

Bulk Metallic Glass Composites

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Metallic glasses have attracted considerable attention due to their unique properties. The recent discovery of new glass-forming compositions makes it possible to produce metallic glasses in bulk shapes. Bulk metallic glasses offer an opportunity to revolutionize the field of structural materials with combinations of strength, elastic limit, toughness, wear resistance and corrosion resistance. The main current technical barrier is their limited ductility. Forming a composite containing ductile crystal phase in a bulk metallic glass matrix has been proven as an effective approach to increase their ductility. Three types of bulk metallic glass composites are discussed: extrinsic composites, *in-situ* composites and nanocrystalline composites. The paper also lists the key issues in the development of bulk metallic glass composites.

KEY WORDS: Metallic glasses; Bulk metallic glasses; Composites; Microstructure; Mechanical properties

1. Introduction

Amorphous alloys or metallic glasses have attracted considerable attention due to their often unique properties, such as mechanical, magnetic, electronic, chemical, optical and other properties. These properties make them of great interest in fundamental studies in solid state physics and very useful for application. In the last two decades metallic glasses have regained more interest due to the discovery of new glass-forming compositions that have a critical cooling rate of less than 100 K/s and can be made glassy in bulk shapes. The availability of bulk metallic glasses opens the materials being used for engineering applications. They offer an opportunity to revolutionize the field of structural materials with combinations of strength, elastic limit, toughness, wear resistance and corrosion resistance.

2. Metallic Glasses

When a conventional metal or alloy cools from the liquid melt, equilibrium is reached when it solidifies into the lowest energy state structure, *i.e.* a crystalline lattice. Most metals crystallize at a temperature just below the melting point in microseconds during solidification. But rather than forming a perfect single crystal, most metals are polycrystalline, with grains of varying shapes and sizes. Grain boundaries and crystal defects represent weak spots of less than optimal atomic packing, where fracture can form and corrosion often starts. Misaligned planes of atoms can easily slip past each other under sufficient stress and heat, allowing dislocations to move. As a result, metals have a much lower strength than their theoretical maximum^[1]. In contrast, if a metal alloy has very slow crystal nucleation and growth kinetics or solidifies at a very high cooling rate, the liquid melt may be frozen as a vitreous solid without crystallization. The atoms retain an amorphous structure, *i.e.* random packing with no long-range order. This material exhibits many different properties.

The first metallic glass was reported in 1960^[2]. Duwez discovered that at a very high cooling rate of 10^6 K/s, $\text{Au}_{80}\text{Si}_{20}$ melt does not have enough time for crystal nucleation and solidifies as a metallic glass. Later on Turnbull's group discovered that Pd-Si and Pd-Cu-Si systems can also form metallic glass at a certain critical cooling rate^[3,4]. The research on metallic glasses gained momentum in early 1970's when Allied Chemical Corporation developed a continuous melt spinning method. Molten metal is poured onto a spinning casting wheel to achieve high cooling rate and produce a continuous ribbon. Metallic glass ribbon could then be produced on a commercial scale for magnetic applications. However, the requirement for high cooling rate still means that metallic glasses can only be produced in very thin shapes, which precludes these materials for any structural applications.

3. Bulk Metallic Glasses

Extensive research has been devoted to increasing the critical casting thickness of metallic glasses. The effort has focused on two areas. One is to develop alloy systems that exhibit high resistance to crystallization. In 1969, Chen and Turnbull formed a metallic glass with a diameter of 0.5 mm in ternary Pd-Cu-Si alloys^[4]. In 1974, Chen obtained a critical casting thickness of 1 mm in Pd-Ni-P alloys^[5] and a slightly greater thickness with Au-Pb-Sb in 1982^[6]. The other development area is to improve the processing method to suppress heterogeneous nucleation in the melt. Beginning in 1982, Turnbull, Drehman, Kui, Greer, and other collaborators used a boron oxide flux to dissolve heterogeneous nucleants into a glassy surface coating along with heating and cooling cycles to poison the nucleants^[7,8]. They increased the critical casting thickness to 10 mm in $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, the first bulk metallic glass (BMG).

