

Review

Bulk glassy and nonequilibrium crystalline alloys by stabilization of supercooled liquid: fabrication, functional properties and applications (Part 1)

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Abstract: Since the stabilization of supercooled liquid in multi-component metallic alloys without any metalloid elements was discovered in 1988, a number of bulk glassy and nonequilibrium crystalline alloys have been fabricated with the aim of clarifying the origin of the novel stabilization phenomenon and searching for useful characteristics. This paper (Part 1) reviews our recent results on multi-component alloy systems in which the stabilization is achieved, some novel atomic configurations in stabilized supercooled liquids, the stabilization mechanism, and the physical, mechanical and chemical properties of the resulting bulk glassy alloys.

Key words: Glass-forming ability; three component rules; multi-component alloy system; novel atomic configuration; computational prediction; mechanical property.

1. Introduction. Metallic alloys without metalloid elements are usually in a metallic bonding state and the diffusion rates of the constituent elements in their liquid phase are very fast at high temperatures just below their melting point. This high diffusivity permits the phase transformation from supercooled liquid to a crystalline state within the extremely short time of less than 10^{-5} s. The phenomenon of instantaneous solidification to crystalline phases has led to progress in physical, chemical and process metallurgy and the development of alloys with a variety of crystalline structures.¹⁾ Recently, this instantaneous solidification has been suppressed through a tremendous increase in the stability of the supercooled liquid against crystallization for a large number of special multi-component metallic alloys, leading to the formation of glassy alloys in a bulk form, even with slow cooling at rates of less than 100 K/s from the liquid phase.²⁾⁻⁹⁾ The development of a number of glassy and metastable crystalline alloys in bulk form, together with the stabilization of supercooled metallic liquids has opened up a new field of basic science and engi-

neering: supercooled liquid metallurgy. This paper introduces the fundamental concepts, present state and future prospects of supercooled liquid metallurgy based largely on the work of our research group.

2. Stabilization of a metallic supercooled liquid. Figure 1 illustrates the continuous cooling transformation (C-C-T) curves of metallic liquids leading to the formations of the conventional crystalline, amorphous and glassy phases.⁴⁾⁻⁶⁾ The incubation time of the C-curve for the transition of supercooled liquid to crystalline phase at the nose temperature can be less than 10^{-5} s for conventional crystalline alloys and on the order of 10^{-4} s for ordinary amorphous alloys, which require high cooling rates of about 10^6 K/s. It is known that the necessity of such a high cooling rate limits amorphous alloy formation to thicknesses of less than about 0.05 mm. These incubation times are too short to permit utilization of the supercooled liquid state for the fabrication of novel metallic materials. This constraint remained unchanged for many years. However, since 1988, the incubation time has been increased significantly, to several thousands of seconds. At present the longest incubation time reaches 6 ks and the lowest crit-

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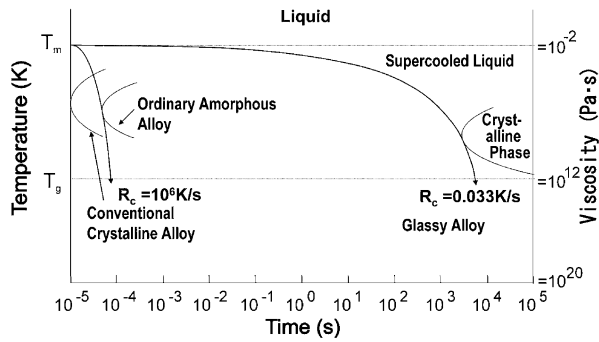


Fig. 1. Schematic illustration of continuous cooling transformation (C-C-T) curves of metallic liquids for different alloys in conventional crystalline, ordinary amorphous and bulk glassy types.

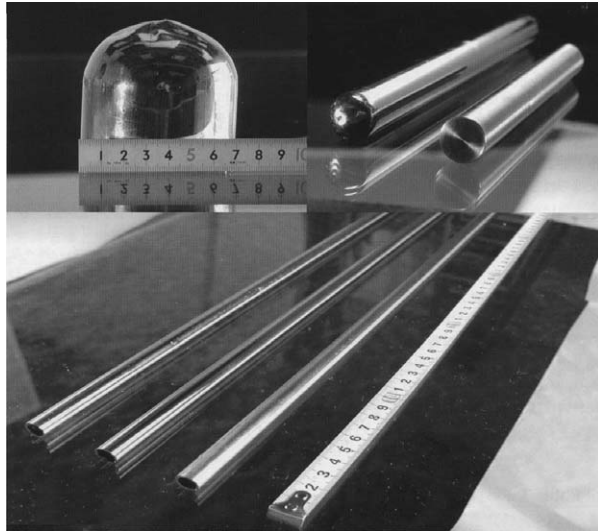


Fig. 2. Shape and surface appearance of some bulk glassy alloys in massive, cylindrical rod and pipe forms produced by water quenching and copper mold casting.

ical cooling rate is as low as 0.020 K/s.¹⁰⁾ Thus, the stability of metallic supercooled liquid has been increased by one million to one hundred million times over the last 15 years. Such a dramatic increase in the stability of the supercooled liquid has enabled us to fabricate various nonequilibrium alloys exhibiting useful engineering properties in a bulk form by conventional casting and water quenching processes. We have fabricated bulk glassy alloys with a variety of shapes, such as a massive ingot 75 mm in diameter and 80 mm high, cylindrical rods 25 mm in diameter and 300 mm long, and long pipes with a 10 mm inner diameter, 2 mm thick and 1.5 to 2 m

Table I. Typical bulk glassy alloy systems reported to date together with the calendar years when the first paper or patent on each alloy system was published

1. Nonferrous alloy systems	Year
Mg-Ln-M (Ln = Lanthanide Metal; M = Ni,Cu,Zn)	1988
Ln-Al-TM (TM = Fe,Co,Ni,Cu)	1989
Ln-Ga-TM	1989
Zr-Al-TM	1990
Zr-Ln-Al-TM (double T_g)	1992
Ti-Zr-TM	1993
Zr-Ti-TM-Be	1993
Zr-(Ti,Nb,Pd)-Al-TM	1995
Pd-Cu-Ni-P	1996
Pd-Ni-Fe-P	1996
Ti-Ni-Cu-Sn	1998
Ca-Cu-Ag-Mg	2000
Cu-Zr (nanophase)	2001
Cu-(Zr,Hf)-Ti (glass, nanophase)	2001
Ca-Cu-Ag-Mg	2001
Cu-(Zr,Hf)-Ti-(Y,Be)	2001
Cu-(Zr,Hf)-Ti-(Fe,Co,Ni)	2002
Pt-Cu-P	2003
Ti-Cu-(Zr,Hf)-(Co,Ni)	2004
Ca-Mg-Zn	2004
2. Ferrous alloy systems	
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
Fe-Ga-(Cr,Mo)-(P,C,B)	1999
Fe-(Nb,Cr,Mo)-(C,B)	1999
Ni-(Nb,Cr,Mo)-(P,B)	1999
Co-Ta-B	1999
Fe-Ga-(P,B)	2000
Ni-Zr-Ti-Sn-Si	2001
Ni-(Nb,Ta)-Zr-Ti	2002
Fe-Si-B-Nb	2002
Co-Fe-Si-B-Nb	2002
Co-Fe-Ta-B-Si	2003
Fe-(Cr,Mo)-(C,B)-Ln	2004

long, as shown in Fig. 2.⁴⁾⁻⁶⁾ The three glassy alloy pipes were made of Zr-Al-Ni-Cu, La-Al-Ni-Cu and Pd-Cu-Ni-P alloys. Based on these recent advances, since about 1990 we have been utilizing a novel type of bulk metallic alloy with a glassy structure, though only crystalline metallic alloys were used during the previous several thousand years.

