

AN INTRODUCTION OF BULK METALLIC GLASSY-CRYSTAL**Patel Ram Suthar**

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ABSTRACT

During the initial phase, precious metals such as Zr and Pd were utilized as the foundation for synthesizing major bulk metallic glasses (BMGs). However, the high cost associated with using precious metals limited the development of bulk metallic glass. In the decade of 1990, the emergence of Fe-based BMGs garnered attention due to its unique blend of properties, such as relatively low material cost, excellent magnetic properties, ultra-high strength, and good corrosion resistance. Nonetheless, the extensive use of Fe-based BMG is limited due to its tendency to fail catastrophically with negligible plasticity at room temperature. Hardness and strength are typically mutually exclusive mechanical properties of a material. Metallic glasses, however, exhibit significantly high strength, nearly twice that of their crystalline counterparts, while simultaneously discouraging low tensile plasticity. Fortunately, significant toughness can be generated in metallic glasses, despite their apparent brittleness and poor plasticity.

Keywords: Crystal, Glasses, PPG, metal-metal, in-situ.**1. INTRODUCTION**

Ancient literature often contains descriptions of various types of crystals, and humans have always been fascinated by them. In ancient times, solid materials were assumed to be crystalline because the available instruments at that time were not advanced enough to view the structure of solids. The emergence of bulk metallic glasses (BMGs) has sparked widespread enthusiasm in the research community due to their technological potential for practical applications and their scientific significance in unraveling glass formation and phenomena. With their disordered atomic structure and intriguing glass-to-supercooled liquid transition, BMGs represent a novel category of structural and functional materials boasting extraordinary properties. These include exceptional strength at low temperatures, remarkable flexibility at high temperatures, as well as a range of superior chemical and physical attributes.

1.1 Crystal

Crystallography deals with the organized arrangement of atoms, ions, or molecules in a crystalline material, which is referred to as the crystal structure. The ordered structures arise from the inherent nature of the constituent particles, forming symmetric patterns that repeat along the three non-coplanar Bravais vectors within the material. Thus, the arrangement of atoms in a crystal is termed the crystal structure.

Materials, in general, can be categorized into three main groups: solids, liquids, and gases. Solids exhibit characteristics such as incompressibility, rigidity, and mechanical strength. Within the category of solids, there are two subdivisions based on molecular structure: crystalline and amorphous. Crystalline solids exhibit a regular arrangement of atoms, molecules, or groupings of atoms in a lattice (Figure-1.1). In contrast, amorphous solids lack a regular array, with the atoms, molecules, or groupings of atoms being randomly organized. An example of an amorphous material is glass (Figure-1.2), which is a uniform solid without a crystalline structure. Glass is typically formed by rapidly cooling a viscous molten material below its glass transition temperature, preventing the formation of a regular crystal lattice. During the glass transition, the dynamics of certain liquids slow down as their temperature decreases.

Amorphous materials, such as glass, are created through rapid cooling of molten substances. This quick cooling process limits the mobility of the material's molecules, preventing them from arranging themselves into a thermodynamically favored crystalline state. Another method for producing amorphous materials, like window glass, is the PPG process (also known as the floating method), which was introduced by Sir Alistair Pilkington in 1952. This process is widely utilized for manufacturing architectural glass worldwide.

1.2 Bulk Metallic Glass

But about six decades ago, scientists working on material knew how to make glassy metals by cooling a metallic liquid so rapidly, so that the internal atomic configurations freeze before the atoms had a chance to arrange themselves into a regular lattice pattern.

Generally, the processing method to make metallic glass involved the chilling rate of 1 Kelvin per

second to 100 Kelvin per second for molten metal. the gold-silicon alloy ($Al_{80}Si_{20}$) was first metallic glass produced in 1957. It is less Brittle than ordinary oxide glass but seems like a metal, so it is opaque, grey, smooth and shiny. Fundamental differentiation of liquid metals alloys from ordinary metal is atomic structure. The liquid metal alloy possesses amorphous atomic structure.

