

Metallic Glasses – Novel materials for applications in Nuclear Fusion

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Abstract—Novel alloys like Metallic Glasses hold the potential to revolutionise many scientific and industrial sectors including Nuclear Fusion. These metallic materials with amorphous atomic structure possess outstanding mechanical properties in combination with high corrosion resistance and high radiation tolerance. They can be made and shaped in unique ways impossible for conventional crystalline materials. Metallic Glasses also offer high compositional flexibility and can be tailored to various specific applications. Here, we give a brief overview on how the fusion sector can benefit from Metallic Glasses and, as examples, highlight some specific use cases. We also outline a pathway for the future development of Metallic Glasses specifically designed for the extreme environments occurring in Nuclear Fusion.

Index Terms—Novel alloys, Amorphous materials, Metallic Glasses, Radiation tolerance, casting, sputtering, structural materials, RF antennae, Nuclear Fusion, corrosion resistance.

I. INTRODUCTION

THE development of novel materials has always been the driver of technological advances. Nuclear Fusion (NF) is no exception. A special class of novel materials hitherto only marginally explored in this sector are Metallic Glasses (MGs). They consist mainly of metallic elements but possess a non-crystalline liquid-like *amorphous atomic structure* (inset of Fig. 2a). Different families of these fascinating materials based on a variety of elements offer a set of unprecedented properties with high appeal for a multitude of applications in NF. These properties, which are often superior to those of their crystalline counterparts with similar composition, can be directly traced back to the amorphous structure [1][2][3]. MGs are usually multi-component alloys. A high diversity in atomic sizes of the components cause the amorphous structure to be “jammed”, i.e. voids of different sizes are filled by atoms of different sizes (inset of Fig. 2a). Weak points like grain boundaries, slip planes and conventional defects (like vacancies) are absent [1]. Under mechanical load the atoms cannot move easily for plastic deformation to take place when the material is strained. The mechanical energy is stored elastically in the atomic bonds and is released when the load is removed. This leads to several

unique mechanical properties of MGs compared to crystalline metallic alloys like the mechanical strength being about three times higher than in crystalline counterparts with the same Young’s modulus (Fig. 3a) and elastic elongation limits of around 2% which is also about three times higher than in crystalline counterparts [1][2][3]. Furthermore, high hardness, high scratch resistance, high wear resistance, as well as high fracture toughness of MGs are observed [1][4]. However, it is often the combination of these properties making MGs uniquely suitable for many applications (Fig. 3b). The superior elastic properties usually also persist at cryogenic temperatures [5]. Research to increase the ductility of MGs is continuously progressing [4][6][7].



Fig. 1. MG rod ($\text{Zr}_{55}\text{Cu}_{30}\text{Ni}_{15}\text{Al}_{10}$, about $\varnothing 10$ mm, 100 mm long) produced at Cranfield University by tilt casting into a copper mould.

The absence of grains and grain boundaries leads to very smooth surfaces of MGs and high corrosion and oxidation resistance. High radiation tolerance as well as self-healing of radiation-induced structural changes has also been reported [8][9]. Both effects are closely related to the creation and temperature dependence of so-called free volume in the amorphous structure which occurs instead of atom-sized vacancies found in crystalline materials [1][9].

It is important to note that not all compositions and various families of MGs exhibit all the properties discussed here to the same extent. Depending on the specific intended application, it will always be necessary to select or tailor appropriate alloys. Currently, the achievable size of MG parts is still limited. Although mostly outweighed by their beneficial properties, overcoming or circumventing this constraint is a major aspect of MG research (cf. Fig. 3c).

MGs show several similarities with “traditional” oxide glasses although their chemical bonding is predominantly metallic in nature while that of oxide glasses is strongly covalent. For example, MGs can be worked similar to oxide glasses allowing completely new ways of processing metallic materials. In the following, after a few theoretical remarks, these properties and some of their possible applications in NF will be discussed.