3. Feature of alloy components. Table I summarizes typical bulk glassy alloy systems reported to date, together with the calendar year when the first paper or patent mentioning each alloy system was published.²⁾⁻⁹⁾ The alloy systems can be divided into nonfer-

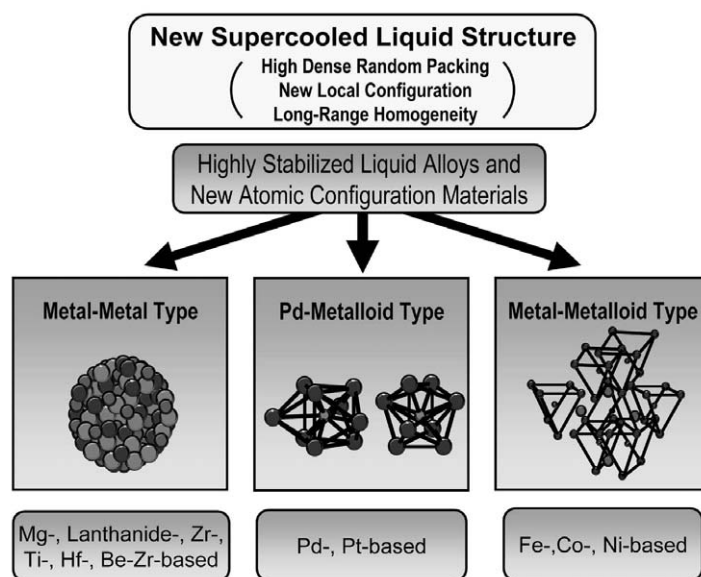


Fig. 3. Schematic illustration of new locally ordered atomic configurations in supercooled liquid and/or glassy phases of metal-metal, metal-metalloid and Pd-based alloy systems.

rous and ferrous alloy types. Nonferrous alloys include Mg-, lanthanide(Ln)-, Zr-, Ti-, Hf-, Pd-, Cu- and Ca-based alloys, while the ferrous include a variety of Fe-, Co- and Ni-based alloys. This table shows clearly that the 5 or 6 years between 1988 and 1993 were foundational for the research field of bulk glassy alloys. Considering that the lanthanides include more than 16 elements, the total number of bulk glassy ternary alloy systems exceeds one thousand. It is also apparent that more than 50% of all alloy systems were developed within the last 7 or 8 years, indicating that this research field is growing significantly even now. Furthermore, it is clear that bulk glassy alloys of the metal-metal type are formed in a number of alloy systems, but not in Fe- and Co-based systems. Thus, most of the bulk glassy alloys found after 1988 consist only of metallic elements and do not include any metalloid elements, in striking contrast to the Pd-Ni-P and Pt-Ni-P alloy systems, which were found to be glassy alloys in the late 1960s.¹¹⁾ Close examination of the alloy components of the more than one thousand alloy systems shown in Table I reveals the existence of three very simple component rules, i.e., (1) multi-component consisting of more than three elements, (2) significant atomic size mismatches above 12% among the main three elements, and (3) suitable negative heats of mixing among the main three elements.⁴⁾⁻⁶⁾ As described later, the total solute content of the bulk glassy alloys that sat-

isfy the three component rules is in the range of 25 to 50 at% where eutectic points are always included. This component rule can be also regarded as the necessary criterion for the generation of eutectics in multi-component alloy systems.

4. Stabilization mechanism. It is important to clarify the reason why alloys that follow the three component rules display a high glass-forming ability through stabilization of their supercooled liquid. We took special notice of the local atomic configurations in the multi-component glassy and liquidus alloys, and tried to clarify the glassy and liquidus structures with various advanced analytical techniques such as anomalous X-ray scattering, neutron scattering, small-angle X-ray scattering, high-resolution transmission electron microscopy (HRTEM) and STEM-high angle angular dark field (HAADF), in addition to density measurement. As a result, it has been reported that the bulk glassy alloys have novel local atomic configurations with the following three features,⁴⁾⁻⁶⁾ i.e., (1) more densely packed atomic configurations, (2) new local atomic configurations which are different from those of the corresponding equilibrium crystalline phases, and (3) long-range homogeneity with attractive interactions. Here, it is important to describe the difference in the local atomic configurations between the metal-metal and the metal-metalloid type glassy alloys. Figure 3 illustrates the

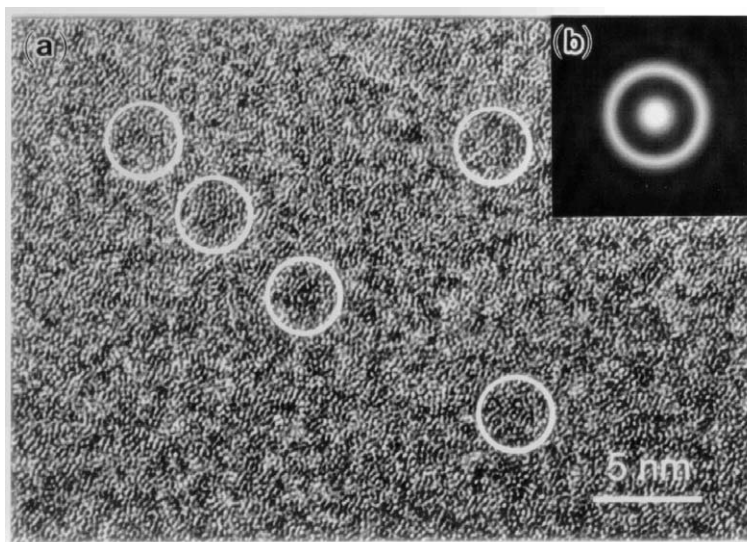


Fig. 4. High-resolution TEM image and selected-area electron diffraction pattern of $\text{Zr}_{70}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{12.5}$ glassy alloy.

local atomic configurations of the three types of bulk glassy alloys. The metal-metal type glassy alloys as exemplified by the Zr-Al-Ni-Cu and Hf-Al-Ni-Cu systems are mainly composed of an icosahedral type short-range ordered atomic configuration, while the metal-metalloid type glassy alloys such as the Fe-Ln-B and Fe-M-B ($M = \text{Zr, Hf, Nb, Ta}$) systems have a network-like ordered structure in which distorted trigonal prisms consisting of Fe and B are connected in edge- and face-shared configurations with Ln or M glue atoms. The Pd-Cu-Ni-P glassy alloys are mainly composed of transformed tetragonal dodecahedrons consisting of Pd, Cu and P and trigonal prisms capped with three half-octahedral polyhedrons consisting of Pd, Ni and P.¹²⁾ Any of these locally ordered atomic configurations can be regarded as more homogeneous, more densely packed and novel structures. Although the bulk glassy alloys include the above-described ordered atomic configurations on a short-range scale, their structures on a longer scale consist of random atomic configurations without any periodic or quasi-periodic atomic array.

Here some experimental data on the local atomic configurations are presented for Zr- and Fe-based bulk glassy alloys. In the high-resolution TEM image of the as-cast $\text{Zr}_{70}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{12.5}$ alloy shown in Fig. 4,¹³⁾ one can see a number of concentric-circle contrast regions with a size of about 0.5 nm, resembling cross sections of onions. This unique contrast image and its size agree well with

the computer simulation contrast image obtained on the assumption of the existence of icosahedral clusters with a size of about 1 nm. Based on the coordination numbers and atomic distances obtained by the anomalous X-ray scattering, the local atomic structure models of Fe-Ln-B and Fe-M-B glassy alloys are shown in Fig. 3.¹⁴⁾ Here, it is important to point out that the formation of the network-like ordered structures consisting of distorted trigonal prisms is attributed to the addition of a Ln or M element with a negative heat of mixing with Fe and B and an atomic size ratio significantly above 12%.

A novel liquid with unique locally ordered atomic configurations in the special multi-component alloys can have a smooth liquid/crystal interface at which it is difficult to accrete new atoms leading to the formation of a crystal nucleus. Consequently, the novel liquid has a high solid/liquid interfacial energy, resulting in the suppression of crystal nucleation. Long-range atomic rearrangements are also suppressed in the liquid, leading to a decrease in atomic diffusivity and an increase in glass transition temperature (T_g). In addition, the liquid requires atomic rearrangements on a long-range scale for the progress of crystallization because of its novel locally ordered atomic configurations, leading to the suppression of the growth reactions needed to form a crystalline phase. Owing to the combination of these three factors, the special multi-component alloys can have higher reduced glass transition temperatures (T_g/T_l) due

Table II. The primary phase in the crystallization process of a number of bulk glassy alloys