A significant breakthrough was made in late 1980s. Inoue and his co-workers at Tohoku University, Japan investigated rare-earth materials with Al and ferrous metals. When studying rapid solidification in these systems, they found exceptional glass forming ability

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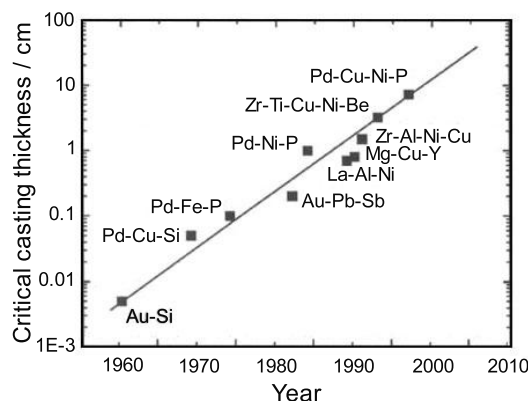


Fig.1 Critical casting thickness for glass formation of the corresponding alloy as a function of the year

in La-Al-Ni and La-Al-Cu alloys^[9,10]. Cylindrical samples with diameters of up to 5 mm or sheets with similar thickness were made fully glassy by casting $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ (or later $\text{La}_{55}\text{Al}_{25}\text{Ni}_{10}\text{Cu}_{10}$ up to 9 mm) into Cu mould. In 1991, the same group developed glassy Mg-Cu-Y and Mg-Ni-Y alloys with the largest glass-forming ability obtained in $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ ^[11]. Also the Inoue group developed a family of Zr-base Zr-Al-Ni-Cu alloys having a high glass-forming ability and thermal stability^[12]. They reported pseudo-ternary, quaternary and quinary materials of La-^[9,10,13], Mg-^[11], Zr-^[12,14], Pd-, Fe-base^[15] alloys that form metallic glass at cooling rates under 100 K/s with critical casting thickness greater than 10 mm. The results also illustrated that bulk metallic glass was far more common than previously thought and was not confined to exotic Pd-base alloys. This discovery means that metallic glasses can be produced in bulk shapes and in a wide range of alloys using conventional metallurgical casting methods. This breakthrough initiated the real start of the BMG technology.

Building on the Inoue work, Johnson from California Institute of Technology developed a family of quinary Zr-Ti-Cu-Ni-Be alloy in 1992^[16]. Alloy $(\text{Zr}_3\text{Ti})_{0.55}(\text{Cu}_5\text{Ni}_4)_{0.225}\text{Be}_{0.225}$, the alloy became known as Vitreloy 1 (Vit1), was developed as the first commercial BMG with a critical casting thickness of up to 100 mm and critical cooling rate for glass formation of 1 K/s. In the next ten years the properties of the alloy Vit1 were investigated extensively.

Figure 1 shows the critical casting thickness of the corresponding alloy as a function of the year^[17]. Starting with the first metallic glass developed by Duwez *et al.*, the critical casting thickness increased by more than three orders of magnitude in the last 40 years. Currently, USA, Europe, Japan, China and Russia are all exercising much effort in the development, application and commercialisation of BMGs, as well as in the scientific understanding of bulk amorphous formation. The US Department of Defense and the US Defense Advanced Research Project Agency each have US\$10 million research programs on BMGs. The Japanese New Energy and Industrial Technology Development Organisation has a similar size five-year program. Eu-

rope is currently running a RTN network program on BMG involving 11 research institutes. The company Liquid Metal Technology manufactures bulk metallic glass products for sporting goods, cases for electronic products, high performance springs, and medical devices.

