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Development and applications of Fe- and Co-based bulk glassy alloys and their prospects

A. Inoue [a,b,d,*], F.L. Kong [a], Q.K. Man [b], B.L. Shen [c], R.W. Li [b], F. Al-Marzouki [d]

[a] International Institute of Green Materials, Josai International University, Togane 283-8555, Japan
[b] Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, China
[c] School of Materials Science and Engineering, Southeast University, Nanjing 211189, China
[d] Department of Physics, King Abdulaziz University, Jeddah 22254, Saudi Arabia

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ABSTRACT

Glassy type metallic alloys exhibit unique characteristics which cannot be obtained for conventional amorphous alloys. For the last more than two decades, a number of bulk glassy alloy (BGA) systems have been developed and centimeter-class BGAs have been prepared in almost all alloy systems. Among them, Fe- and Co-based BGAs have attracted much attention and have been commercialized in various fields. This paper reviews recent developments and applications of Fe- and Co-based BGAs and their future prospects are also described.

1. Introduction

Around 1990, metallic glassy alloys in bulk form were found to be formed in La- and Mg-based systems by copper mold casting [1,2]. Subsequently, arc-melted Zr-based alloy ingots, just cooled on water-cooled copper hearth, were found to keep a glassy structure [3]. The ingot showed very shiny surface luster and had good ductility which could not be cracked by hitting with a hammer. Since the findings of these new phenomena, a great number of studies were carried out with the aims of searching new BGA systems, clarifying the fundamental properties including glass-forming ability (GFA), glassy structure and finding novel application fields [4–6]. As one of important results obtained for the last two decades, the lowest cooling rate for glass formation reaches 0.067 K/s, which is about 10^8 times smaller than that for ordinary amorphous alloys requiring melt quenching [7]. It is recognized that the thermal stability of supercooled liquid against crystallization increases dramatically and the enhanced stability has opened a new research field of metallic liquids. The maximum diameter (D_m) reaches about 8 cm for Pd–Cu–Ni–P system [8], 3 cm for Zr–Al–Ni–Cu [9,10], 5 cm for Zr–Ti–Be–Ni–Cu [11], 1.5–3 cm for Ni–Pd–P–B [12], and Cu–Zr–Al–Ag–Pd [13] and 7.3 cm for Cu–Zr–Al–Ag–Be [14]. In addition, glassy alloy plates with uniform thickness of 0.3–1 mm and large surface area aspect ratios have been produced as secondary forming materials [15]. Glassy alloy balls with diameters of 2–10 mm are also available for the Zr- and Cu-based alloys [5].

The significant developments of BGAs have enabled the utilization of new bulk metallic materials consisting of a glassy structure since 1990, in addition to conventional bulk metallic crystalline materials which have been used by human beings for several thousand years. Table 1 summarizes the application fields that have been developed at present for glassy type alloys in Japan. The fields have been extended very widely.

Nowadays, sustainable developments have been desired to create low-carbon, resource-circulating and nature harmonious societies. We have been requested to contribute to sustainable development and low-carbon society through the developments of highly functional Fe- and Co-based BGAs and their industrialization. This review focuses on soft magnetic Fe- and Co-based alloys belonging to bulk glassy, nanocrystalline and bulk nanocrystalline types.

2. Fe-based bulk glassy alloys

2.1. Alloy components

Looking at the development history of Fe-based amorphous and glassy alloys, the first amorphous phase was synthesized for Fe–P–C system in 1967 by Paul Duwez's group [15], followed by the formation and licence of Fe- and Co-based amorphous alloys by Allied Chemical Corporation in 1975 [16] and their commercialization in the early 1980s. Subsequently, the synthesis of Fe-based BGAs by copper mold casting was made for Fe–Al–Ga–P–C–B alloys with a large supercooled liquid region before crystallization by Inoue et al. in 1995 [17].

Table 2 summarizes typical Fe-based BGAs developed up to date. The alloys can be classified to ferromagnetic and paramagnetic types at room temperature. As the former type, one can see Fe–(Al, Ga)-metalloid (P, C, B, Si) [17], FeC20(Fe–C–Si)–B

* Corresponding author at: International Institute of Green Materials, Josai International University, Togane 283-8555, Japan. Tel.: +81 475 53 2166.
E-mail address: ainouebmg@yahoo.co.jp (A. Inoue).