Phase	System	Typical alloy composition (at%)
Big cube	Zr-Al-Ni-Cu	$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$
	Zr-Al-Ni-Cu-(Cr,Mo)	$Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}(Cr,Mo)_5$
	Zr-Ni-(Fe,Co)	$Zr_{70}Ni_{10}(Fe,Co)_{20}$
	Hf-Al-Ni-Cu	$Hf_{65}Al_{7.5}Ni_{10}Cu_{17.5}$
Icosahedral	Zr-Al-Cu-O*	$(Zr_{65}Al_{7.5}Cu_{27.5})+O$
	Zr-Al-Ni-Cu-O*	$(Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5})+O$
	Zr-Ti-Al-Ni-Cu-O*	$(Zr_{59}Ti_3Al_{10}Ni_8Cu_{20})+O$
	Zr-Al-Ni-Cu-(Ag,Pd,Au,Pt)	$Zr_{65}Al_{7.5}Ni_{10}Cu_{7.5}(Ag,Pd,Au,Pt)_{10}$
	Zr-Al-Ni-Cu-(Nb,Ta,V)	$Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}(Nb,Ta,V)_5$
	Zr-Al-Ni-(Ag,Pd,Au,Pt)	$Zr_{65}Al_{7.5}Ni_{10}(Ag,Pd,Au,Pt)_{17.5}$
	Zr-Al-Cu-Pd	$Zr_{65}Al_{7.5}Cu_{17.5}Pd_{10}$
	Zr-Ni-(Pd,Au,Pt)	$Zr_{70}Ni_{10}(Pd,Au,Pt)_{20}$
	Zr-Cu-Pd	$Zr_{70}Cu_{10}Pd_{20}$
	Zr-Pd	$Zr_{70}Pd_{30}$
	Zr-Pt	$Zr_{80}Pt_{20}$
	Hf-Al-Ni-Cu-Pd	$Hf_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$
	Hf-Al-Ni-Ag	$Hf_{65}Al_{7.5}Ni_{10}Ag_{17.5}$
	Hf-Cu-(Pd,Pt)	$Hf_{70}Cu_{20}(Pd,Pt)_{10}$
	Ti-Zr-Ni	$Ti_{45}Zr_{38}Ni_{17}$
	Ti-Zr-Ni-Cu	$Ti_{60}Zr_{15}Ni_{15}Cu_{10}$
Complex fcc	Fe-(Nb,Ta,W)-B	$Fe_{70}(Nb,Ta,W)_{10}B_{20}$

to a decrease in liquidus temperature (T_l) and an increase in T_g .

We have tried to clarify the characteristics of the primary crystallization phase from the supercooled liquid because this phase is expected to be closely related to the locally ordered atomic configuration of the supercooled liquid. Table II summarizes alloy systems examined in the present study and the primary crystallization phase in their alloy systems.^{15),16)} Careful scrutiny of the metal-metal type glassy alloys shows that the primary crystallization phase can be limited to a big-cube or an icosahedral phase across a variety of alloy systems. In the Zr- and Hf-based glassy alloys with the largest supercooled liquid region, the primary crystallization phase is a big cube type Zr_2Ni phase with a large lattice parameter of 1.12 nm including 96 atoms. In addition, the big cube phase always includes local icosahedral-type ordered atomic configurations. When elements with nearly zero or positive heats of mixing with the other constituent elements are added, the primary crystallization phase changes to an icosahedral phase.^{17),18)} It is thus concluded that the addition of elements leading to deviation from the three component rules causes the precipitation of the icosahedral phase. The precipitation of the icosahedral phase takes place very homogeneously at high volume fractions of approximately 70% in

the glassy matrix and its particle size is as small as 10 to 20 nm. It has also been clarified that the critical size for the transition from the glassy phase to the icosahedral phase lies in the vicinity of 0.5 nm, from examination of the high-resolution TEM image and nano-beam electron diffraction patterns shown in Fig. 5.¹³⁾ These results indicate that the metal-metal type bulk glassy alloys in the Zr-, Hf- and Ti-based alloy systems are composed mainly of icosahedral-type ordered atomic configurations with a size less than 0.5 nm.

5. Predictions of glass-forming ability and glass-forming composition ranges. By using the dominant three factors for stabilization of supercooled liquid, the glass-forming ability of special multi-component alloys has been estimated.^{6),19)} For estimation purposes, the atomic size mismatch and negative heats of mixing were changed to the thermodynamic parameters of mismatch entropy for the assumption of a hard-sphere model, and mixing enthalpy for the assumption of a regular solution model. The calculation model was created on the basis of an equation that was proposed for the evaluation of the critical cooling rate for oxide glasses,²⁰⁾ and the relationship that includes their two thermodynamic factors to estimate the critical cooling rate (R_c) is expressed by equation [1]¹⁹⁾:

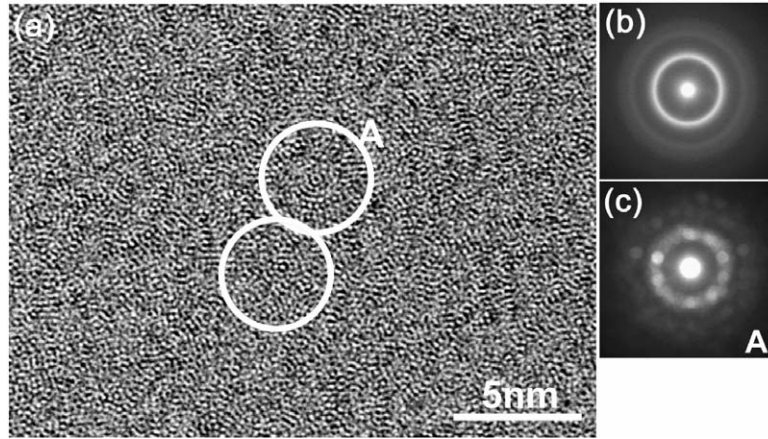


Fig. 5. TEM data of $\text{Zr}_{70}\text{Pd}_{30}$ alloy annealed at 690 K for 120 s. (a) High resolution TEM image, (b) selected-area electron diffraction pattern taken from an area $1\mu\text{m}$ in diameter, and (c) nano-beam electron diffraction pattern taken from the area marked with A in (a).

$$R_c = Z \frac{k_B T_m^2}{a^3 \eta_{T=T_m}} \exp \left[0.75 \times \left(\frac{\Delta H - T_m \Delta S^{\text{ideal}}}{300R} \right) - 1.2 \times \frac{T_m S_o}{300R} \right], \quad [1]$$

where Z is a constant, k_B is the Boltzmann constant, T_m is the melting temperature, a is the mean atomic distance, $\eta_{T=T_m}$ is the viscosity at T_m , and R is the gas constant. An important concept of the calculation method expressed by equation [1] is that equation [1] has the constant Z as a probability factor,^(6),19),21) and that Z is described by a thermodynamic function associated with the Gibbs free energy consisting of the enthalpy ΔH and entropy ΔS terms of the liquid state. This probability term Z indicates the stability of the supercooled liquid at room temperature. Calculations were carried out for three groups: pure metals, typical glass-forming systems, and the latest metallic glasses with a high glass-forming ability found after 1990. The calculation results are summarized in Fig. 6. As shown in Fig. 6, the R_c for Ni metal, Co- and Pd-Cu-based metallic glasses obtained by equation [1] are 9.1×10^8 , 1.2×10^5 and 1.6×10^{-2} K/s, respectively, which are in agreement with the values 3×10^{10} , 3.5×10^5 and 1×10^{-1} K/s, respectively, obtained from the T-T-T diagram calculated by Davies.⁽²¹⁾ Thus, the R_c obtained from equation [1] can predict rather well the order of magnitude of the experimental data for a number of bulk glassy alloys. In addition to the success in obtaining R_c for metallic glasses, the following points are clarified by equation [1]^(6),19): (1) T_m^2/η characterizes R_c as is typical for a Pd-Cu-based metallic glass with a low melting point as well as high viscosity at the melting point; (2) negative heats of mixing and atomic size mis-

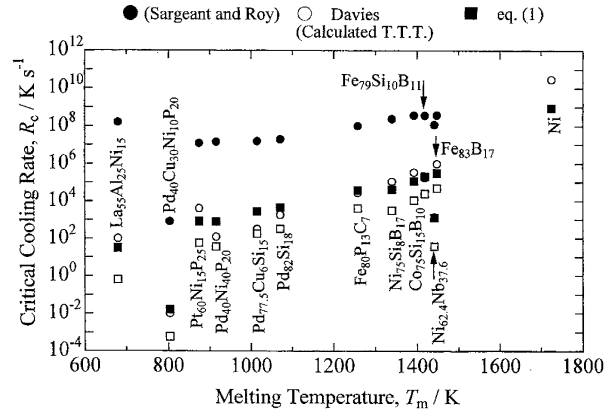


Fig. 6. Relationship between critical cooling rate (R_c) and melting temperature (T_m) for Ni and typical metallic glasses.

matches above approximately 12% cause the reduction of R_c from 10^{-2} to 10^{-7} K/s and from 10^{-1} to 10^{-2} K/s, respectively, and (3) the reduction of R_c is understood as a stabilization of the liquid state.

