

# Research

## Advanced Materials and Materials Genome—Review

### Bulk Glassy Alloys: Historical Development and Current Research

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**ABSTRACT** This paper reviews the development of current research in bulk glassy alloys by focusing on the trigger point for the synthesis of the first bulk glassy alloys by the conventional mold casting method. This review covers the background, discovery, characteristics, and applications of bulk glassy alloys, as well as recent topics regarding them. Applications of bulk glassy alloys have been expanding, particularly for Fe-based bulk glassy alloys, due to their unique properties, high glass-forming ability, and low cost. In the near future, the engineering importance of bulk glassy alloys is expected to increase steadily, and continuous interest in these novel metallic materials for basic science research is anticipated.

**KEYWORDS** bulk glassy alloys, mold casting, metallic materials, structural relaxation

#### 1 Background and discovery

It is important to point out that the development of bulk glassy alloys was not intentional; back in the mid-1980s, no one believed that such alloys could exist. In fact, these new materials were created spontaneously during long-term basic studies on the structural relaxation of amorphous alloys. The first trigger for the discovery of bulk glassy alloys was the use of amorphous alloys with tiny glass-transition phenomenon for structural relaxation studies. These studies were carried out by examining changes in apparent specific heat and enthalpy with alloy composition, cooling rate, annealing, deformation, and preparation techniques through accurate differential scanning calorimetry (DSC) measurements [1–5].

In this series of structural relaxation studies, it was important to use amorphous alloys with a glass transition and supercooled liquid region before crystallization in order to obtain highly reliable data. Back in 1982, some noble metal base amorphous alloys, such as Pd-Ni-P, Pt-Ni-P, and Pd-Cu-Si systems, were known as metallic glasses with distinct glass transition and supercooled liquid regions [6–9]. We

studied the structural relaxation behaviors of Pd-Ni-P, Pt-Ni-P, and Pd-Cu-Si glassy alloy wires with different diameters of 80–250  $\mu\text{m}$ , produced by the in-rotating-water melt spinning method, and Pd- and Pt-based glassy alloy rods with diameters of 1–2 mm, prepared by water quenching. We compared these with glassy alloy ribbons of 20–40  $\mu\text{m}$  in thickness that were produced by the melt spinning method [9, 10]. Based on these systematic measurements, we reported that the structural relaxation behavior was strongly dependent on alloy composition, preparation technique, and cooling condition.

The relaxation study was subsequently shifted to focus on Fe-, Co-, Ni-, and Zr-Cu-based amorphous alloys, which were regarded as more important engineering materials [1, 2, 7, 11]. The Fe-based alloys used for DSC measurement in those days were mainly an amorphous material, without a glass transition and supercooled liquid region. With the aim of obtaining more reliable quantitative data on structural relaxation, we began to search for amorphous alloys with faint glass transition behavior in Fe-, Co-, Ni-, and Zr-Cu-based systems around 1983.

As an alternative research field, we found Al-based amorphous alloys with high strength, good bending ductility, and faint glass transition in Al-Ln-LTM (where Ln indicates any lanthanide metal, and LTM = Fe, Co, Ni, Cu) [12, 13] and Al-Zr-LTM [11, 14] systems in 1987. Several months later, Professor Poon's group also reported high-strength Al-based amorphous alloys in the same Al-Ln-LTM system [15]. Since these findings, several research groups have continuously developed new Al-based amorphous alloys with distinct glass transition and supercooled liquid for many years [16–18]. In addition, researchers have carried out a number of studies on various fundamental properties of these materials, including thermal stability and crystallization behavior [19, 20].

It is obvious that the three base elements in the Al-based glassy alloys Al-Ln-LTM and Al-Zr-LTM are the same as those in the Ln-based bulk glassy alloys in the Ln-Al-LTM system and the Zr-based bulk glassy alloys in the Zr-Al-LTM system, respectively [21, 22]. Therefore, we extended our

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study to include alloys from these systems as well.