4. Bulk Metallic Glass Composite

The mechanical properties of bulk metallic glasses are in many cases superior to their crystalline counterparts. The tensile strength of BMGs is very high ($\sigma_y > 2$ GPa, even 5 GPa was reported in some alloy systems), and the elastic strain limit is about 2%, much higher than common crystalline metallic alloys (<1%). BMGs also exhibit good fracture toughness ($> 55 \text{ MPa}\cdot\text{m}^{1/2}$) and very good hardness. Very high strength (also specific strength, σ/ρ) and high elastic limit make BMGs excellent candidates for structural applications. However, all the BMGs discovered so far exhibit very limited plasticity. Upon yielding, bulk metallic glasses often show plastic flow in absence of work-hardening and a tendency towards work-softening leads to shear localization with the formation of shear bands at 45° to the applied stress. The localization of plastic flow into shear bands leads to the lower resistance to shear band propagation^[18]. So that the materials usually fail catastrophically immediately after yield on one domain shear band. The low overall ductility largely limits industrial and structural applications for BMGs where reliability is critical (*e.g.* automotive and aerospace applications). To obtain more tolerance to damage and to enable structural use, ductility or plasticity need to be enhanced by controlling shear band formation and propagation.

In the last few years, attempts have been made to form bulk metallic glass matrix composites with a two-phase microstructure to improve the ductility of BMGs. Here the amorphous BMG acts as the matrix and a crystalline-phase reinforcement material acts as a "crack-stopper" by adding impediments to shear band propagation; the second phase could also act to initiate more shear bands, which would also distribute the deformation. The reinforcement can be either extrinsic (metal or ceramic fibres or particles) or intrinsic (*in-situ* precipitation of reinforcement from the melt during cooling or by partial crystallization through heat treatment). The two-phase BMG matrix composite combines the high strength of the monolithic BMG with the advantages of crystallinity: increased ductility, fracture toughness and plastic strain-to-failure.

4.1 Extrinsic BMG composites

In extrinsic BMG composites, external reinforcement will be included into BMG matrix. The appropriate sized reinforcement is introduced and dispersed in the BMG liquid melt before casting. There are two types of reinforcement: metal fibres and particles. The selection of reinforcement requires the fibres/particles to have high Young's modulus and

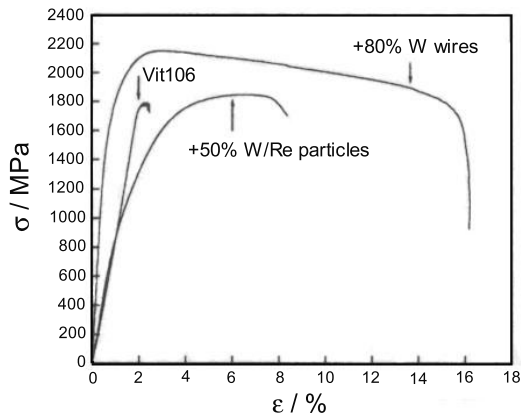


Fig.2 Compressive stress-strain curves of $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ (Vit106) bulk metallic glass and composites reinforced with tungsten fibre and mixed tungsten/rhenium particles (with given volume fraction)^[20]

melting points, limited reactivity with BMG matrix, and similar thermal expansion coefficients to that of the matrix.

Extrinsic BMG composites with low volume fraction of reinforcement can be produced using melt injection casting method, which is commonly used for BMG fabrication. For extrinsic BMG composites with high volume fraction of reinforcement, usually the so-called melt infiltration casting technique is employed^[19]. A reinforcement preform is prepared and placed in a sealed end quartz or steel tube. The tube is necked a few centimetres above the reinforcement. Ingots of the BMG matrix material are then placed into the tube above the neck. The tube is placed in an electrical resistance furnace and is connected to a three-way valve, which can switch to vacuum pump and Ar supply. The tube is usually evacuated and flushed with Ar gas several times to purge residual oxygen prior to heating. Then the tube is heated to well above the melting temperature of the glass former. The superheat is important to dissolve the residual oxides and other impurities that degrade the glass-forming ability of the alloy. Then the tube is pressurized with Ar to allow the infiltration of the molten matrix material into the reinforcement. Finally, the sample is quickly quenched in a supersaturated brine solution.