Furthermore, the glass-forming composition ranges and the best alloy compositions with the largest supercooled liquid region prior to crystallization have also been predicted by using Miedema's semi-empirical model⁽²²⁾ and quasi-chemical model⁽²³⁾ including interaction parameters among constituent elements. For the criterion $\Delta H(\text{SS}) - \Delta H(\text{Glass}) > 0$ for glass formation, it has been reported that the glass-forming composition ranges in La-Ni-Al and Zr-Al-Ni systems agree rather well

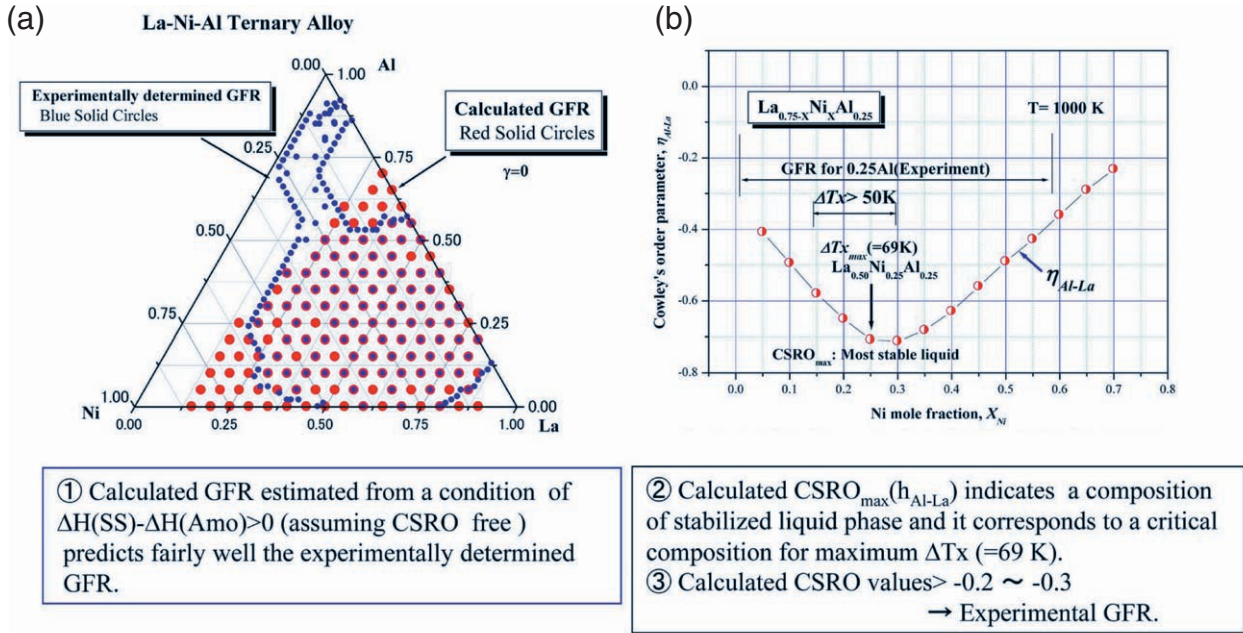


Fig. 7. (a) Glass-forming composition range (GFR) in La-Ni-Al system, and (b) the relationship between Cowley's order parameter and the supercooled liquid region prior to crystallization in La-Ni-Al alloys.

with the experimental data, as exemplified by the La-Ni-Al system in Fig. 7 (a).²⁴⁾ It has also been recognized that the alloy composition having the most negative Cowley's order parameter²⁵⁾ has the largest supercooled liquid region prior to crystallization, as shown for La-Ni-Al alloys in Fig. 7 (b).²⁶⁾ The good correspondence between Cowley's order parameter and the stability of supercooled liquid indicates that the high stability of supercooled liquid against crystallization may originate from the development of short-range ordered atomic configurations such as icosahedral or a network-like atomic configuration, which is consistent with the interpretation above.

6. Experimental determination of thermodynamic properties. The use of bulk glassy alloys of the Pd-Cu-Ni-P system whose supercooled liquid forms have high stability against crystallization has enabled us to measure specific heat as a function of temperature over the whole supercooled liquid region. Based on the experimental data on specific heat, the temperature dependence of enthalpy, entropy and Gibbs free energy has been determined quantitatively as shown for Pd₄₀Cu₃₀Ni₁₀P₂₀ alloy in Fig. 8.²⁷⁾ The extremely high glass-forming ability of the Pd-based alloy is partly due to the low Gibbs free energy for the liquid/crystal transition.

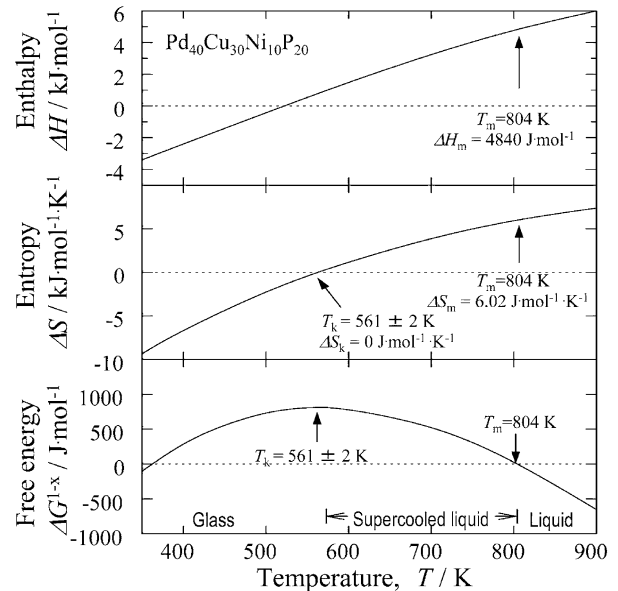


Fig. 8. Temperature dependence of enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) for Pd₄₀Cu₃₀Ni₁₀P₂₀ glassy alloy.

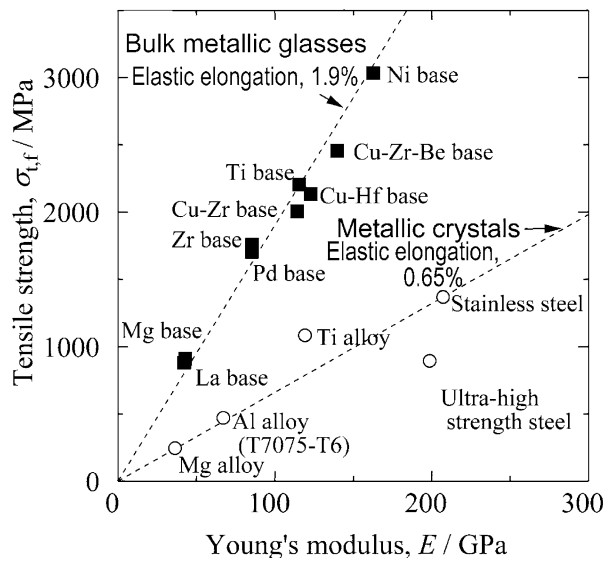


Fig. 9. Relationship between tensile strength ($\sigma_{t,f}$) and Young's modulus (E) for bulk glassy alloys. Data for crystalline metallic alloys are also shown for comparison.

In addition, the fictive glass transition temperature can also be determined from the temperature dependence of entropy. It is believed that the present result is the first report of thermodynamic properties determined on the basis of experimental measurement data over the entire supercooled liquid region for metallic materials.

7. Mechanical properties. *7-1. Tensile and compressive strength.* We have found that bulk glassy alloys produced by the combination of new alloy components, novel local ordered atomic configurations and three dimensional material form exhibit unique mechanical properties which are significantly different from those of crystalline alloys. Figure 9 summarizes the relationship between tensile strength and Young's modulus for typical bulk glassy alloys,⁴⁾⁻⁶⁾ together with corresponding data for conventional crystalline alloys. A good linear relationship can be seen between the two kinds of alloys, with the linearity much better for bulk glassy alloys. In comparison with the tensile strength of conventional crystalline alloys at the same Young's modulus, the strength values of the bulk glassy alloys are about three times higher. On the other hand, the Young's moduli of the bulk glassy alloys at the same tensile strength are about a third as high as those for crystalline alloys. In addition, the slope of the linear relationship corresponds to an elastic elongation limit on the basis of Hook's law. The elastic elongation limit is 1.9%

for bulk glassy alloys, being much larger than that (0.65%) of conventional crystalline alloys. The much better linearity relation for all bulk glassy alloys indicates that the deformation and fracture modes are dominated by long-range disordered atomic configurations. Figure 9 also shows that a high tensile strength exceeding 2000 MPa, which has not been obtained with conventional crystalline alloys, can be achieved by choosing Ni-, Cu- and Ti-based bulk glassy alloys.