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Table 1
Application fields for bulk glassy type alloys in Japan and their responding characteristic.

Application fields	Characteristic
Structural materials	High strength, high hardness, high fracture strength
Sensor materials	High magnetostriction, giant magneto-impedance effect
Spring materials	High fatigue strength
Sporting goods materials	High strength and large elastic elongation limit
Wear resistant coating materials	High wear resistance
Corrosion resistant materials	High corrosion resistance
Magnetic materials	Excellent soft-magnetic properties, high electrical resistivity
Micro-technology materials	Micro-formability, transferability
Nano-technology materials	Nanoscale imprintability
Data storage materials	
Biomedical materials	Biocompatibility, high wear and corrosion resistance
Fuel cell separator materials	

Table 2
Typical Fe-based bulk glassy alloys developed up to date.

Ferromagnetic alloys	Non-ferromagnetic alloys
Fe–(Al,Ga)–(P,C,B)	Fe–(Cr,Mo)–(C,B)
Fe–(P,Si)–(B,C)	(Fe,Ni)–(Cr,Mo)–(B,Si)
Fe–Ga–(P,C,B,Si)	Fe–(Cr,Mo)–(C,B)–Ln
Fe–(Cr,Mo)–(P,C,B,Si)	
Fe–(Zr,Hf,Nb)–B	
Fe–Co–Ln–B	
Fe–(Nb,Cr)–(B,Si)	
Fe–(Nb,Cr)–(P,B)	
Fe–(Zr,Hf,Nb)–B–Ln	

(Fe-metalloid) [18,19], Fe–LTM(Cr, Mo)-metalloid [20], Fe–ETM(Zr, Hf, Nb)-metalloid [21], Fe–LTM-metalloid–(Y, Ln) (Ln = lanthanide metal) [22] and Fe–ETM–(B, Si)–(Y, Ln) [23]. The latter type alloys are obtained for Fe–(Cr, Mo)–(C, B) [24], (Fe, Ni)–(Cr, Mo)–(B, Si) [25] and Fe–(Cr, Mo)–(B, C)–(Y, Ln) [26–28].

These new Fe-based BGAs have been developed on the basis of the following guidelines, i.e., (1) multicomponent systems consisting of three or more elements, (2) significant atomic size mismatches among the main elements, (3) many atomic pairs with negative heats of mixing and (4) minor addition of Al, Ga, ETM, LTM and Y or Ln for enhancement of the three component rules.

2.2. Concrete results

2.2.1. Fe–(Ga, Mo)–(P, C, B, Si) alloy series

Glassy alloy rods of 2.5 mm in diameter are formed for $Fe_{77}Ga_3P_{9.5}C_4B_4Si_{2.5}$, showing a supercooled temperature interval of 45 K, by copper mold casting [29]. The bulk GFA exhibits rather high saturation magnetization (B_s) of 1.4 T and low coercive force (H_c) of 3 A/m. The replacement of Ga by Mo causes an increase of D_m to 4 mm for $Fe_{75}Mo_4P_{10}C_4B_4Si_3$ [30]. This alloy exhibits good combination properties, i.e., 1.27 T for B_s, 1.5 A/m for H_c and 25,230 for effective permeability (μ_e) at 1 kHz and 1 A/m. By partial replacement of Fe with Co, the D_m increases further to 5 mm for $Fe_{66}Co_{10}Mo_{3.5}P_{10}C_4B_4Si_{2.5}$ [31], in conjunction with good soft magnetic properties of 1.23 T for B_s, 1.0 A/m for H_c and 4.0×10^5 for maximum permeability (μ_{max}) [31].

