

Bulk Metallic Glasses a review

Ms. Uma V. Gaikwad¹

*(Assistant Professor, Priyadarshini Bhagwati C.O.Engg. Nagpur, India)

Abstract: This paper aims to revive the interest of Bulk Metallic glasses and to show its current applications in industry. The discovery of bulk metallic glasses (BMGs) has stimulated widespread research enthusiasm because of their technological promise for practical applications and scientific importance in understanding glass formation and glass phenomena. Arising from their disordered atomic structure and unique glass-to-supercooled liquid transition, BMGs represent a new class of structural and functional materials with extraordinary properties including extreme strength at low temperature and high flexibility at high temperature, along with a number of superior chemical and physical properties. This article covers the general properties of BMGs based on a review of the historical milestones in metallic glass research, and recent progress on several fundamental issues in the development of a comprehensive understanding of the strength, ductility and glass-forming ability of BMGs and, more importantly,

Recent advances in the applications of BMGs in microelectromechanical systems (MEMS), biomedicine and nanotechnology are also reviewed.

Keywords: metallic glasses; deformation; strength; plasticity, transition metals

I. INTRODUCTION

The discovery of bulk metallic glasses (BMGs) has stimulated widespread research enthusiasm because of their technological promise for practical applications and scientific importance in understanding glass formation and glass phenomena. Arising from their disordered atomic structure and unique glass-to-supercooled liquid transition, BMGs represent a new class of structural and functional materials with extraordinary properties including extreme strength at low temperature and high flexibility at high temperature, along with a number of superior chemical and physical properties. This article covers the general properties of BMGs based on a review of the historical milestones in metallic glass research, and recent progress on several fundamental issues in the development of a comprehensive understanding of the strength, ductility and glass-forming ability of BMGs and, more importantly, the correlation of these parameters with atomic structure, focusing on the outstanding questions and critical issues that appear to warrant future research. [1]

Bulk metallic glasses, formed at very low critical cooling rates, are fundamentally different from traditional amorphous alloys, which are usually formed at very high cooling rates in order to suppress the nucleation of crystalline phases. The high cooling rates required for the formation of traditional glassy alloys restrict the range of possible structures that can be prepared to powders, films and ribbons. Of the extensive family of glasses, BMGs are probably the youngest, possessing a number of characteristics, such as amorphicity and high strength, that are shared by other glasses, including the most familiar window (oxide) glasses. However, the most important feature of BMGs that, along with other glasses, distinguish them from general amorphous materials is the glass transition that transforms supercooled liquids into a glassy state when cooled from high to low temperature and vice versa. [1]

Metallic glasses are therefore scientifically defined as amorphous alloys that exhibit a glass transition, from which derives their unique properties of extreme strength at low temperature and high flexibility at high temperature, along with thermodynamic and physical properties that change abruptly at the glass transition temperature (T_g).[4]

Research on metallic glasses is closely related to that on metallic liquids. It is known that the atomic configurations of molten metals and alloys are disordered. The noncrystalline structure is expected to be retained if the liquids can be quenched at a sufficiently high cooling rate to suppress the formation of equilibrium crystalline phases. The critical cooling rate required to freeze the liquid structure is estimated to be on the order of 10^5 – 10^6 K s⁻¹ for alloys. This assumption was proved experimentally in 1959 by a research group at Caltech, who reported the first glassy alloy with a composition of Au₇₅Si₂₅ produced by splat quenching [1]. In this pioneering work, the Au₇₅Si₂₅ melt was quenched using a cold metal plate instead of the water or oil used traditionally. The good contact between liquid droplets and the cold metal avoids the formation of gaseous layers that limit the heat release during solidification. Moreover, the droplets spread into a thin layer for rapid thermal diffusion when striking the solid, cold metal plate. [1]

X-ray diffraction analysis revealed the disappearance of all crystalline structure and the formation of a noncrystalline structure in the resultant micrometer-sized flakes. Following this discovery, a large number of metallic glasses were found in various alloy systems, and rapid research progress was made in the search for new metallic glasses. [1]

Up till now researchers have found that noble metal based alloys, such as Pd-Cu-Si and Pd-Ni-P [2-3]. These alloys have very low critical cooling rates of $\sim 10 \text{ K s}^{-1}$ and can make glassy samples with a bulk size of $\sim 10 \text{ mm}$ in thickness [5]. Unfortunately, these pioneering works on the development of BMGs did not make a big impact in the materials science community. One reason is that, although the noble metals of palladium and platinum are good for improving glass-forming ability, they are too expensive to be used for a wide range of applications. The breakthrough in BMG research came with the discovery of multicomponent glass formers by Inoue and co-workers at Tohoku University [8,9]. These new bulk glassy alloys exhibit excellent glass-forming ability and very low critical cooling rates for bulk glass formation, similar to those of the noble metal-based metallic glasses.