More recently, it was also found that the strength of bulk glassy alloys increased to 3200 – 5200 MPa by choosing Fe- and Co-Fe-based alloy components, though the mechanical tests were made in a compressive deformation mode. The fracture strength and Young's modulus at room temperature are 3200 MPa and 160 GPa, respectively, for $\text{Fe}_{77}\text{Ga}_3\text{P}_{9.5}\text{C}_4\text{B}_4\text{Si}_{2.5}$ glassy alloy rod,²⁸⁾ 3400 MPa and 180 GPa, respectively, for $(\text{Fe}_{0.75}\text{B}_{0.2}\text{Si}_{0.05})_{96}\text{Nb}_4$,²⁹⁾ 4250 MPa and 210 GPa, respectively, for $[(\text{Fe}_{0.6}\text{Co}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$,³⁰⁾ 5185 MPa and 268 GPa, respectively, for $\text{Co}_{43}\text{Fe}_{20}\text{Ta}_{5.5}\text{B}_{31.5}$,^{30),31)} and 5550 MPa and 280 GPa, respectively, for $\text{Co}_{52}\text{Fe}_{10}\text{Ta}_{4.5}\text{Mo}_2\text{B}_{31.5}$.³²⁾ It is also apparent that these high-strength glassy alloys exhibit distinct plastic strain before final rupture. A number of shear deformation bands are observed on their lateral surfaces and the final fracture occurs along the maximum shear stress plane, which is inclined by about 45 degrees to the direction of the applied load. The high values of fracture strength and Young's modulus for the Fe- and Co-Fe-based bulk glassy alloys lie on the same straight line which is extrapolated from the linear relationship between tensile strength and Young's modulus for bulk glassy alloys in Mg-, Ln-, Pd-, Zr-, Ti-, Cu- and Ni-based systems. This good agreement indicates that the deformation and fracture modes of bulk glassy alloys are independent of alloy components and strength levels. The ultra-high strength exceeding 5000 MPa is believed to be the highest value yet obtained for any kind of metallic material including crystalline and glassy alloys.

7-2. Bending and torsional strength. Although the uniaxial tensile fracture strength of Zr- and Pd-based bulk glassy alloys is in the range of 1600 – 1800 MPa, it is important to report the bending fracture strength of their bulk glassy alloys because the bulk glassy alloys are likely to be used under bending stress conditions. The Zr- and Pd-based bulk glassy alloy sheets with thicknesses up to about 6 mm prepared by the squeeze casting technique were found to exhibit much higher bending fracture strength as compared with the tensile fracture strength. Figure 10 shows the bending flexural stress-

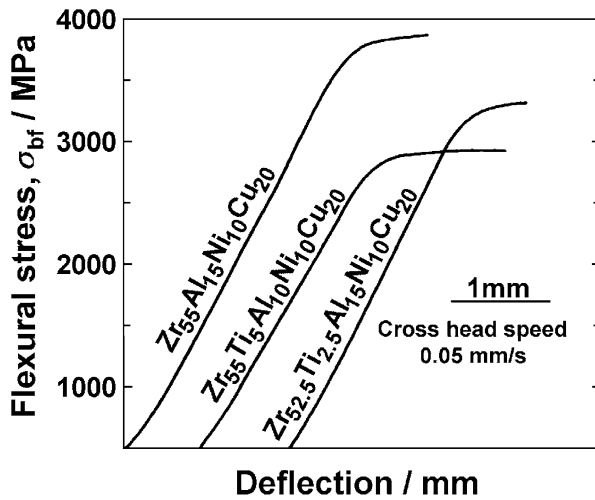


Fig. 10. Flexural stress-deflection curves of bulk glassy Zr-based alloy sheets with thicknesses of 3 and 4 mm prepared by squeeze casting.

deflection curves of $\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}$, $\text{Zr}_{55}\text{Ti}_5\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{20}$ and $\text{Zr}_{52.5}\text{Ti}_{2.5}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}$ glassy alloy sheets subjected to the three-point bending test at room temperature. By applying the load at three points and causing bending, a tensile force is created in the material opposite the mid-point. Fracture begins at this location. The flexural strength ($\sigma_{b,f}$) and flexural modulus ($E_{b,f}$) are evaluated by the following equations [2] and [3], respectively.³³⁾

$$\sigma_{b,f} = (3FL)/(2wh^2) \quad [2]$$

$$E_{b,f} = (L^3F)/(4wh^3\delta) \quad [3]$$

Here, F is the fracture load, L is the distance between the two outer points, w is the width of the specimen, h is the height of the specimen, and δ is the deflection of the beam up to fracture. The terms $\sigma_{b,f}$, $E_{b,f}$ and h are evaluated to be as high as 2930 MPa, 92 GPa and 2.4 mm, respectively, for the $\text{Zr}_{55}\text{Ti}_5\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{20}$ sheet, 3895 MPa, 115 GPa and 2.5 mm, respectively, for the $\text{Zr}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}$ sheet and 3300 MPa, 104 GPa and 2.1 mm, respectively, for the $\text{Zr}_{52.5}\text{Ti}_{2.5}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{20}$ sheet. We have also reported^{34),35)} that $\sigma_{b,f}$ is 1800–1900 MPa for the $\text{Zr}_{60}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{20}$ bulk glassy alloys with a cylindrical form prepared by the conventional copper mold casting method. Similar $\sigma_{b,f}$ values have also been reported for the bulk glassy alloy prepared by the powder metallurgy method consisting of extrusion of atomized glassy powders in the supercooled liquid region.³⁴⁾ In

comparison with the previous data on $\sigma_{b,f}$, the $\sigma_{b,f}$ values of the present bulk glassy alloys prepared by squeeze casting are as much as 1.5–2.5 times higher. Thus, the squeeze casting method is useful for the production of Zr-based bulk glassy alloys with much higher $\sigma_{b,f}$ values. It is generally known³⁶⁾ that the bending flexural strength for oxide glasses is sensitive to residual stress, and the existence of residual compressive stress in the outer surface region induces a significant increase in $\sigma_{b,f}$. Furthermore, a residual compressive stress in the outer surface region can be introduced by quenching.³⁶⁾ Quenching treatment has been used as an effective strengthening method for oxide glasses. Furthermore, the existence of residual compressive stress is effective in increasing the bending flexural strength and bending fatigue strength. No significant increase in tensile fracture strength has been recognized, presumably because of preferential crack initiation in the inner region with residual tensile stress. In the squeeze casting method, a much higher cooling rate is achieved in the outer surface region of the metallic liquid because of its direct contact with copper mold. The significant difference in the cooling rate between the outer surface region and the inner region induces residual compressive stress in the outer surface region and residual tensile stress in the inner region. The residual compressive stress can yield an increase in the bending flexural strength to about 4000 MPa which is about 2 times higher than that (1800–1900 MPa) of the ordinary bulk glassy alloys in which compressive residual stress is not present in the outer surface region.

The torsional elastic and rupture strength values of bulk glassy alloys were measured by using rod specimens of 10 mm in diameter and comparison with conventional plain carbon (0.4 mass% C) steel.³⁷⁾ The size and dimensions of the specimens satisfy the JIS criterion. The elastic twist angle was measured to be about 16 degrees for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ glassy alloy rod and 4 degrees for the carbon steel. In addition, the elastic shearing stress of the glassy alloy rod was about 900 MPa which was about three times higher than that (300 MPa) of the plain carbon steel. This difference is nearly the same as those for the uniaxial tensile strength and Young's modulus.

7-3. Impact fracture strength and fracture energy. The Charpy test specimen has a U-shaped notch and a shape and size in conformity with JIS-No.3 (2.5 mm in width) type.³⁸⁾ The fracture stress and displacement at the impact fracture and the impact fracture energy were measured at room temperature with a Charpy

testing machine. The initial angle of the arm was 143.5 degrees and the velocity at impact was 3.761 m/s. From data on the Charpy impact load-displacement curves for the $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ and $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ glassy alloy sheets prepared by copper mold casting, the maximum load was measured as 4.3 kN for the Zr-based alloy and 4.7 kN for the Pd-based alloy. Consequently, the maximum impact fracture stress was evaluated as 1615 and 1749 MPa, respectively. The impact fracture stress was nearly the same as the static tensile fracture strength (about 1570 MPa³⁹⁾ for the Zr-based alloy and 1680 MPa⁴⁰⁾ for the Pd-based alloy) obtained over the wide strain rate range of $10^{-4} - 10^{-1} \text{ s}^{-1}$ for the cast bulk glassy alloys, and the maximum displacement was as large as 0.44 – 0.43 mm. Furthermore, the impact fracture energy was measured as 63 kJ/m² for the Zr-based alloy and 70 kJ/m² for the Pd-based alloy.^{5),41)}

It has also been pointed out that the Charpy impact fracture energy of the Zr-based bulk glassy alloys is strongly dependent on the preparation method, and increases significantly for squeeze-cast glassy alloy sheets. Figure 11 shows the compositional dependence of the Charpy impact fracture energy for $\text{Zr}_{70-x-y}\text{Ti}_x\text{Al}_y\text{Ni}_{10}\text{Cu}_{20}$ glassy alloy sheets with a thickness of 2.5 mm prepared by the squeeze casting method.^{5),41)} The impact fracture energy exceeds 100 kJ/m² at 10%Al and tends to decrease with any change in deviation from the Al content. On the other hand, the change in the impact fracture energy with Ti content is less significant for the 10% Al-containing alloys with Ti contents below 5 at%. It is noteworthy that very high impact fracture energies of 120 – 135 kJ/m² are obtained for $\text{Zr}_{55-60}\text{Ti}_{0-5}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{20}$ glassy alloy sheets.