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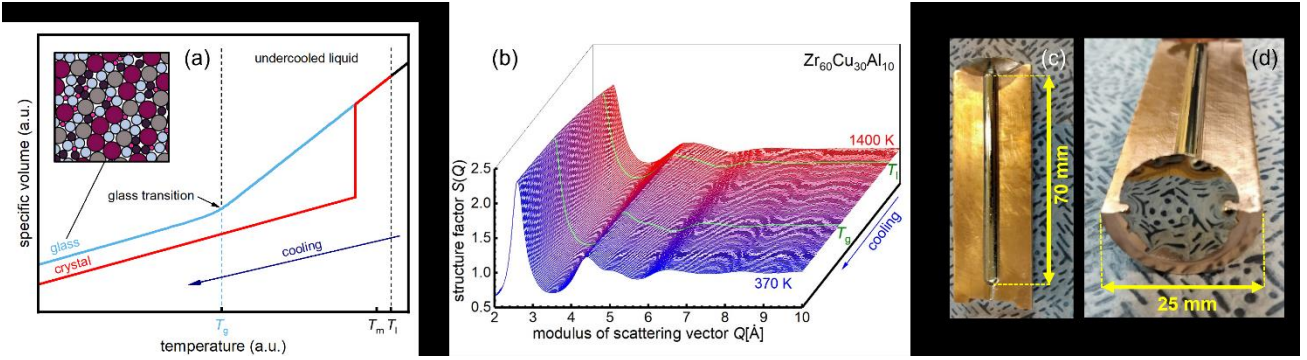


Fig. 2. (a) Schematic temperature dependence of the specific volume of a model alloy quenched from the liquid phase at high temperature. Depending on the cooling rate the (undercooled) liquid can crystallise (in this example slightly below the melting temperature T_m) or vitrify at the glass transition temperature T_g . The inset shows a sketch of a 2-dimensional 5-component model glass highlighting the multi-component nature of MGs with high diversity of atomic sizes causing the jammed structure responsible for the outstanding properties of MGs. **(b)** The structure factor $S(Q)$ of the MG forming alloy $Zr_{60}Cu_{30}Al_{10}$ ($T_l = 1207$ K) taken by synchrotron X-ray diffraction during cooling and vitrification [10]. No significant structural change at $T_g = 671$ K is visible, highlighting the very similar structure of liquid and glass rationalising the small solidification shrinkage during casting of MG parts. **(c)** Rod-shaped MG ($Zr_{55}Cu_{30}Ni_{15}Al_{10}$) prepared by suction casting into a water-cooled copper mould (Cranfield University) with one half of the mould removed after casting and **(d)** surplus material remaining outside the mould highlighting the typical smooth surface of MGs without additional treatment (cf. the reflection of the structured blue background).

II. THEORETICAL REMARKS

In the simplest view, a solid with an amorphous atomic structure is called a glass. Most commonly glasses, including MGs, are created when a (metallic) liquid is cooled rapidly enough that crystallisation is avoided and the amorphous atomic structure of the liquid is retained during solidification [1]. This special kind of solidification is called *vitrification* and takes place at the so-called *glass-transition temperature* T_g which is much lower than the liquidus temperature T_l (and the melting temperature T_m) of the alloy. Between T_l and T_g the alloy is in its *undercooled* (or *supercooled*) liquid (UCL) state. From above T_l down to T_g the alloy's viscosity increases by up to 15 orders of magnitude [1]. The high degree of undercooling does not only cause the density of the UCL to approach that of the crystallised material of the same composition but also leads to only a very small volume change during vitrification (Fig. 2a). The latter can also be seen to result from the very similar atomic structure of the MG compared to that of the UCL at T_g (Fig. 2b).

The propensity of an alloy to form a glass is called glass-forming ability (GFA) and can be expressed by the critical cooling rate R_c necessary to obtain the glassy state or by the maximal thickness t_{max} the material can be cast in with fully amorphous structure. The high diversity in atomic sizes mentioned above enhances the GFA as the jammed structure hinders diffusion of the atoms in the UCL state to reach their, energetically more favourable, positions in a crystalline structure of the same composition. Other factors, like chemical bonding characteristics between the components (electronic band structure), affect GFA as well [1][11][12][13][14].