The alloy composition region where glass transition was observed was extended significantly in Ln-rich Ln-Al-LTM and Zr-rich Zr-Al-LTM alloys, as compared to Al-rich Al-Ln-LTM and Al-Zr-LTM alloys, which agrees with typical bulk glassy alloy systems used today. As a result, we succeeded for the first time in producing La-Al-(Ni, Cu) [23] and Zr-Al-(Ni, Cu) [24, 25] multicomponent amorphous alloys with distinct glass transition and a large supercooled liquid region above 80 K. Subsequently, by utilizing the highly stabilized supercooled liquid, we tried to prepare bulk glassy alloys by copper-mold casting, water quenching, and die casting. As a result, we succeeded in forming bulk glassy alloys in La-Al-(Ni, Cu) systems by a casting process using copper molds in 1989. The success of these bulk glassy alloys in the La-Al-Ni system [26]—followed by the formation of Mg-Ln-LTM bulk glassy alloys with diameters up to 4 mm by injection copper-mold casting [27] and with diameters near 1 cm by high-pressure die casting [28]—led to the opening up of a bulk glassy alloy age in conjunction with the advent of a copper-mold casting age.

In 1990, we found that glassy alloys in the Zr-Al-Ni-Cu system exhibit a large supercooled liquid above 100 K [29]. These alloys can be made in the form of arc-melted buttons with a mass of about 25 g and a height of 7–8 mm by melting and cooling the alloys on a water-cooled copper hearth [22, 30]. Over several years of development starting in 1989, we found a large number of bulk glassy alloys in more than 100 kinds of alloy systems including Ln-Al-(Ni, Cu), Mg-Ln-(Ni, Cu), and Zr-Al-(Ni, Cu) systems. We also demonstrated that these glassy alloys can be deformed with a large elongation over  $10^{4\%}$  by viscous flow in the supercooled liquid region [14, 23, 30]. In addition, we reported that these bulk glassy alloys exhibit high yield and fracture strength, high hardness, large elastic elongation, and low Young's modulus; and that the differences in fracture strength, Young's modulus, and elastic elongation between glassy alloys and crystalline alloys are as large as about three times [30]. For six years, until 1992, all the data on bulk glassy alloys and their fundamental properties was reported only by our group; no other research groups reported data on bulk glassy alloys during this period. Therefore, in those days we were suspicious about the academic importance and future prospect of bulk glassy alloys, stabilized metallic supercooled liquid, and multicomponent-type new alloys.

## 2 Development and characteristics

Finally, in 1993, Johnson's group reported that a bulk glassy alloy rod with a diameter of 12 mm had been formed in the Zr-Ti-Be-Ni-Cu system by water quenching [31]. Since then, studies on stabilized supercooled liquid and bulk glassy alloys attracted rapidly increasing interest. Over the next 20 years, stabilized supercooled liquids and bulk glassy alloys became the most active research field in materials science and engineering, including physics and chemistry. Researchers are attracted to this wide academic field due to the strangeness of the high stability of supercooled liquids against crys-

tallization for metallic alloys in which constituent elements can be easily moved in the high temperature region, as well as the unique fundamental and engineering properties of these substances, which differ significantly from those for crystalline alloys.