In comparison with the Charpy impact fracture energies for other metallic crystalline alloys, one can notice that the impact fracture energies exceed that (100 – 120 kJ/m²) for conventional age-hardened Al-based high-strength alloys prepared by powder metallurgy.⁴²⁾ The comparison allows us to conclude that the bulk glassy alloys prepared by squeeze casting possess the impact fracture energies that are high enough to allow their use as structural materials.

We further examined the impact fracture mode of a Zr-based glassy alloy with high impact fracture energy. The fracture surface of the cast glassy Zr-Al-Ni-Cu specimen with a U-shaped notch prepared by copper mold casting consisted of a vein pattern in the region near the U-shaped notch and changed to an equiaxed dimple-like pattern which occupied most of the region of the fracture surface. Neither the shell-like pattern nor

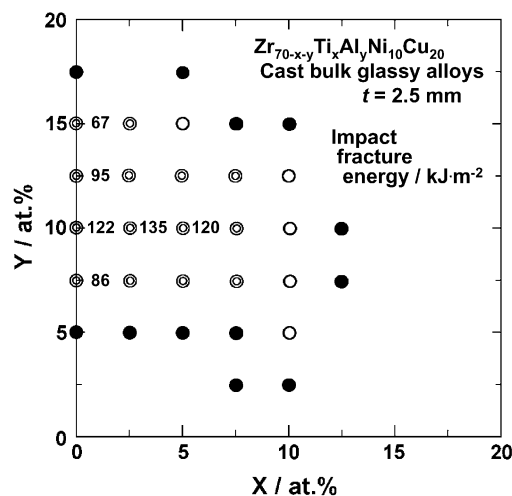


Fig. 11. Compositional dependence of the Charpy impact fracture energy for the $\text{Zr}_{70-x-y}\text{Ti}_x\text{Al}_y\text{Ni}_{10}\text{Cu}_{20}$ glassy alloy sheets with a thickness of 2.5 mm prepared by squeeze casting.

the featureless cleavage-like pattern typical of embrittled glassy alloys was observed over the whole fracture surface. The fracture surface appearance indicates clearly that the cast bulk glassy alloy has high ductility, leading to severe deformation even in the impact fracture mode. Furthermore, we observed secondary failures and a change in the fracture surface appearance from an equiaxed dimple-like pattern to a vein pattern near the failures. The secondary failures appeared to be closely related to casting defects. That is, the casting defect seemed to correspond to the boundary plane between the early solidified glassy region and the later solidified glassy region. The glassy phase region near the boundary plane is subjected to subsequent heating. The subsequent heating seems to cause a decrease in ductility as compared with the as-cast glassy phase without subsequent heating, leading to the generation of the secondary failures. Although the complete eradication of boundary planes between early and late solidified glassy alloys is very difficult to achieve in the casting process, a decrease in the number of such interfaces is expected to cause a further increase in impact fracture energy.

7-4. Fracture toughness. In addition to the large elastic elongation limit, high Charpy impact fracture energy and large bending deflection, it is important to present data on the fracture toughness and fracture mechanics of bulk glassy alloys to support the use of bulk glassy alloys as high-strength structural materials.

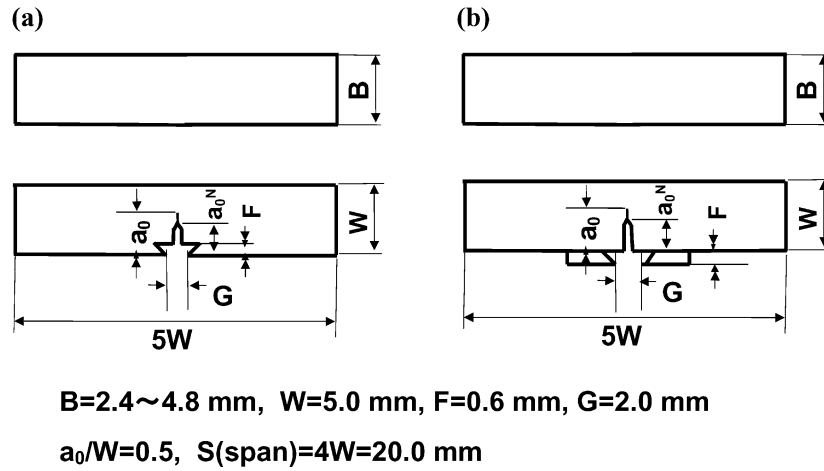


Fig. 12. Size and shape of $Zr_{55}Al_{10}Ni_5Cu_{30}$ glassy alloy specimens used for measurement of fracture toughness.

There is a high likelihood that bulk glassy alloys contain some flaws. We want to know the maximum stress that a bulk glassy alloy can withstand if it contains flaws of a certain size and geometry. Fracture toughness represents the ability of the glassy alloy containing a flaw to withstand an applied load. As compared with the results of an impact test, fracture toughness is a quantitative property of the alloy.^{43),44)} Figure 12 shows the outer shape and size of $Zr_{55}Al_{10}Ni_5Cu_{30}$ glassy alloy specimens used to measure fracture toughness.⁴⁵⁾ Fracture toughness tests with uniaxial tensile and three-point bending loads were carried out under the standard criterion of ASTM E399 where the stress field near the crack tip was controlled by linear fracture mechanics and the small-scale yielding condition. Standard compact specimens with a thickness of 2.3 – 3.2 mm were used. The ratio of thickness to width was fixed at 1:4. The fatigue cracking and the fracture toughness tests were performed with the same servo-hydraulic fatigue machine. One $MPa\sqrt{m}/s$ was used for the fracture loading rate. The load-displacement relationships were plotted by using the output of a load-sensing transducer and the output of a clip-in displacement gauge.

Table III summarizes the K_{IC} and the criterion of the plane-strain condition $2.5(K_{IC}/\sigma_y)^2$ in all fracture toughness tests.^{45),46)} The specimen thickness B satisfied the criterion values in all tests. The K_{IC} lies in the range from about 40 $MPa\sqrt{m}$ for the uniaxial tensile load condition to about 50 $MPa\sqrt{m}$ under a three-point bending load.

There is a tendency for K_{IC} to be higher in the latter testing condition. We have also confirmed that the fracture toughness of the Zr-Al-Ni-Cu bulk glassy alloys shows higher values of 55 – 76 $MPa\sqrt{m}$ for some fatigue pre-crack specimens, though the critical value of the $2.5(K_{IC}/\sigma_y)^2$ term is larger than the specimen thickness and hence the toughness value is regarded as K_Q .

Figure 13 shows the slip lines that occurred in the fracture toughness test under a uniaxial tensile load in the vicinity of the fatigue crack tip on the specimen surface.⁴⁶⁾ In the material with a K_{IC} value of 41 $MPa\sqrt{m}$, long bent slip lines with a length of several tens to hundred μm were observed. Figure 14 shows the fracture surfaces of a cast glassy specimen with the fatigue crack tip.⁴⁶⁾ In Fig. 14(b), a pair of white lines shows the cross sectional profile of the crack obtained by stereo-matching observations of fracture surfaces. In the deep region of the material, plane-strain type slip lines were continuous and crack tip openings (width; 5 – 10 μm), as in the stretch zone in ductile crystalline alloys, were discrete along the fatigue crack front on the fracture surfaces. In the surface region shown with a large circle in Fig. 14(a), cracks propagated along the outermost long bent slip line and the cracks also propagated almost the same distance in the depth direction as shown in Fig. 14(c). The length of this plane-stress type crack was about double the plastic zone size calculated under plane-stress conditions with fracture mechanics. It is presumed that this difference is related to a unique property of the bulk glassy alloy, which easily slips off along one

Table III. Fracture toughness values and test conditions of bulk glassy alloys

Alloy	Width W (mm)	Thickness B (mm)	Notch Fracture Crack (mm)	Test Condition	$P_{\max}$ (kN)	K_{IC} (MPa $\sqrt{m}$)	$2.5(K_{IC}/\sigma_f)^2$ (mm)	K_{IC} results
* ¹ Material Su-1	9.20	2.31	* ³ 4.98	Tensile	0.825	41.1	2.03	Valid
* ¹ Material Su-2	9.20	2.30	* ³ 5.32		0.687	39.1	1.84	Valid
* ² Material Sq-1	4.944	2.436	* ⁴ 2.57	Bending	0.818	50.3	1.95	Valid
* ² Material Sq-2	4.958	2.462	* ⁴ 2.60		0.859	53.4	2.2	Valid
* ² Material Sq-3	5.005	2.473	* ⁴ 2.63		0.708	46.9	1.69	Valid
* ² Material Sq-4	4.973	2.028	2.50		0.637	48.1	1.78	Valid

*¹ Material Su: $Zr_{55}Al_{10}Ni_5Cu_{30}$ at% made by the suction casting method

*² Material Sq: $Zr_{55}Al_{10}Ni_5Cu_{30}$ at% made by the squeeze casting method

*³ Crack length a = Notch length (3.30 mm) + fatigue crack length

*⁴ Crack length a = Notch length (1.20 mm) + fatigue crack length

The notch plane in the specimen (*¹ Material Su) was machined in the direction normal to the boundary plane of molten metal.