Johnson's group^[19~21] has investigated a composite of Vit1 reinforced with carbon, tungsten and steel fibres, and $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ reinforced with a ductile metal fibres, such as W and Mo, and particles such as SiC, WC, W, Ta and Mo. Hu and Zhang's group has fabricated $(Zr_{55}Al_{10}Ni_5Cu_{30})_{98.5}Si_{1.5}$ composites reinforced with tungsten fibre^[22]. The reinforcement in extrinsic composite effectively obstructs shear band propagation and prompts the multiple shear bands formation. The compressive strain to failure in these extrinsic BMG composites is increased by over 900% compared to the unreinforced BMG materials^[20], as shown in Fig.2.

For extrinsic composite, the control of interface properties is critical. Understanding the wetting beh-

aviour of the liquid glass-forming alloy and the reinforcement is important before synthesizing the composites. The wettability is usually quantified by the interface contact angle. As the temperature increases, the equilibrium contact angle decreases and the system has better wetting behavior. However, an increase in temperature also increases the chemical reactivity between the matrix and the reinforcement. In some cases surface treatment or surface coating might be necessary. Careful consideration should be taken to determine the infiltration temperature, time and pressure during the process.

4.2 *In-situ* BMG composites

In a well-designed alloy system, through controlled crystallization, the ductile phase may be *in-situ* precipitated while the remaining liquid solidifies as a bulk metallic glass. Johnson's group reported^[23] that, upon cooling the composition in the neighborhood of Vit1 ($Zr_{56.2}Ti_{13.8}Nb_5Cu_7Ni_{5.5}Be_{12.5}$), a micrometer-sized ductile β -ZrTi (body-centered cubic) precipitates and shifts the composition of the remaining liquid close to that of Vit1, so the remaining liquid solidified as a bulk metallic glass. The element Nb was added to stabilize the ductile bcc phase over the α -ZrTi (hcp) phase. The resulting two-phase microstructure effectively modifies shear band formation and propagation. A high density of multiple shear bands evolves upon loading, which results in a significant increase of ductility both in tension and compression, toughness, and impact resistance compared to the monolithic glass. The overall (tensile and compressive) plastic strain of this *in-situ* composite is about 5%. Most recently He *et al.* reported^[24] an *in-situ* Ti-base composite with ductile β -Ti (Ta, Sn) dendritic precipitates in a nanostructured matrix, which exhibits up to 14.5% compressive plastic strain.

In *in-situ* BMG composites, the reinforcement/matrix interface is expected to be stronger and it more effective in transferring stress. Ductile precipitates might be more efficient in the ductilization of BMGs than brittle precipitates, as ductile particles can act as attraction or pinning centres during shear band propagation and serve as heterogeneous sites for the initiation of multiple shear bands. Also, in order to maximise the interaction between shear band and the *in-situ* precipitates, it is crucial to have a suitable match between the microstructural length scale of the precipitates (particle size and particle spacing) and the mechanical length scale of the shear band (shear band width and spacing, *etc.*).

4.3 Nanocrystalline BMG composites

In this route, *in-situ* nanocrystalline BMG composites are obtained through the annealing of BMG precursors. In 2000, Inoue produced BMG nanocomposites with improved plasticity of up to 2.5% by annealing glassy precursor alloys^[25]. In the Zr-base system, elements such as Ag, Ti and Pd have been added to examine the effect on the formation of nanocrystalline structure^[26,27]. The precipitates appear to have a spheroidal morphology with a size range of

5~10 nm for Pb-containing alloy and 10~15 nm for Ti-containing alloy. The plastic strain increased to 2.5%. They concluded that if the system satisfies the following criteria, a composite structure consisting of nanoscale crystalline particles embedded in a metallic glass matrix can be formed^[28]: (1) multi-stage crystallization process, (2) existence of homogeneous nucleation sites in BMG matrix, (3) suppression of growth reaction caused by segregation of a solute element with low atomic diffusivity at the nanocrystal/amorphous interface, and (4) high thermal stability of the remaining amorphous matrix. Hu's group recently synthesized a Cu-based BMG composite containing *in-situ* formed TiC particles^[29]. The ductility was improved together with the yield and fracture strengths.