Here, I list some features of crucial findings on bulk glassy alloys over the last 20 years [30, 32]: ① the proposal of an alloy component rule leading to the stabilization of supercooled liquid for metallic alloys, ② the formation of bulk glassy alloys with centimeter-class diameters for Zr-Al-(Ni, Cu) [33–35] and Zr-Ti-Be-Ni-Cu [31] systems in 1993–1995, ③ the first synthesis of ferromagnetic Fe-(Al, Ga)-(P, Si)-(B, C) bulk glassy alloys in 1995–1996 [36, 37], ④ the effectiveness of adding minor elements without any compound-forming ability to the main solvent element in order to increase the glass-forming ability [38–40], ⑤ the formation of Cu-based bulk glassy alloys in Cu-Zr-(Ti, Hf) and Cu-Zr-Al-(Ti, Hf) systems [41, 42], ⑥ the formation of Cu-Zr-Al-Ag bulk glassy alloys with centimeter-class diameters [43], ⑦ the formation of Fe-Cr-Mo-B-C bulk glassy alloys with high strength and high corrosion resistance [44, 45], ⑧ the formation of Ti-based bulk glassy alloys in an Ni-free Ti-Zr-Ni-Pd system with centimeter-class diameters [46] and good biocompatibility [47], ⑨ the formation of Fe-Cr-Mo-C-B-Ln bulk glassy alloys with centimeter-class diameters [48–51], ⑩ the formation of Co-based bulk glassy alloys with nearly zero saturation magnetization and high effective permeability in the Co-Fe-B-Si-Nb system [52], ⑪ the formation of Ni-based bulk glassy alloys with centimeter-class diameters in the Ni-Pd-P-B system [53], ⑫ the formation of Fe-(Si, P)-(B, C) bulk glassy alloys with good soft magnetic properties and high saturation magnetization [54], ⑬ the formation of Mg-based [55] and Ln-based [56] bulk glassy alloys with centimeter-class diameters, ⑭ the production of Pd-Ni-Cu-P bulk glassy alloys with the largest diameter of 72–80 mm [57, 58], ⑮ the production of a Zr-Cu-Al-Ag-Pd-Be bulk glassy alloy with a diameter of 73 mm [59], ⑯ the production of ultrahigh-strength bulk glassy alloys with fracture strengths exceeding 5000 MPa for the Co-Fe-Ta-B-based system [60, 61], and ⑰ the formation of Co-Fe-Nb-Dy-B bulk glassy alloys with a large supercooled liquid region exceeding 130 K and a large magneto-impedance effect [62] (as well as the formation of Fe-Si-Nb-Dy-B bulk glassy alloys with a large supercooled liquid region exceeding 100 K and a large giant magneto-impedance effect [63]).

In addition to bulk glassy single-phase alloys, various kinds of mixed-phase bulk alloys consisting of nanocrystalline [64], nanoquasicrystalline [65], and dendritic crystal [66, 67] dispersion phases embedded in a glassy matrix have been prepared by intentionally deviating the alloy composition from the optimum composition where the largest bulk glassy alloys are obtained; the ductility of these mixed-phase alloys is significantly better than that of single-phase alloys. The strength of mixed-phase alloys can also be increased by the dispersion of the nanocrystalline and nanoquasicrystalline phases, although the dispersion of the dendrite phase causes a decrease in yield strength owing to the large size. The dispersion effect of ZrC, TaC, and WC particles on the

mechanical properties of bulk glassy alloys has also been examined for a Zr-based system [68].

The characteristics of bulk glassy alloys as compared to crystalline alloys are: ① higher yield and fracture strength, ② larger elastic elongation, ③ lower Young's modulus, ④ higher fatigue strength, ⑤ similarly high fracture toughness, ⑥ higher corrosion resistance, ⑦ higher precise castability, ⑧ much better viscous flow workability, ⑨ better nanoscale imprintability, ⑩ higher surface smoothness, ⑪ higher light reflectivity, ⑫ similarly good low-temperature ductility, ⑬ higher resistance to irradiation-induced embrittlement, ⑭ higher machinability, and ⑮ lower sensibility to characteristics caused by the dissolution of impure elements [30, 32]. One can also utilize various joining methods for bulk glassy alloys such as electron-beam welding, laser welding, friction welding, and liquid joining [69].

Techniques and processes for producing bulk glassy alloys have also been developed in conjunction with findings on alloy composition and unique characteristics of bulk glassy alloys [69]. The production methods reported to date include injection casting, suction casting, squeeze casting, tilt casting, cap casting, water quenching, twin-roller casting, unidirectional casting, high-velocity spray deposition, warm pressing, and warm rolling [69]. Injection casting and suction casting are regarded as the most popular casting methods.