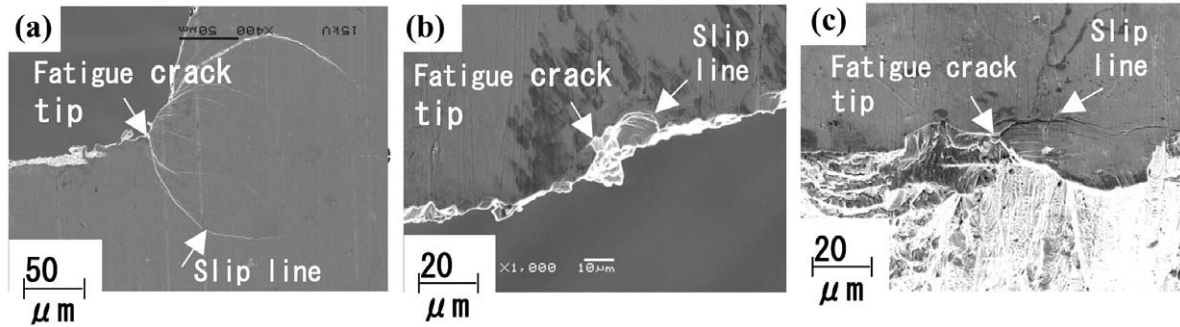


Fig. 13. Slip lines after fracture in the vicinity of the fatigue pre-crack tip on the $Zr_{55}Al_{10}Ni_5Cu_{30}$ glassy alloy specimen surface.

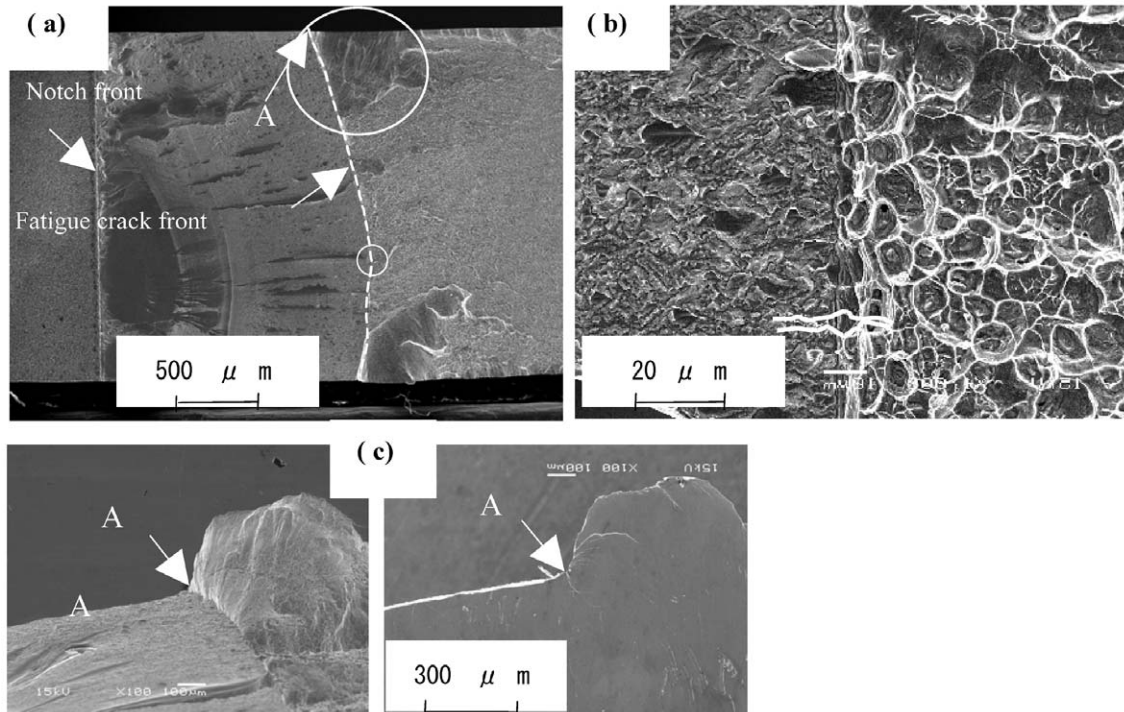


Fig. 14. Fracture surface near the fatigue pre-crack tip for the $Zr_{55}Al_{10}Ni_5Cu_{30}$ glassy alloy specimen under a uniaxial tensile load.

(a) General view, (b) enlarged view of (a)-small circle region, and (c) views near the specimen surface.

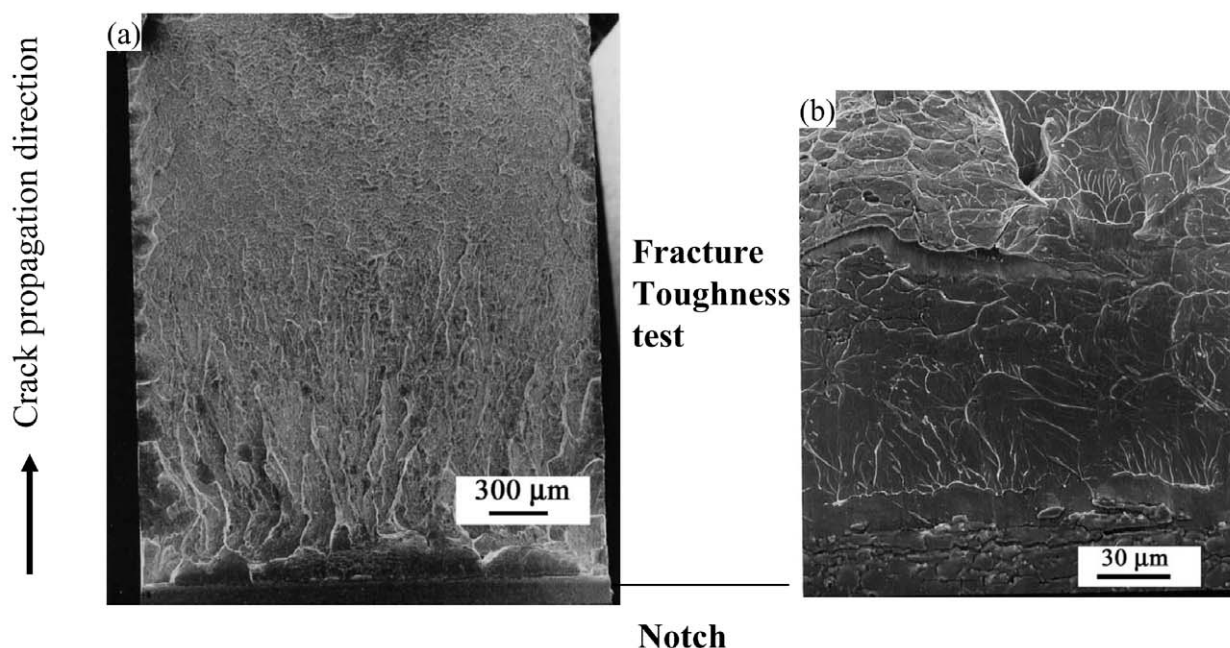


Fig. 15. Fracture surface near the fatigue pre-crack tip for the $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ glassy alloy specimen under a three-point bending load.

slip plane. Therefore, specimen thickness may require further attention in fracture toughness testing of bulk glassy alloys with a large K_{IC} .