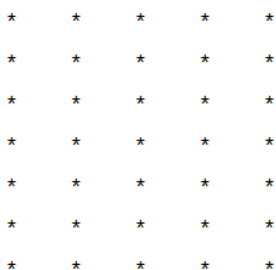


Fig.-1.1

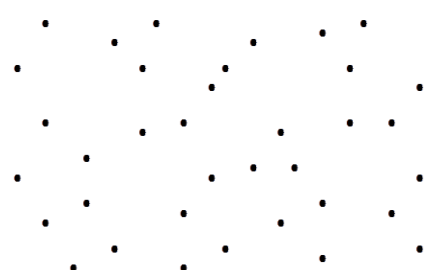


Fig.-1.2

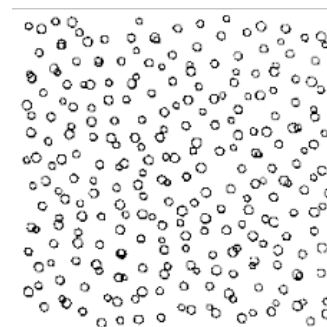


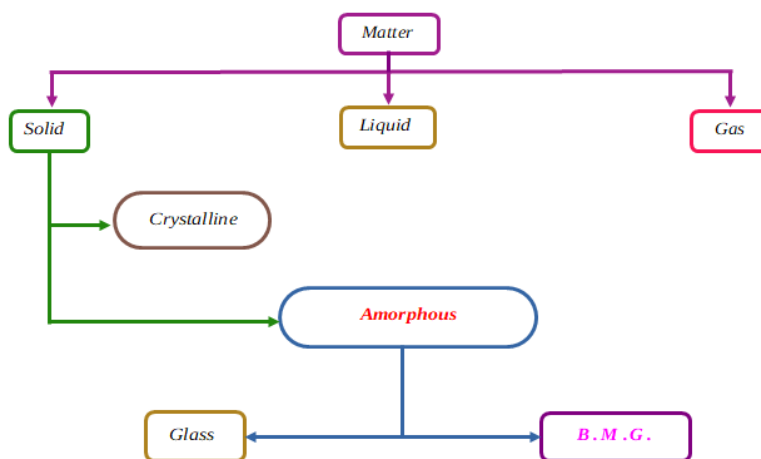
Fig.-1.3

There is no discernable pattern exist in the atomic structure of liquid metal alloys as it is a contrast to the crystalline structure. In the amorphous glassy structure, the atoms are tightly packed so that the displacement of an atom is obstructed. The unusual atomic structure in glassy metals is responsible for the distinctive magnetic properties and mechanical properties.

Bulk metallic glasses possess a unique combination of properties, displaying characteristics of both glasses and metals. They are strong, opaque, and malleable like ordinary metals, yet brittle like glasses. It's important to note that an amorphous metal is typically an alloy rather than a pure metal. Alloys consist of constituent atoms of different sizes and natures, resulting in a small volume in the

molten state and higher viscosity compared to pure metals. This structural arrangement also contributes to the alloy's resistance to plastic deformation.

Amorphous crystal bulk metallic glasses exhibit less brittleness and greater toughness compared to ceramics and ordinary silica glasses. Furthermore, amorphous materials generally have lower thermal conductivity compared to crystalline metals. Alloys that include elements like boron, silica, and phosphorus, along with magnetic materials such as nickel, iron, and cobalt, demonstrate high magnetic susceptibility, low coercivity, and high resistivity. This combination minimizes losses caused by eddy currents in the presence of varying magnetic fields. This particular property makes them suitable for transformer cores.