Centimeter-class bulk glassy alloys have been prepared in almost all bulk glassy alloy systems. The maximum diameters reported to date are 20–73 mm for Zr-based alloys, 12 mm for Ti-based alloys, 15–18 mm for non-ferromagnetic Fe- and Fe-Co-based alloys, 80 mm for Pd-based alloys, 40 mm for Pt-based alloys, 30 mm for Cu-Zr-based alloys, 20 mm for Ni-based alloys, 15 mm for Mg-based alloys and 25 mm for Ln-based alloys. A diameter of 5 mm has been achieved for ferromagnetic Fe-based bulk glassy alloys, which can be regarded as one of the most important engineering materials, and a diameter of 0.8–1 mm for Al-based glassy alloys [70, 71]. If a new bulk glassy alloy composition can be developed with a larger diameter than Fe- and Al-based alloys, but in conjunction with their unique characteristics, the engineering value of bulk glassy alloys is expected to increase significantly.

### 3 Applications

In this section, I summarize the past and present-day applications of bulk glassy alloys. The first successful application was the use of Zr-Al-Ni-Cu [72] and Zr-Ti-Be-Ni-Cu [73] bulk glassy alloys for golf clubs (drivers, irons, and putters) starting in the mid-1990s and continuing for about a decade. The advantages of bulk glassy alloys are: ① high yield and fracture strength, ② high fatigue strength, ③ high fracture toughness, ④ large elastic elongation, ⑤ high corrosion resistance, ⑥ high glass-forming ability, ⑦ good castability, and ⑧ good machinability. Due to the advantageous mechanical properties and formability of the material, a driver club made of Zr-based bulk glassy alloys has a longer flight distance, a longer impacting time, and feels good to use because of the

high repulsion energy resulting from the large elastic elongation. In Japan, no difficulties were encountered in the application of golf clubs made with Zr-Al-Ni-Cu bulk glassy alloys, indicating a high reliability of the product. Unfortunately, however, the application of Zr-based bulk glassy alloys to golf clubs was stopped around 2005 because the repulsion ratio of the glassy alloy clubs was too high to lie within golfing equipment limitation rules.

Other applications of bulk metallic glasses (BMGs) include: baseball bats; tennis racket frames; casings for cell phones; watch and electric magnetic devices; connecting parts for optical fibers; optical mirrors; ornamental parts; micro-gear motor parts; magnetic inductor cores; choke coil cores; electric-magnetic shielding; surface coating; magnetic rotating sensors; magnetic torque sensors; machinery parts; and antennas [32, 33, 74].

Among these applications, magnetic inductor cores, choke coil cores, surface coating, and magnetic torque sensors seem to be of particular importance because they are produced in much greater quantities than the other applications. Two materials are used for induction cores: Licalloy™ [75], based on Fe-Cr-(P, Si)-(B, C), and SENNTIX [76], based on Fe-Cr-Nb-(P, Si)-B. These inductor cores are made through the following simple process: ① the mass production of glassy alloy powders by water atomization, ② the blending of glassy alloy powders and polymer resin, ③ the formation of thin resin film on the powder surface, ④ the formation of consolidated cores by cold pressing, and ⑤ the annealing of the core to reduce internal stress and to strengthen contacted and bonding states among powders. The consolidated powder cores exhibit good high-frequency permeability in a high-frequency range up to the MHz region, although their saturation magnetization values are not always high. Due to their good high-frequency permeability, which cannot be obtained for other soft magnetic materials such as Sendust and Permalloy, Licalloy™ magnetic cores have been used as various kinds of inductors since 2004, and SENNTIX cores since 2009. Production quantities of these products are estimated to reach tens of million pieces per year.

