Research
Engineering 2015, 1(2): 185–191
DOI 10.15302/J-ENG-2015038

Advanced Materials and Materials Genome—Review

Bulk Glassy Alloys: Historical Development and Current Research

Akihisa Inoue[1,2]

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 μm, 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 μm 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

---

[1] Tohoku University, Sendai 980-8577, Japan; [2] International Institute of Green Materials, Josai International University, Togane 283-8555, Japan
E-mail: ainoue@imr.tohoku.ac.jp

Received 18 June 2015; received in revised form 28 June 2015; accepted 30 June 2015

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 crystallization 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