In a bulk glassy alloy subjected to the three-point bending test, a distinct vein fracture pattern is also observed in the fracture surface region near the fatigue crack tip as shown in Fig. 15.⁴⁷⁾ These fracture toughness results demonstrate clearly that these bulk glassy alloys have high plastic deformability even near a preexisting fatigue crack tip. It is also noteworthy that the K_{IC} values are much higher than those ($24 - 36 \text{ MPa}\sqrt{\text{m}}$)⁴⁸⁾ for age-hardened Al-based alloys and comparable to those ($50 - 95 \text{ MPa}\sqrt{\text{m}}$)⁴⁸⁾ for commercial Ti-based alloys. The present K_{IC} values are also nearly the same as that ($50 \text{ MPa}\sqrt{\text{m}}$)⁴⁹⁾ of Zr-Ti-Cu-Ni-Be bulk glassy alloy. Here, it is particularly important to point out that K_{IC} decreases to about $1 \text{ MPa}\sqrt{\text{m}}$ for the Zr-Ti-Cu-Ni-Be glassy alloy containing nanocrystalline particles,⁵⁰⁾ while the Zr-Al-Ni-Cu base bulk glassy alloys containing nanocrystalline particles exhibit remarkably improved K_Q values of $100 - 160 \text{ MPa}\sqrt{\text{m}}$ ⁵¹⁾ which significantly exceed those of conventional Ti alloys and alloy steels. We have also measured the fracture toughness of Zr-based glassy alloys with a thickness of 3 mm having only the U-shaped notch and no fatigue pre-crack tip. It has been reported that the

toughness values are in the range of $65 - 72 \text{ MPa}\sqrt{\text{m}}$ for $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$ and $67 - 75 \text{ MPa}\sqrt{\text{m}}$ for $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{29}\text{Nb}_1$.⁴⁵⁾ In any event, it is concluded that the Zr-based bulk glassy alloys have high enough K_{IC} values for use as structural materials.

7-5. Fatigue strength. We have further examined fatigue strength and fatigue crack propagation behavior for bulk glassy alloys with smooth and notched shapes.⁵²⁾⁻⁵⁵⁾ Figure 16 shows the relationship between the ratio of cycled applied stress to uniaxial fracture strength and the number of cycles up to failure for Zr-Al-Ni-Cu, Zr-Ti-Cu-Ni-Be and Pd-Cu-Ni-P bulk alloys in glassy single phase and glassy plus nanocrystalline mixed states. The fatigue strength endurance limit defined by the minimum applied cycle stress ratio at 10^7 cycles is about 0.04 for two kinds of Zr-based bulk glassy alloys and 0.23 for the Pd-based glassy alloy. In addition, the fatigue limit of the Zr-Al-Ni-Cu glassy alloy was increased significantly to 0.13 by the homogeneous dispersion of nanocrystalline particles with a size of about 5 nm in the glassy phase matrix. It has been reported that crack initiation in the Zr-based bulk glassy alloys with glassy single or nanocrystalline mixed phase occurs at a very early stage of about 7% of the total number of cycles to failure, and that most of the

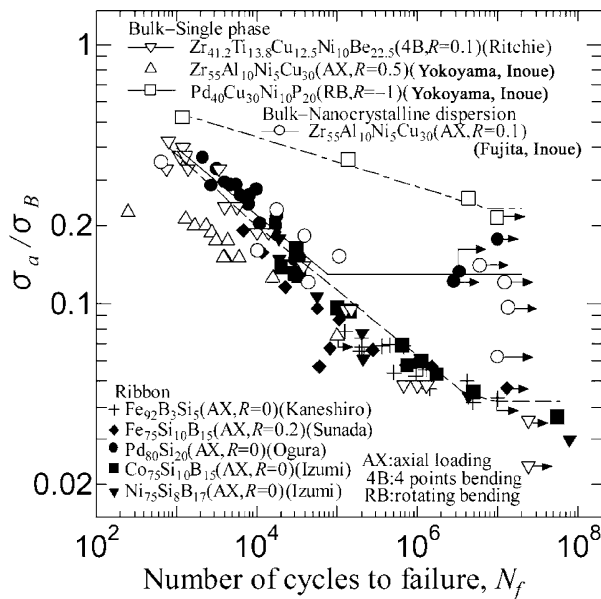


Fig. 16. Relationship between the ratio of cyclic applied stress to fracture strength (σ_a/σ_B) and number of cycles to failure (N_f) for bulk glassy single-phase and glassy plus nanocrystalline phase alloys. Data for amorphous alloy ribbons are also shown for comparison.

cycles are spent on the propagation of fatigue cracks. We have also examined the relationship between fatigue crack propagation rate (da/dn) and the normalized stress intensity factor range ($\Delta K/E$) for Zr-Al-Ni-Cu and Pd-Cu-Ni-P glassy alloys. The fatigue crack propagation rate is proportional to the stress intensity factor range in spite of different fatigue test conditions and can be measured as 1.7×10^{-6} mm/cycle at $\Delta K/E = 3 \times 10^{-5} \sqrt{\text{m}}$ for the former alloy and 1.2×10^{-6} mm/cycle at $\Delta K/E = 5 \times 10^{-5} \sqrt{\text{m}}$ for the latter. In addition, the amplitude of displacement at the fatigue crack tip as a function of cycle remains unchanged for the un-ruptured specimen tested under a low applied stress level and decreases gradually for the ruptured specimen tested under a high applied stress level. The gradual decrease suggests that structural relaxation-induced hardening occurs in the vicinity of a fatigue crack tip.

8. Corrosion resistance. It is known that amorphous type alloys without grain boundaries exhibit high corrosion resistance when they contain corrosion-resistant elements such as Cr, Mo, Nb, Ta and P.⁵⁶⁾ However, these corrosion-resistant alloys had the disadvantages of low glass-forming ability and extreme brittleness. The low glass-forming ability resulted in the limitation of

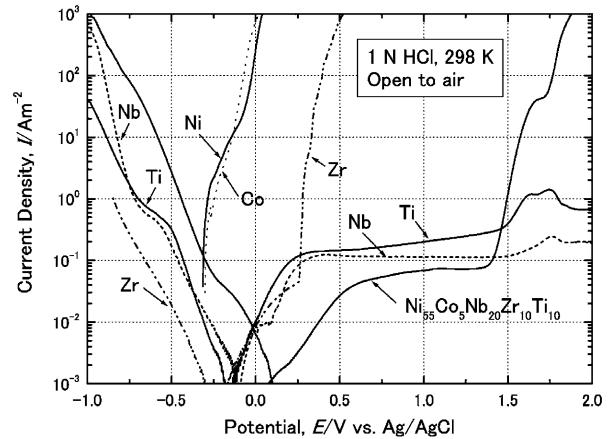


Fig. 17. Cathodic/anodic polarization curves of $\text{Ni}_{55}\text{Co}_5\text{Nb}_{20}\text{Zr}_{10}\text{Ti}_{10}$ glassy alloy in 1N HCl solution open to air at 298 K.

amorphous alloy thickness to less than about 0.03 mm. Bulk glassy alloys in metal-metal system without metal-loids are expected to simultaneously possess high glass-forming ability and engineering properties that are in demand for useful applications. It is important to develop glassy alloys simultaneously exhibiting high glass-forming ability, good mechanical properties and high corrosion resistance. Newly developed Ni-based bulk glassy alloys with high tensile strength and good ductility exhibited high corrosion resistance in various chemical solutions such as 1N HCl, 6N HCl, 1N H_2SO_4 and 3% NaCl.^{57,58)} Figure 17 shows cathode/anode polarization curves in 1N HCl at 298 K for a $\text{Ni}_{55}\text{Co}_5\text{Nb}_{20}\text{Zr}_{10}\text{Ti}_{10}$ glassy alloy rod with a diameter of 3 mm. The Ni-based bulk glassy alloy has a higher pitting corrosion potential and a much lower anodic current density than pure metals such as Ni, Co, Ti, Zr and Nb. The addition of Ta to the Ni-based glassy alloy causes a further enhancement of corrosion resistance. It has also been recognized that the addition of Nb or Ta to $(\text{Cu}_{0.6}\text{Hf}_{0.25}\text{Ti}_{0.15})_{100-x}\text{M}_x$ ($\text{M} = \text{Nb}$ or Ta) bulk glassy alloys drastically increases their corrosion resistance through an increase in the pitting corrosion potential and a decrease in the anode current density.⁵⁹⁾ We could not detect any weight loss for the Cu-based glassy alloys containing 8 at%Nb in 1N HCl and 4 at%Nb in 3% NaCl. The simultaneous achievement of high strength, high ductility, high bulk glass-forming ability and high corrosion resistance had not previously been obtained for any kind of amorphous alloys, and this is encouraging for the future development of the Ni- and Cu-based bulk glassy

alloys as new types of functional materials based on their chemical properties.

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