In nanocrystalline BMG composites, the selection of additional elements and the control of the heat treatment process are the two key issues. The additional element will change the single-stage crystallization mode to a two-stage crystallization mode. Selection should be based on the calculation of their heats of mixing (ΔH_{mix}) against the other constituent elements. The change of ΔH_{mix} in the system causes a change of microscopic heterogeneity in the system, leading to the precipitation of a primary crystalline phase from the amorphous matrix.

5. Key Issues

Bulk metallic glass composites have shown encouraging results to overcome the main current technical barrier for these materials to be used as structural materials. Some of the key issues need to be addressed in the area of development of BMG composites are listed as follows:

(1) Alloy design for BMG matrix: For extrinsic BMG composites, the introduction of a second crystalline phase into the melt might be expected to induce heterogeneous nucleation and crystallization of the glass-forming liquid on undercooling. Therefore the alloy composition of BMG matrix must be carefully designed to have very good glass-forming ability and also be robust against heterogeneous nucleation at the surface and interface of the matrix and reinforcement.

For intrinsic BMG composites, the alloy composition is more critical, because on one hand the melt needs to be able to partially crystallize to form the chosen reinforcements upon either cooling or subsequent heating; on the other hand, crystallization needs to be suppressed in the rest of the melt in order to form BMG as the matrix.

(2) Reinforcement selection: Reinforcement selection needs to consider the following three aspects: (a) the nature of the reinforcement itself: *i.e.* ductile or brittle, Young's modulus, melting point *etc.*, (b) its integrity with the matrix, such as physical wettability, chemical reactivity and structural matching, (c) residual internal stress build-up from the unequal coefficients of thermal expansion of the matrix and reinforcement.

(3) Reinforcement/matrix interaction: the reported

results for the ductility of BMG composites are not always consistent. Some report the ductility of the two-phase BMG composites are seriously degraded^[30], and others^[31] report that the ductility is very sensitive to any fluctuation of composition, casting and processing conditions. We believe the inconsistent results about the ductility in BMG composites are related to the interaction between the reinforcement and the matrix in BMG composites. At this stage there is no systematic study on determination of the effect of the dispersion of reinforcement phase, matrix/reinforcement interface and internal stresses caused by the two-phase microstructure on the mechanical properties. There is no knowledge of how to engineer reinforcement phases (of varying length scale, morphology, volume and distribution) and reinforcement/matrix interfaces (of varying interface microstructure, chemical reactivity, physical wettability and thermal stress issue) to effectively improve the ductility. The features of the reinforcement, the nature of the interface and the internal stress in the composite will each have different effects on shear band behaviour and hence different effects on ductility.

(4) Processing issues: For extrinsic BMG composites, the issues such as pretreatment of reinforcement, casting temperature and filtration conditions are crucial to fabrication of composites. For intrinsic composites, solidification conditions from the melt and heat treatment conditions for recrystallization are the key issues to control the size, morphology and volume fraction of the precipitated crystalline phases.

(5) Fracture mechanism and modelling: Fracture behavior in BMG is very unique. Unlike crystalline materials where after yielding plastic deformation occurs by the motion of dislocations, BMGs exhibit highly localized inhomogeneous deformation behaviour. It is believed that impediment to shear band propagation and initiation of multiple shear bands are responsible for the plasticity in BMGs. So far, most investigations of shear band and fracture behaviours stop at the scanning electron microscopy (SEM) level, and studies at the transmission electron microscopy (TEM) level are very limited.

Based on the fundamental understandings of fracture mechanisms in BMG and BMG composites, and the controlling influences of reinforcement phase properties, various length-scales and dispersion of the reinforcement, reinforcement/matrix interface and internal stresses on the mechanical properties of the materials, it is desirable to develop computer models to simulate the deformation behaviour of the composite materials and then to predict the material performance according to the composite material design. Such models can provide powerful tools to tailor and engineer ductile BMG composites.