It is important to point out the reason why Fe-based bulk glassy alloys have succeeded in gaining valuable mass applications. This reason is their high glass-forming ability, which enables the mass production of glassy alloy powders over the whole particle size range, even when using the simple mass-production process of water atomization. When the same water atomization process is applied to ordinary Fe-based amorphous alloys such as Fe-Si-B and Fe-P-B systems, the resulting powders are composed of amorphous and crystalline mixed phases and hence do not have good soft magnetic properties.

In addition to the mass production application of soft magnetic Fe-based glassy alloy consolidated cores, non-ferromagnetic Fe-based bulk glassy alloys in the Fe-Cr-Mo-C-B system have been used as coating materials with high hardness, high wear resistance, high corrosion resistance, and high heat-resistant strength [77, 78]. These rather thick Fe-based glassy alloy plates with wide surface areas are produced from Fe-based bulk glassy alloys using the high-velocity supercooled



liquid spray-coating technique. The same high-velocity spray-coating technique has also been used to form a soft magnetic Fe-based glassy alloy layer on various kinds of rotators made of ordinary metallic alloys, giving this material applications for torque sensors and rotation sensors [79].

## 4 Recent topics

In this section, I discuss recent topics involving bulk glassy alloys, including ductile Fe-based bulk glassy alloys, high entropy bulk glassy alloys, and the stable structural relaxation of bulk glassy alloys.

### 4.1 Ductile Fe-based bulk glassy alloys

Various kinds of Fe-based bulk glassy alloys have been developed since the first synthesis in 1995 [34], and have been reported to exhibit high fracture strength (3000–4500 MPa), high Vickers hardness (900–1200), and high Young's modulus (190–210 GPa) in the absence of distinct plastic strain at room temperature [80, 81]. In addition, their fracture toughness values are under  $5 \text{ MPa}\cdot\text{m}^{1/2}$ . The lack of both ductility and fracture toughness has prevented the application of Fe-based bulk glassy alloys as three-dimensional structural materials. Therefore, there has been a strong demand to develop Fe-based bulk glassy alloys with high strength, high ductility, and high fracture toughness. Although a number of studies on the development of ductile Fe-based bulk glassy alloys have been carried out in the last two decades, little has been reported on the synthesis of highly ductile Fe-based bulk glassy alloys.

However, Fe-based bulk glassy alloys of 1–2 mm in diameter in the Fe-Ni-P-C system were prepared by water quenching and exhibited a high fracture strength of 2000–2500 MPa and compressive plastic strains above 10% [82]. Very recently, it was also found that Fe-based nanocrystalline (bcc + amorphous) ribbons in the Fe-Co-B system exhibit good bending ductility as well as high saturation magnetization (above 1.7 T). Further progress in alloy designs on the basis of this new data and knowledge is expected to enable the development of various Fe-based bulk glassy alloys with high ductility in conjunction with other useful characteristics.

### 4.2 High entropy bulk glassy alloys

It is generally known that the glass-forming ability of an alloy is enhanced with increases in configuration entropy, from the thermodynamics of nonequilibrium phase formation from liquid. Based on this concept, a  $\text{Ti}_{20}\text{Zr}_{20}\text{Hf}_{20}\text{Cu}_{20}\text{Ni}_{20}$  bulk glassy alloy with an equal atomic composition was formed and its fundamental properties were examined [83]. However, no further report on the formation of a bulk glassy alloy with an equal atomic composition was made in the 10 years following this study. On the other hand, a recent study on crystalline high entropy (HE) alloys has attracted significant and increasing interest [84]. It was demonstrated that the multiplication of alloy components causes the formation of a supersaturated face-centered-cubic (fcc) or body-centered-cubic (bcc) solid solution with fine grain sizes, and that these solid solutions exhibit low diffusivity of the constituent ele-

ments as well as high elevated-temperature strength.