2. HISTORY OF DEVELOPMENT OF BMG (BULK METALLIC GLASS)

In 1969 an amorphous sphere with a diameter of 0.5 mm formed ternary palladium, silicon copper, at a cooling rate of 100 Kelvin per second to 1000 Kelvin per second. The supercooled liquid range was extended up to 40 Kelvin in some alloys for crystallization and glass transition temperature. It was the path for the first detailed studying of metallic glass regarding crystallization. In 1974 crystal thickness of 1 mm was obtained from Pd-Ni. In the 1980s diameter of the amorphous sphere was extended up to 5 mm. The scientist has capable to discover strongly glass forming at the larger under cooling with the low critical cooling rate of 1 Kelvin per second to the 100 Kelvin per second with multi-component alloys like- titanium,

magnesium lanthanum, zirconium, iron, copper etc. just similar to ordinary oxide glasses. The large undercooling and low critical cooling rates allow scientists an increase in the time for transition from milliseconds to minutes before crystallization, so they make a greater critical casting thickness of 1 cm by conventional good moulding.

In the 1980s cast, glass reaches up to 5 mm thick using copper moulds.

In the 1990s cast glass reached up to 9 mm thick.

In 1992s critical casting thickness of 15 mm was achieved for Zr-Al-Ni at an extended supercooled liquid in the region of 125 Kelvin.

The first commercial BMG (bulk metallic glass) was the Vitreloy 1 (41.2% Zr, 13.8% Ti, 12.5% Cu, 10% Ni and 22.5% Be) developed by NASA with a critical casting thickness of up to 10 centimetres.

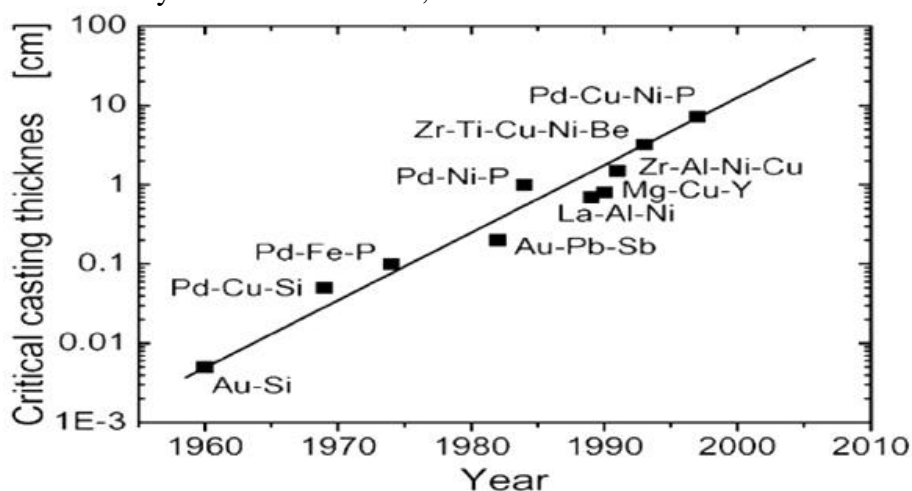


Figure : Evolution of the critical casting thickness for bulk metallic glasses over the past forty years (Loffler,2003), Zhiying Zhang; Elastic Properties of Bulk-metallic Glasses Studied by Resonant Ultrasound Spectroscopy Reference: University of Tennessee, Knoxville Trace: Tennessee Research and Creative Exchange, Doctoral Dissertations, Graduate School, 8-2008

3. CATEGORIZATION OF BMGS

Over the past 50 a long time, a wide range of metallic glasses have been created. Despite the fact that there are different categories, these might be generically categorised into two categories as metal-metalloid or metal-metal types.

3.1 Metal-metalloid Type BMGs

The metal particles make up generally 80% of a common place metal-metalloid-type glass, whereas the metalloid molecules, which are commonly B, C, P, and Si, make up 20%. The add up to rate of the metal molecules is generally 80%, whether they are all of one sort or a blend of a few metals. Comparable to the past case, the metalloid component may comprise of a single kind of

metalloid atom or a combination of a few metalloid atoms, with a add up to metalloid molecule substance of around 20%. $Fe_{80}B_{20}$, $Fe_{40}Ni_{40}B_{20}$, $Pd_{80}Si_{20}$, $Ni_{49}Fe_{29}B_6P_{14}Si_2$, $Pd_{77}Cu_6Si_{17}$, $Fe_{40}Ni_{40}P_{14}B_6$, $Fe_{70}Cr_{10}P_{13}C_7$, $Ni_{75}Si_8B_{17}$, and some exotic compositions such as $W_{35}Mo_{20}Cr_{15}Fe_5Ni_5P_6B_6C_5Si_3$ are a few compositions in this category that have experienced broad inquire about. (The subscripts appear the nuclear extents of the alloy's constituent components.)