2.2.2. Fe–Co–Ni–B–Si–Nb alloy series

The addition of small amounts (2–4 at.%) of Nb to Fe–Si–B alloys was found to cause the change from amorphous to glassy type with glass transition, followed by supercooled liquid region over the whole composition range [32]. BGAs were formed over the whole composition range of $[(Fe_{1-x-y}Co_xNi_y)_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ and their D_m was 5 mm for $[(Fe_{0.5}Co_{0.5})_{75}B_{20}Si_5]_{96}Nb_4$ alloy [33]. The D_m for the $[(Fe_{0.5}Co_{0.5})_{75}B_{20}Si_5]_{96}Nb_4$ alloy increases to 7.7 mm by B_2O_3 flux melting [34]. The Fe-rich alloy exhibits rather high B_s of over 1.3 T [35], while the Co-rich alloy has low H_c below 1 A/m because of very low saturated magnetostriction (λ_s) of 5×10^{-7} under the field of 250 kA/m. The nearly zero λ_s alloy exhibits high μ_e exceeding largely 10^4 in a wide frequency range up to at least 100 kHz, as exemplified in Fig. 1 [36]. This good high-frequency permeability characteristic appears to be maintained up to several MHz range.

2.2.3. Fe–Mo–Si–B–P alloy series

For $Fe_{76}Si_{9-x}B_{10}P_5Mo_x$ series, the D_m and B_s were, respectively, 3 mm and 1.45 T for x = 1, 3.5 mm and 1.40 T for x = 2 [37]. Besides, the alloys with 1% and 2% Mo show appreciable plastic strains in conjunction with fracture surface consisting of several step zones. Even for the Mo-free Fe–Si–B–P alloys, BGAs were obtained in the diameter range up to 2.5 mm and the $Fe_{79}Si_6B_{10}P_5$ alloy exhibits distinct plastic strain of 1.1% [38]. The Fe–Si–B–P alloys exhibit very high B_s exceeding 1.6 T and the maximum value reaches 1.62 T for $Fe_{80}Si_5B_{10}P_5$ [39]. The Fe–Si–B–P glassy alloys also exhibit low H_c of 1.6–1.9 A/m and high μ_e of 16,500–17,200 at 1 kHz. It is noticed that high B_s exceeding 1.6 T in conjunction with good soft magnetic properties is obtained for Fe-metalloid alloy system.

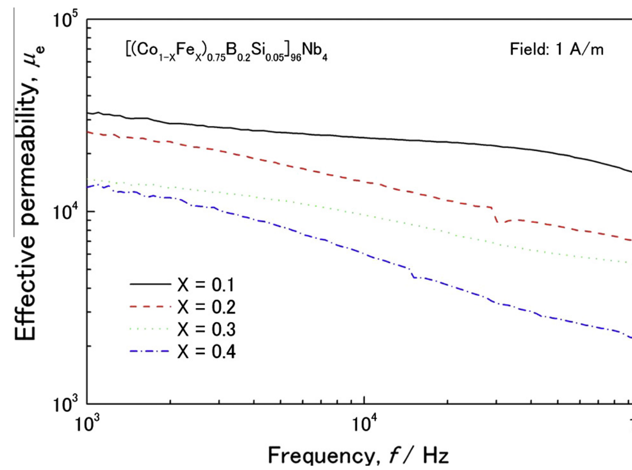

Fig. 1. Effective permeability as a function of applied field frequency for the $[(Co_{1-x}Fe_x)_{0.75}B_{0.2}Si_{0.05}]_{96}Nb_4$ (x = 0.1, 0.2, 0.3, and 0.4) glassy alloys annealed for 300 s at temperature of T_g−50 K.

2.2.4. Fe–Dy–B–Si–Nb alloy series

The influence of Ln addition on GFA, thermal stability and soft magnetic properties was examined for Fe–Dy–B–Si–Nb alloy series [40]. The 4%Dy-containing alloy shows a D_m of 4 mm and very large λ_s of 65×10^{-6} which are attractive for application to a sensitive magnetostriction sensor.

3. Features of Fe-based bulk glassy alloys

Fe-based BGAs possess unique features of lower H_c and higher electrical resistivity which have not been obtained for amorphous and nanocrystalline Fe-based alloys [41]. The lower H_c has been thought to originate from the lower internal stress on the basis of the relation that H_c is dominated by some factors such as thickness of domain wall, B_s, anisotropy constant and internal stress [42]. With the aim of investigating the presumption, a number of data for BGAs and amorphous alloys were re-plotted in the relation between H_c and the ratio of λ_s to B_s [43]. In the relationship, the data has a linear relation and its slope is much smaller for the BGAs than for the amorphous alloys. The slope corresponds to the volume and density of internal defects in the glassy and amorphous alloys. The smaller slope implies that the BGAs include considerably lower