By heating an MG above T_g , the material re-enters the UCL state, i.e. a highly viscous metallic liquid is present again which is of high relevance for several unique ways of processing MG alloys. Both, this transformation (i.e. on

heating) and the aforementioned vitrification (i.e. on cooling) are summarised under the term *glass transition*.

The many existing MG families (Fig. 3) and the usually high number of components in an MG allows for high adaptability to specific applications and given constraints (in NF for example related to high-shielding but low-activation behaviour). Addition of desired component elements may not only enhance applicability but also GFA [11]. A particular example is boron with both high neutron-capture cross section and small atomic size. The potential design space for desirable MGs is immensely big [15]. MGs share some aspects, especially their multi-component nature, with High-Entropy Alloys (HEAs) as another class of novel materials currently gaining a lot of attention. Several HEAs with properties relevant for NF, foremost high radiation tolerance, are amorphous when prepared as thin films [16][17][18].

III. MAKING AND SHAPING METALLIC GLASSES

One of the most important ways to manufacture parts of MGs is by casting in combination with rapid solidification. Techniques range from simple tilt casting (Fig. 1) over suction casting (Figs. 2c,d and 4l), die casting (Fig. 4g) to centrifugal casting. Other techniques starting in the liquid phase include melt spinning, planar-flow casting or splat quenching [1]. The small solidification shrinkage during vitrification (Fig. 2a) allows for *near net-shaped casting* of MG parts of various shapes and sizes. Such parts (e.g. Fig. 4a) can then be used with little to no need for further machining [5][19] which adds an important sustainability aspect to MGs.

Besides vitrification from the melt, MGs can also be prepared as films e.g. by sputtering, flash evaporation, electrodeposition, thermal spraying or interdiffusion of multilayers [1].

When heated above T_g , MG alloys can be shaped by blow moulding (similar to glassblowing of oxide glasses done since

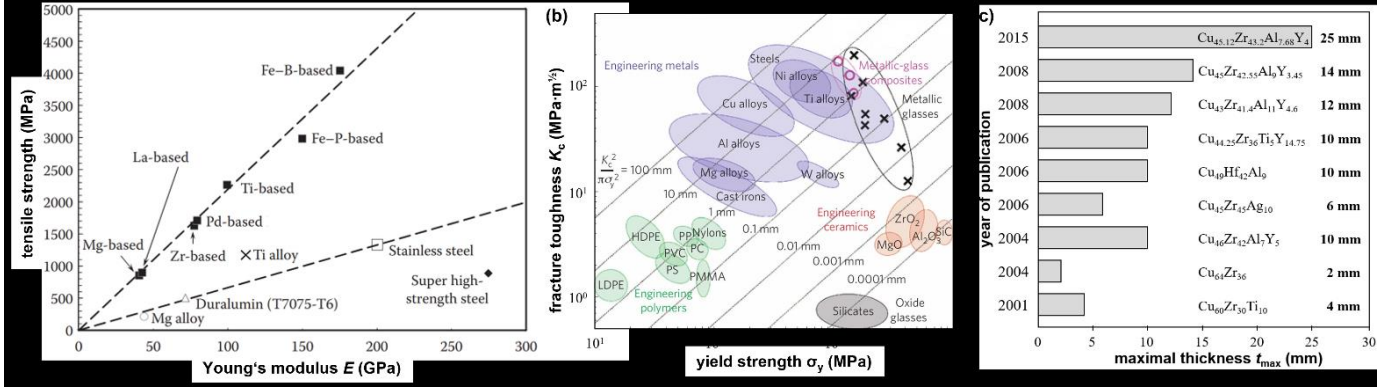


Fig. 3. (a) Relationship between tensile strength and Young's modulus for members of various MG families (black squares) in comparison to crystalline alloys with similar composition (a very similar relationship holds for Vickers hardness versus Young's modulus), adapted from [1]. (b) Fracture toughness K_{IC} versus yield strength σ_y for Ti-, Zr-, Fe- and Pd-based MGs (crosses) and MG composites (circles) in comparison with data for metallic-glass composites, oxide glasses, ceramics, polymers and crystalline engineering metals, adapted from [4]. (c) Compositional tuning of MGs to successively increase GFA (given in terms of the maximal casting thickness t_{max}) exemplified by a Cu-based family of MG (which also shows high resistance against He^{2+} irradiation [20]), adapted from [1].