II. MECHANISMS OF BMG FORMATION

As aforementioned, deep eutectic points in binary and ternary alloy systems have been widely used as an indication for seeking good glass formers. However, it is impossible to represent more than three components on a phase diagram, and the eutectic transitions in qua-ternary and higher systems are rarely known. Therefore, it is difficult to locate the compositions for best glass formers in multicomponent alloy systems. Most multicomponent metallic glasses found so far have been identified by trial and error, and the development of new BMGs requires considerable experience and involves major commitments in time and resources. There is thus a compelling demand for research that uncovers the underlying mechanisms for the formation of BMGs.

Empirical rules

Following the discovery of multicomponent bulk glass formers, there have been many discussions on the underlying mechanisms of BMG formation. The excellent glass-forming ability of the new alloys has been generally attributed to the increased atomic packing density in the multicomponent system, as there are more atoms of the 'right' size to fill free space in the randomly packed glass structure. This appears to be true since the total energy of alloys with directionless metallic bonding depends on the packing density; denser packing leads to lower energy and thereby higher stability. Besides consideration of the packing density, the improved glass-forming ability of the multicomponent systems has also been nominally understood by the 'confusion principle', i.e., the more elements involved, the lower the chance that the alloy can select viable crystal structures, and hence the greater the chance of glass formation [5].

Since the discovery of metallic glasses by Duwez in 1959, a number of empirical rules on metallic glass formation have been suggested in consideration of factors such as atomic size, interatomic bonding, electron density and other structural features [7]. Although these empirical rules work for certain alloys, they frequently fail for others.

By statistically analyzing hundreds of alloys that have excellent glass forming ability, Inoue suggested a more comprehensive set of empirical rules for the formation of BMGs [9] alloys should be multicomponent systems consisting of more than three elements, there should be a significant difference in the atomic size ratios ($>12\%$) among the three main constituent elements, and the three main constituent elements should have negative heats of mixing. Although most of the best glass formers follow those empirical rules, implying certain physical principles indeed play vital roles in the formation of BMGs in multicomponent systems, the empirical rules represent only the bare essentials for glass formation and are not sufficient for designing new alloys. The definite physical mechanisms for BMG formation therefore remain unclear, and the laws for quantitative composition design of bulk metallic glasses are still unknown.

Atomic Structure

The atomic structure is the foremost striking characteristics of the BMG' as it fundamentally differentiates from ordinary metals. The figure below shows TEM micrograph where the atomic structure of BMG versus the atomic structure of conventional metal zirconium is shown. The atomic structure of conventional metal is a periodic structure in which the layout of atomic species shows repeating patterns over an extended range. This atomic structure called "crystalline" and is said to have long range order. By contrast no discernable patterns exist in the atomic structure of BMG's, which is called amorphous and said to have no long range order. For the first time, amorphous atomic structure became possible for the solid bulk forms of metals with discovery of BMG's. This unique atomic structure places BMG's in new domain of properties unattainable by ordinary metals. [1]

III. STRUCTURAL ORIGINS OF METALLIC GLASS FORMATION

As the key to glass formation is avoiding the occurrence of detectable crystals during cooling from liquid to a temperature below the glass transition point, the kinetics of crystal formation in supercooled liquids has been considered as the controlling factor for glass formation. According to the homogeneous crystal nucleation theory, crystal nucleation rates depend strongly on the diffusivity of alloy melts, which is a function of viscosity from the Stokes–Einstein equation. Therefore, dense liquids with high viscosity are expected to have a more stable liquid state and better glass-forming ability. The disordered atomic structure of metallic glasses has been examined extensively by various experimental methods, including X-ray and neutron diffraction, EXAFS and nuclear magnetic resonance [13,15]. However, these experiments give only average and one-dimensional structural information, although plausible three-dimensional structural models can be reconstructed by trial and error using reverse Monte Carlo and ab initio molecular dynamics (MD) simulations [1]. The main problem is that these methods cannot give unique atomic configurations, particularly for multicomponent alloys. In this sense, experimental observations of the local atomic structure of disordered metallic glasses are still lacking, and definite evidence of the local atomic order suggested by various theoretical models remains inconclusive.