Very recently, some data on HE bulk glassy alloys was presented for the HE  $\text{Pd}_{20}\text{Pt}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{P}_{20}$  [85] and pseudo-HE  $\text{Zr}_{55}\text{Al}_{10}\text{Fe}_6\text{Co}_6\text{Ni}_6\text{Cu}_6\text{Ag}_5\text{Pd}_6$  [86] alloys. The pseudo-HE Zr-based bulk glassy alloy has a diameter of 6 mm, a higher crystal nucleation rate, and a much lower crystal growth rate in the crystallization reaction as compared with the ordinary  $\text{Zr}_{55}\text{Al}_{10}\text{Ni}_5\text{Cu}_{30}$  bulk glassy alloy. Even after a long time annealing around the crystallization temperature, no distinct grain growth of a crystalline phase was recognized, resulting in a mixed structure of nanoscale crystalline phase embedded in glassy matrix. It has thus been clarified that increased multiplication of alloy components causes the suppression of atomic rearrangement, resulting in an increase in the stability of the glassy phase through a remarkable decrease in growth rate. The subsequent systematic and detailed study on high-order multicomponent bulk glassy alloys is expected to produce more functional bulk glassy alloys with novel characteristics.

### 4.3 Stable structural relaxation

A glass transition and a supercooled liquid region are always observed before crystallization for bulk glassy alloys, while amorphous alloys crystallize without these regions. The high stability of the supercooled liquid, leading to the appearance of a wide supercooled liquid region, enables the formation of bulk glassy alloys. High stability of the supercooled liquid is ordinarily recognized for alloys with the following three component rules: ① They are multicomponent, consisting of three elements or more; ② they have significant atomic size mismatches (above 12%) among the main constituent elements; and ③ they have negative heats of mixing [22, 32]. The unique medium-range network atomic configurations that can spontaneously form in a supercooled liquid with the three component rules can suppress the long-range rearrangement that is necessary for the progress of crystallization, resulting in the formation of bulk glassy alloys. On the other hand, amorphous alloys do not have special medium-range atomic configurations and this lack results in the direct crystallization of the amorphous phase without a glass transition and a supercooled liquid region. In order to suppress the crystallization reaction of a supercooled liquid, very high cooling rates are required to form an amorphous phase. Little is known about the influence of such significant differences in atomic configurations on the structural relaxation behavior.

Very recently, we carried out studies on the structural relaxation behavior upon annealing for typical BMGs such as Zr-Al-Ni-Cu, Zr-Al-Cu, Ni-Pd-P-B, and Pd-Ni-P-B systems in comparison with numerous data on structural relaxation for amorphous alloys. Although the number of metallic elements for bulk glassy alloys is larger than that for amorphous alloys, the structural relaxation of Zr-based bulk glassy alloys takes place in a monotonous mode where the structural relaxation reaction increases gradually with increasing annealing temperature and does not show the two-stage structural relaxation behavior that is common for metal-metalloid amorphous alloys containing two metallic elements and for

metal-metal Zr-Cu-Ni and Zr-Cu-Co alloys. The single-stage relaxation mode for bulk glassy alloys is due to the more homogeneous medium-range network atomic configurations, in agreement with the mechanism for high stability of the supercooled liquid. A systematic study on structural relaxation for various types of bulk glassy alloys will shed some light on the differences in the structures and atomic mobility of bulk glassy alloys and amorphous alloys.

## 5 Conclusions

Although the research field of bulk glassy alloys usually includes various kinds of composites such as nanocrystal + glass, nanoquasicrystal + glass, dendrite + glass, and compound + glass, this review focuses on bulk glassy alloys without an intentionally dispersed second phase. For about 25 years, since the first synthesis of bulk glassy alloys in 1989, Japan has been the most active country in the bulk glassy alloy field; until 2007, Japan produced the largest number of published papers in this field. Today, however, the countries with the largest number of papers published in this field are China, the US, Germany, and then Japan. In recent years, research activity in this field has increased rapidly in China and gradually in the US and Germany. This steady increase in research activity in countries other than Japan is expected to cause continuous development of bulk glassy alloys as basic science and engineering materials, in contrast to the nearly saturated development of crystalline bulk metals.

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