3.2 Metal-metal Type BMGs

Atoms are solely included within the metal-metal sort of metallic glasses, not the metalloid shape. In this category, amalgams counting $Mg_{70}Zn_{30}$,

$\text{Fe}_{90}\text{Zr}_{10}$, $\text{Cu}_{57}\text{Zr}_{43}$, $\text{La}_{80}\text{Au}_{20}$, and $\text{Ni}_{60}\text{Nb}_{40}$ have been broadly considered. A noteworthy refinement between the compositions of metal-metalloid-type and metal-metal-type metallic glasses is promptly clear. There's no such compositional limitation within the case of metal-metal-type metallic glasses, but the metalloid component is ordinarily around 20% and the leftover portion is metallic within the metal-metalloid-type glasses. The second metal component might range in size from 9 to 10 at. percent to about 50 at. Percent.

4. GROUPS OF BMGS

There are five different groups of BMGs which are as follows-

- Group-I Cu-Zr-Al, Cu-Hf-Al
- Group-II Fe-(B, Si)-Nb, Fe-Nb-B, Fe-Zr-B, (Fe, Co)-Ln-B, (Co, Fe)-Ta-B, Fe-(Cr, Mo)-(C,B)
- Group-III Fe-(Al, Ga)-(P, C, B)
- Group-IV Ni-Nb-Ti, Cu-Zr-Ti, Cu-Hf-Ti
- Group-V Ni-Pd-P, Cu-Pt-P, Pd-(Ni, Cu)-P, (Pd, Pt)-Cu-P

5. COMPOSITES OF BMGS

Compared to monolithic materials, composites based on bulk metallic glasses (BMGs) exhibit significantly improved mechanical properties, particularly enhanced plasticity. Recent efforts have focused on the synthesis and analysis of BMG composites due to this unique characteristic. Qiao et al. provided a recent overview of metallic glass matrix composites.

In BMG composites, the reinforcing phase, also known as the second phase, is crystalline, and its volume percentage varies depending on the desired properties. The volume fraction of the reinforcing phase in BMG composites is carefully selected based on the desired qualities. In some cases, a high volume fraction of up to 80% has been chosen to achieve exceptional plasticity. However, not all studied composites have contained such a large amount of crystalline reinforcement.

BMG composites can be categorized as either ex situ or in situ composites, depending on the method used for their fabrication. In in situ composites, the second phase precipitates from the metallic glass either during casting or subsequent processing of the fully glassy alloy. As a result, the interface between the glassy matrix and the crystalline reinforcement is clean and robust. On the other hand, in the ex situ method, the reinforcement phase is introduced separately during the casting or processing of the alloy and remains "as is" without

significant interaction with the matrix. Consequently, the interface between the matrix and the reinforcement may not be as strong. Additionally, the volume fraction of the reinforcement phase tends to be smaller in the in situ technique compared to the ex situ method.

5.1 "in situ" Composites

The in situ composites are normally produced by adjusting the chemical composition of the alloy. When the alloy composition is chosen in such a way that it does not correspond exactly to the real glass-forming composition, then the product of solidification will not be a homogeneous glassy phase. Instead, a crystalline phase will coexist with the glassy phase. This method has been adopted in a variety of instances to produce the in situ composites

In the in situ method, the alloy is melted and forged directly into the mold. If the composition deviates extensively from the glass-forming composition range, the second (crystalline) segment forms and its quantity fraction is decided via the extent of deviation from the glass-forming composition range. The structure of the crystalline phase is normally dendritic since it types immediately from the melt. Instead of at once casting from the liquid state, if the alloy is homogenized in the soft (liquid + solid) vicinity and then cast, the crystalline phase bought will have a spherical form, and this is expected to in addition improve the mechanical properties.