IV. DYNAMICS OF METALLIC GLASS FORMATION

In view of the thermodynamic relationship between structure and phase stability in crystalline materials, the atomic origins of BMG formation have been discussed intensively from geometrical and topological perspectives of the dense atomic packing as introduced above.

In principle, the formation of metallic glasses is a competition between the stability of supercooled liquids and the formation kinetics of rival crystalline phases [18]. As both liquid stability and crystallization kinetics are time-related, and as metallic glasses are essentially out-of-equilibrium systems, the formation of BMGs involves structural evolution in time and thus may not be studied in terms of thermodynamics alone. Therefore, it seems to be more appropriate to explore the glass forming mechanism and glass forming ability from the perspective of the dynamics of supercooled liquids. Several kinds of temperature dependent relaxations have been observed experimentally in metallic glasses.

In the supercooled liquid state, α - or structural relaxation corresponds to an increase in shear viscosity and shear modulus during cooling, resulting in change of the glass formers from liquid behavior to viscoelastic behavior. In general, superior glass formers exhibit slower dynamics and a longer α -relaxation time at temperatures above the glass transition point. This is simply because the slow dynamics offers a low critical cooling rate for glass formation and, thus, has been used to explain the effect of alloying on the improved glass-forming ability of BMGs empirically [10-13].

V. MICROMECHANISMS OF MECHANICAL PROPERTIES

One of the most notable properties of BMGs is their extreme hardness and strength, which makes them attractive for applications where strength is critical. Nevertheless, the underlying deformation micro mechanisms that govern the strength and ductility of BMGs remains poorly known [15]. For crystalline metals and alloys, the factors controlling their mechanical properties have been well investigated through the development of dislocation and electronic theories, which can explain, in general, the atomic and electronic origins of the strength and ductility of crystalline materials. For disordered materials such as metallic glasses, however, the definite correlation between mechanical behavior and atomic and electronic structures has not been properly established. It has long been recognized that the mechanical properties of metallic glasses are closely related to the chemical and physical properties of their component elements [3]. The significant differences in mechanical performance, such as strength and ductility, that are observed with changes in the chemical composition of metallic glasses indicate the existence of an intrinsic relationship between the mechanical properties and the atomic and electronic structures of metallic glasses. However, the underlying mechanisms have not been well understood and the physical picture appears to be much more complicated than that for crystalline materials [17]. Ductility and composite effects. Although BMGs possess very high strength compared to their crystalline counterparts, they generally suffer from low ductility at low temperature. Room-temperature plastic deformation of metallic glasses has been known to occur through shear band movement, in which plastic flow driven mainly by shear stresses is localized within a nano-scale zone [16,17]. Due to structural and/or thermal softening, these bands are preferential sites for further plastic flow and lead to final failure in a brittle manner that typically breaks a sample along a single shear band without detectable plastic strains. Therefore, highly localized shearing and resultant strain softening are responsible for the poor ductility of BMGs. It has been recognized that the ductility improvement of BMGs largely depends on suppression of the localized strain softening caused by shear bands[1]

VI. FORMATION OF POROUS BULK GLASSY ALLOYS

From the review article it was also found that the ductility of a Pd₄₀Cu₃₀Ni₁₀P₂₀ bulk glassy alloy increased even by homogeneous dispersion of spherical pores into glassy matrix [22]. In addition to the increase in ductility, the porous bulk glassy alloys exhibited the decreases in specific weight, Young's modulus and strength as well as the increase in absorption energy required up to fracture [22]. The porous bulk glassy alloys containing spherical pores with sizes from 15 to 33 μm in a wide volume fraction range from 2 to 70% can be formed by use of significant difference in solubility limit of hydrogen between supercooled liquid and glassy solid. The 0.2% proof stress and Young's modulus as a function of porosity can be estimated by taking the stress concentration effect around pores into consideration. The simultaneous achievement of high ductility and high fracture absorption energy as well as light weight and low stiffness is important for future extension of application fields for bulk glassy alloys. Porous bulk glassy alloys have been also produced by the precompaction and sintering method [22], by the sequent processes of homogeneous mixing of bulk glassy alloy powder and sodium chloride, followed by dissolution of sodium chloride with water [22], and by the formation of immiscible type glassy alloy, followed by dissolution of less-noble glassy phase field with some acids [1]

Recently, various casting techniques of molten alloy to produce bulk glassy alloys with desired outer shapes have been developed to full fill their engineering needs [1]. As a result, we can utilize glassy alloy rods with diameters of 3 to 5 mm and a length of about 1 m, glassy alloy sheets with dimensions of 0.3-2x125x200 mm and spherical glassy alloy balls with diameters of 3-10 mm. The combination effect of unique properties, these useful forms and simple net-shape production process is expected to open up much wider application fields. [22]

VII. RECENT ADVANCES IN APPLICATIONS

BMGs have been used as one of the best soft magnetic materials for a wide range of applications from electronic devices to automobiles and long-distance electric power transmission. Combining high strength and low density, BMGs have also been exploited as light-weight structural materials for applications in which weight and strength are critical. As these applications have been detailed in previous publications, the present review focuses on recent progress in applications in biomedicine, nanotechnology and microelectromechanical systems (MEMS).