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REFERENCES

- [1] M.Telford: *Materials Today*, March, 2004, 36.
- [2] W.Clement, R.H.Willens and P.Duwez: *Nature*, 1960, **187**, 869.
- [3] H.S.Chen and D.Turnbull: *J. Chem. Phys.*, 1968, **48**, 2560.
- [4] H.S.Chen and D.Turnbull: *Acta Metall.*, 1969, **17**, 1021.
- [5] H.S.Chen and D.Turnbull: *Acta Metall.*, 1974, **22**, 1505.
- [6] M.C.Lee, H.S.Chen and D.Turnbull: *Appl. Phys. Lett.*, 1982, **40**, 382.
- [7] A.L.Drehman, A.L.Greer and D.Turnbull: *Appl. Phys. Lett.*, 1982, **41**, 716.
- [8] H.W.Kui, A.L.Greer and D.Turnbull: *Appl. Phys. Lett.*, 1984, **45**, 615.
- [9] A.Inoue, T.Zhang and T.Masumoto: *Mater. Trans. JIM*, 1989, **30**, 965.
- [10] A.Inoue, K.Ohtera, K.Kita and T.Masumoto: *Jpn. J. Appl. Phys.*, 1988, **27**, L2248.
- [11] A.Inoue, A.Kato and T.Zhang: *Mater. Trans. JIM*, 1991, **32**, 609.
- [12] T.Zhang, A.Inoue and T.Masumoto: *Mater. Trans. JIM*, 1991, **32**, 1005.
- [13] A.Inoue, T.Zhang and T.Masumoto: *Mater. Trans. JIM*, 1990, **31**, 177, and 1991, **31**, 425.
- [14] A.Inoue, T.Zhang, and N.Nishiyama: *Mater. Trans. JIM*, 1993, **34**, 1234.
- [15] A.Inoue: *Acta Mater.*, 2000, **48**, 279.
- [16] A.Peker and W.L.Johnson: *Appl. Phys. Lett.*, 1993, **63**, 2342.
- [17] J.F.Loffler: *Intermetallics*, 2003, **11**, 529.
- [18] E.Pekarskaya, C.P.Kim and W.L.Johnson: *J. Mater. Res.*, 2001, **16**, 2513.
- [19] R.D.Conner, R.B.Dandliker and W.L.Johnson: *Acta Mater.*, 1998, **46**, 6089.
- [20] H.Choi-Yim, R.Busch and W.L.Johnson: *J Appl. Phys.*, 1998, **83**, 7993.
- [21] R.D.Conner, R.B.Dandliker and W.L.Johnson: *J. Mater. Res.*, 1999, **14**, 3292.
- [22] K.Q.Qiu, A.M.Wang, H.F.Zhang, B.Z.Ding and Z.Q.Hu: *Intermetallics*, 2002, **10**, 1283.
- [23] C.C.Hays, C.P.Kim and W.L.Johnson: *Phys. Rev. Lett.*, 2000, **84**, 2901.
- [24] G.He, J.Eckert, W.Loser and L.Schultz: *Nature Mater.*, 2003, **2**, 33.
- [25] C.Fan, C.F.Li, A.Inoue and A.Hass: *Phys. Rev. B*, 2000, **61**, 3761.
- [26] A.Inoue, C.Fan and A.Takeuchi: *Adv. Mater.*, 1998, **4**, 373.
- [27] C.Fan and A.Inoue: *Mater. Trans. JIM*, 1999, **40**, 42.
- [28] A.Inoue: *Acta Mater.*, 2000, **48**, 279.
- [29] H.Fu, H.Zhang, H.Wang, Q.Zhang and Z.Q.Hu: *Scripta Mater.*, 2005, **52**, 669.
- [30] A.Lenard, L.Q.Xing, M.Heilmaier, A.Gebert, J.Eckert and L.Schultz: *Nanostruct. Mater.*, 1998, **10**, 805.
- [31] G.He, J.Eckert, W.Loser and L.Schultz: *Proc. Mater. Res. Soc.*, CC11.12.1, 2003.