If the second segment is received at some stage in subsequent processing of the thoroughly solidified casting, the microstructure of the section can be controlled. The grain dimension and structure of the second phase can be different. For example, if the glassy alloy is annealed at a low temperature, the grain dimension of the crystalline section will be of nanometric dimensions. Thus, different probabilities exist to achieve the favoured measurement and form and quantity fraction of the reinforcement phase thru this route.

5.2 "ex situ" composites

This strategy of creating the BMG composites has been exceptionally critical since one seem introduce a really huge volume division of the moment crystalline stage. The sorts of reinforcements used have been immaculate metals (tantalum, tungsten, molybdenum, nickel, copper, and titanium), alloys (1080 steel, stainless steel, and brass), and non metallics (SiC, precious stone, and graphite). Long

and persistent filaments, brief filaments, and particulates have been utilized. Particulates and short strands have been straightforwardly included to the soften and composites have been created. But, for long and ceaseless strands, the dissolve penetration method has been most commonly utilized.

6. Uses of BMGs

BMGs typically have exceptionally high hardness, yield strength, elasticity, high-temperature process ability, and excellent resistance to corrosion that are superior to their crystalline counterparts. Their use in normal daily life is as follows-

6.1 In Electrical and Electronics

Bulk metallic glasses have high electrical resistance, so they are used to make accurate standard resistance, magnetic resistance sensors and computer memories.

6.2 In Nuclear Reactor Engineering

Bulk metallic glasses are useful in preparing containers for nuclear waste disposal and magnets for fusion reactors because their magnetic properties are not affected by radiation. Chromium

and phosphorus-based metal glasses are used on the inner surface of reactor vessels because of their high corrosion resistance.

6.3 Defence

Instruments used by the military must be stronger, lighter and more effective at high stress and high temperatures. Now a day BMG composite KEPs can replace metallic material as it has a density similar to metallic materials and more of this it has self-sharpness behaviour.

6.4 Sports

The Golf Club head made from BMG (bulk metallic glass) is about twice as hard and nearly four times as elastic as the Ti drivers. Ti transfers only 70% of impact energy to a ball whereas BMG transfers impact energy to the ball is nearly 99%. BMGs are used to make such type of equipment that requires good rebound. Sports Equipment like a baseball bat, softball bat fishing equipment, hunting bows, scuba gear, gun, the frame of a bicycle etc.

6.5 Medical equipment

Instruments used in medical applications must be non-allergenic, and highly biocompatible.

REFERENCES

- Barsanescu, P. (2015). Extension of Mohr-Coulomb Theory for Ductile Materials. *Experimental Mechanics*, 55(7), 1389–1393. <https://doi.org/10.1007/s11340-015-0026-0>
- Battezzati, L., Baldissin, D., Habib, A., & Rizzi, P. (2009). Mechanical behaviour of metallic glasses related to thermal properties. *Journal of Physics: Conference Series*, 144, 012088. <https://doi.org/10.1088/1742-6596/144/1/012088>
- Bradt, R. C. (Ed.). (2005). *Fracture mechanics of ceramics. 14: Active materials, nanoscale materials, composites, glass and fundamentals: [proceedings of the 8th International Symposium on Fracture Mechanics of Ceramics, held February 25 - 28, 2003, at the University of Houston, Houston, Texas] / ed. by R. C. Bradt.*
- Byrne, C. J., & Eldrup, M. (2008). Bulk Metallic Glasses. *Science*, 321(5888), 502–503. <https://doi.org/10.1126/science.1158864>
- Chen, M. (2008). Mechanical Behavior of Metallic Glasses: Microscopic Understanding of Strength and Ductility. *Annual Review of Materials Research*, 38(1), 445–469. <https://doi.org/10.1146/annurev.matsci.38.060407.130226>
- George, T. F., Letfullin, R. R., & Zhang, G. (2011). *Bulk metallic glasses*. Nova Science Publishers. <http://site.ebrary.com/id/10686266>
- Hofmann, P. (2015). *Solid state physics: An introduction* (Second edition). Wiley-VCH, Verlag GmbH & Co. KGaA.
- Huang, X., Ling, Z., & Dai, L. H. (2014). Ductile-to-brittle transition in spallation of metallic glasses. *Journal of Applied Physics*, 116(14), 143503. <https://doi.org/10.1063/1.4897552>
- Laughlin, D. E., & Hono, K. (2014). *Physical metallurgy* (5th edition). Elsevier.
- Liao, Bing., Wu, S., & Yang, L. (2017). Free volume: An indicator of the glass-forming ability in binary alloys. *AIP Advances*, 7(10), 105101. <https://doi.org/10.1063/1.4996056>
- Liu, Y. H. et al., 2007. Super Plastic Bulk Metallic Glasses at Room Temperature. *Science*, 315(5817), 1385–1388. <https://doi.org/10.1126/science.1136726>
- Liu, Z. Q., Qu, R. T., & Zhang, Z. F. (2015). Elasticity dominates strength and failure in