Biomedical materials

Metals and alloys have been widely used as biomedical materials and are indispensable in the medical field. For example, about 70% of the structural materials employed in implants are metallic materials that are used to replace hard tissues or as hard-tissue prostheses, including bone screws, bone plates, artificial hip joints, knee joints and dental implants. The advantages of BMGs compared with conventional crystalline metals and alloys include superior strength, high elasticity and excellent wear and corrosion resistance, attributable to the lack of grain boundaries and crystal defects that usually lead to weakening of material strength, intergranular corrosion and stress-corrosion cracking in biological environments. Corrosion testing of BMGs has demonstrated that these materials have much better corrosion properties in physiological solution compared to many common metallic biomaterials [1]. Moreover, the relatively flexible composition of BMGs and the large number of glass formers makes it possible to design and select glassy alloys without toxic elements for full biocompatibility. Recently, *in vitro* and *in vivo* experiments have demonstrated that BMGs are, in general, nontoxic to cells and compatible with cell growth and tissue function. Importantly, BMGs have much lower Young modulus than crystalline metals, allowing BMGs to be more compatible with bone, reducing the stress-shielding effect that can cause disuse atrophy of cortical bone. Therefore, BMGs possess attractive properties for load-bearing biomedical-implant applications.

Bulk metallic glasses have also been suggested for application as soft tissue stents due to their high flexibility, providing enhanced compliance with blood vessel biomechanics and thereby minimal damage to vessels [2]. More recently, magnesium-based BMGs have been developed for application as biodegradable implants [2]. In addition to their higher strength and elasticity in comparison with the crystalline biodegradable magnesium based alloys, biodegradable metallic glasses also show a distinct reduction in hydrogen evolution *in vivo* which is a general problem that occurs as a result of biocorrosion in physiological solution and forms an unwanted gas pocket around the implants. Owing to the broad solubility of the glassy alloys, the chemical composition of BMGs can also be optimized to match the biocorrosion characteristics of the environment, providing control over degradation and hydrogen evolution rates, which is very difficult to achieve using crystalline alloys.

Nanotechnology and MEMS

Like other glassy materials, such as oxide glasses and amorphous polymers, BMGs have a wide supercooled liquid range when heated from room temperature. Within this temperature window, BMGs

transform into a viscous supercooled liquid with significant softening and, thus can be shaped by Newtonian viscous flow under very small applied forces. This unique property of glassy materials endows BMGs with extraordinary formability and superplasticity, comparable to those of polymers and window glasses. Bulk metallic glasses are quite stable in the supercooled state and, after thermal processing, can be slowly cooled back to the strong glassy state with negligible volume shrinkage. This outstanding thermal formability of BMGs useful for applications in nanotechnology and MEMS [22].

In micro and nano-machines, as well as MEMS, three-dimensional structures or surface nano-patterns are frequently required, which are traditionally fabricated by lithography and chemical or ion etching.

Such processes originate in semiconductor technology and are generally limited to silicon and related materials. The micro- and nano-fabrication of metallic materials for such applications is either expensive or lacks the accuracy required for precision processes [22]. Utilizing the excellent thermal formability of BMGs, supercooled liquid fabrication provides an alternative and economic approach for the fabrication of micro- and nano-sized metallic parts and surface patterns for MEMS and micro and nano-machines. By applying plastic processing techniques, micro- or nano-patterns can be easily transferred to BMG surfaces from stiff dies and molds by thermal imprinting. The sub-nanoscale structural homogeneity also makes patterned BMGs of interest for optical applications [1]. Using a die-forging technique, free-standing BMG micro-parts of as small as 1 μm have been produced for micro-machines. [2,3]

The ultra-high strength and lack of grains and grain boundaries give these metallic glass micro-parts mechanical performance superior to that of their crystalline counterparts, which are limited by the characteristic length of their microstructures. Sputtered BMG films have also been used to fabricate actuators and micro-cantilevers for MEMS applications [19]. Recently, the dimensions of BMG patterns and parts have been further reduced to scales on the order of tens of nanometers by superplastic deformation [20] and thermoplastic forming [21,22].

