanical strength and plastic elongation is the same as that for the nanocrystalline alloys and the mechanisms summarized in Table 2 can be also applied for the icosahedral-based alloys.

9. Conclusions

We have succeeded in preparing the bulk amorphous alloys containing nanocrystalline or nanoquasicrystalline particles with significantly improved mechanical properties by controlling the compositions and thermal treatment conditions. In particular, the bulk amorphous alloys containing fine crystalline particles with a size of about 5 nm prepared by the cooling rate control process are promising for practical high-strength materials because of the simple direct production method. It is therefore expected that the
further optimization of the alloy component and the structure-control method can result in a new bulk material with other useful properties through a unique structure modification.

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