- metallic glasses. *Journal of Applied Physics*, 117(1), 014901. <https://doi.org/10.1063/1.4905349>
13. Louzguine-Luzgin, D. V. et al., 2011. Deformation and Fracture Behavior of Metallic Glassy Alloys and Glassy-Crystal Composites. *Metallurgical and Materials Transactions A*, 42(6), 1504–1510. <https://doi.org/10.1007/s11661-010-0391-3>
14. Mota, R. M. O. et al., 2017. Criticality in Bulk Metallic Glass Constituent Elements. *JOM*, 69(11), 2156–2163. <https://doi.org/10.1007/s11837-017-2415-6>
15. Petrusenko, Y., Bakai, A., Neklyudov, I., Mikhailovskij, I., Bakai, S., Liaw, P. K., Huang, L., & Zhang, T. (2011). Defects and Plastic-Deformation Modes of Bulk-Metallic Glasses. *Metallurgical and Materials Transactions A*, 42(6), 1511–1515. <https://doi.org/10.1007/s11661-011-0693-0>
16. Sakaguchi, R. (2004). Prediction of composite elastic modulus and polymerization shrinkage by computational micromechanics. *Dental Materials*, 20(4), 397–401. <https://doi.org/10.1016/j.dental.2003.11.003>
17. Sun, G. Y., Chen, G., & Chen, G. L. (2011). Design, synthesis, and characterization of bulk metallic glass composite with enhanced plasticity. *Journal of Materials Science*, 46(15), 5216–5220. <https://doi.org/10.1007/s10853-011-5458-z>
18. Suryanarayana, C., & Inoue, A. (2013). Iron-based bulk metallic glasses. *International Materials Reviews*, 58(3), 131–166. <https://doi.org/10.1179/1743280412Y.0000000007>
19. Tong, P., Louca, D., Gu, X.-J., Poon, S. J., Shiflet, G. J., & Proffen, T. (2011). Fluctuations of the Local Atomic Environment with Chemical Alloying in Fe Bulk Metallic Glasses. *Metallurgical and Materials Transactions A*, 42(6), 1481–1485. <https://doi.org/10.1007/s11661-011-0695-y>
20. Vasiliev, V. V., & Morozov, E. (2014). *Advanced Mechanics of Composite Materials*. Elsevier Science. <http://qut.eblib.com.au/patron/FullRecord.aspx?p=293959>
21. Wang, A.-K. et al., 2014. Correlation between Atomic Size Ratio and Poisson's Ratio in Metallic Glasses. *Chinese Physics Letters*, 31(6), 066102. <https://doi.org/10.1088/0256-307X/31/6/066102>
22. Wang, W. H. (2006). Correlations between elastic moduli and properties in bulk metallic glasses. *Journal of Applied Physics*, 99(9), 093506. <https://doi.org/10.1063/1.2193060>
23. Wolf, S. E. et al., 2021. Design of a homologous series of molecular glassformers. *The Journal of Chemical Physics*, 155(22), 224503. <https://doi.org/10.1063/5.0066410>