Metallic glass nanowires fabricated by these methods show interesting multi-harmonic oscillations with possible applications in mechanical and magnetic sensors. The development of such nano-sized BMG structures may lead to a host of applications of BMGs in nanotechnology and bionanotechnology.

VIII. CONCLUSION REMARKS

Research over the past 20 years has produced a large number of BMGs and composites in various alloy systems, rousing intense research interest for the search for novel physical and chemical phenomena in non-equilibrium, disordered, multicomponent solids. Bulk metallic glasses hold great promise for structural and functional applications and are viewed as one of the most important metallic materials owing to their unique properties of extreme strength at room temperature and high flexibility at high temperature. However, as outlined in this review, many fundamental questions remain and our understanding of the properties and structures of BMGs is far from comprehensive.

Researchers are continuing to explore the atomic-scale mechanisms of BMG formation and to search for new bulk glassy alloys and composites with improved glass-forming ability as well as enhanced strength and ductility. Recent applications of BMGs in biomedicine, MEMS and nanotechnology have opened innovative fields for future intense research.

Although no bulk glassy alloy was found in any alloy systems of Fe, Co, Ni, and Cu bases before 1994, we can produce, at present, bulk glassy alloys with diameters of over 10 mm in all these alloy systems. Considering the significantly rapid progress of bulk glass-forming ability for the last one decade, it is expected that the subsequent study leads to the production of bulk glassy alloys with diameters of 30 to 50 mm. When we consider the future prospects of bulk glassy alloys, the key point is attributed to the possibility that much larger scale bulk glassy alloys with diameters of over 30mm are formed in engineering important alloy systems such as Fe-, Co-, Ni-, and Cu-based alloys. Thus, we are approaching a new metallic age that bulk glassy alloys can be used widely as base materials in social life.

REFERENCES

- [1]. Mingwei Chen, A brief overview of bulk metallic glasses, Review article, 82 Npg asia materials | vol 3 | September 2011 |82–90 (2011)
- [2]. H. S. Chen, Rep. Prog. Phys.43, 353 (1980).
- [3]. H. S. Chen, Acta Metall. 22, 1505 (1974).
- [4]. A. J. Drehman, A. L. Greer, D. Turnbull, Appl. Phys. Lett.41, 716 (1982)
- [5]. H. W. Kui, A. L. Greer, D. Turnbull, Appl. Phys. Lett.45, 615 (1984)
- [6]. A. L. Greer, Nature 366, 303 (1993).
- [7]. I. Gutzow, D. Kashchiev, I. Avramov, J. Non-Cryst. Solids 73 , 477 (1985).
- [8]. A. Inoue, T. Zhang, T. Masumoto, Mater. Trans. JIM 31, 177 (1990)

- [9]. Inoue, *Acta Mater.*48, 279 (2000)
- [10]. Y. Q. Cheng, E. Ma, H. W. Sheng, *Appl. Phys. Lett.*93 111913 (2008).
- [11]. S. M. Chathoth, B. Damaschke, M. M. Koza, K. Samwer, *Phys. Rev. Lett.* Y. T. Shen, T. H. Kim, A. K. Gangopadhyay, K. F. Kelton, *Phys. Rev. Lett.*102, 057801 (2009).
- [12]. H. Tanaka, *J. Phys. Condens. Matter* 15, L703 (2003)
- [13]. H. W. Sheng, W. K. Luo, F. M. Alamgir, J. M. Bai, E. Ma, *Nature* 439 , 419 (2006).
- [14]. D. Ma, A. D. Stoica, X. L. Wang, *Nature Mater.*8, 30 (2009)
- [15]. Spaepen, *Acta Metall.*25, 407 (1977).
- [16]. A. S. Argon, *Acta Metall.* 27, 47 (1979)
- [17]. Z. P. Lu., C. T. Liu, *Phys. Rev. Lett.* 91, 115505 (2003).
- [18]. H.-W. Jeong, S. Hata, A. Shimokohbe, J. *Microelectromech. S.*12, 42 (2003)
- [19]. K. S. Nakayama et al., *Adv. Mater.*22, 872 (2010).
- [20]. G. Kumar, H. X. Tang, J. Schroers , *Nature* 457, 868 (2009).
- [21]. N. Nishiyama et al., *Intermetallics* 18, 1983 (2010)
- [22]. A. Inoue, X.M. Wang and W. Zhang” Developments and applications of bulk Metallic glasses *Rev.adv.mater.sci.* 18(2008) 1-9