centuries) to create seamless hollow shapes that can include undercuts, thermoplastic forming (e.g. moulding, rolling, extrusion) [21], electromagnetic pulsing [22] or imprinting on various length scales [21]. This offers ways of net-shaping metallic materials impossible in the crystalline case and allows for the production of parts with complex geometries and very fine details combined with the other outstanding properties of MGs outlined above. A wide UCL region $\Delta T_X = T_X - T_g$ of an MG is important in this respect, where T_X is the temperature above which the alloy adopts a crystalline structure and loses the unique properties associated with the glassy state. The same applies to additive manufacturing of MGs [23], which is increasingly coming into focus, as well as their welding and brazing [24]. In short, MGs can be stronger than steel while being as mouldable as plastic. So-called MG composites, i.e. alloys containing crystalline regions within a glassy matrix, can help to overcome current plasticity limitations of MGs [25]. Fig. 4 gives an overview of MG parts produced by various different techniques, mostly those unique to MGs.

IV. METALLIC GLASSES FOR NUCLEAR FUSION

As mentioned, it is possible to tailor the compositions of MGs to a wide variety of applications including those highly relevant for NF. For instance, MGs based on refractory metals can have high densities necessary for radiation shielding combined with high-temperature stability [26][27] and the discussed unique beneficial properties of MGs. While this class needs further exploration, already developed classes of MGs are promising for applications in NF exploiting their ability to outperform currently used crystalline materials. Both classes will be addressed in the following.

NF comprises a huge variety of environments with vastly different needs of materials. They range from the extremely harsh conditions with high temperatures and radiation levels in and close to the reactor cores to supporting infrastructure further away from it, where shielding capability and activation behaviour is less relevant, to cryogenic environments.

The response of MGs to a wide variety of different types of radiation, including neutrons, hydrogen (protons), helium (α particles) and heavier ions with various kinetic energies and fluences has been examined [8][20][28][29][30][31][32]. While investigations using neutrons with energies and fluences occurring in NF are scarce, several studies using heavy ions to emulate such conditions were conducted (cf. ref. [8] for a comparison). In general, a high radiation tolerance, in some cases even outperforming tungsten, has been found, but the effects on structure depend strongly on the particular compositions and conditions [9][30][33][34]. For instance, no crystallisation was observed in $Zr_{50}Cu_{40}Al_{10}$ MG under irradiation with Xe^+ ions of 200 MeV kinetic energy and a fluence of $1 \cdot 10^{14}$ ions/cm² [8] and changes mainly occur in the configuration of free volume. On the other hand, nanocrystals were found in $Zr_{61.5}Cu_{21.5}Fe_5Al_{12}$ after irradiation by 300 keV Ar^+ ions and a fluence of $3 \cdot 10^{15}$ ions/cm² [8]. Irradiation-induced nanometre-sized Hf precipitates in the amorphous matrix of $W_{24}Ta_{40}Cr_{18}V_5Hf_{13}$ were found to enhance the radiation tolerance as they may act as sinks for an irradiation-induced increase of free volume [17]. This highlights again the opportunities of the big palette of MGs to flexibly select appropriate alloy compositions for particular environments and applications. Reconfiguration of free volume is also made responsible for observed self-healing of irradiation-induced structural changes in MGs [8][9][33] which can be enhanced by elevated temperatures [8].

Harnessing the beneficial response to radiation together with the unique shaping capabilities of MGs could enable compact shielding encapsulating diagnostic equipment. The smooth surface of MGs would make radiation-tolerant optical diagnostic mirrors possible, surpassing the performance of polycrystalline mirrors which suffer from erosion due to differently orientated crystal grains on their surfaces [20] [28][32][35][36][37][38]. MGs can also act as flexible support structures for mirrors with high tilting angles [39].

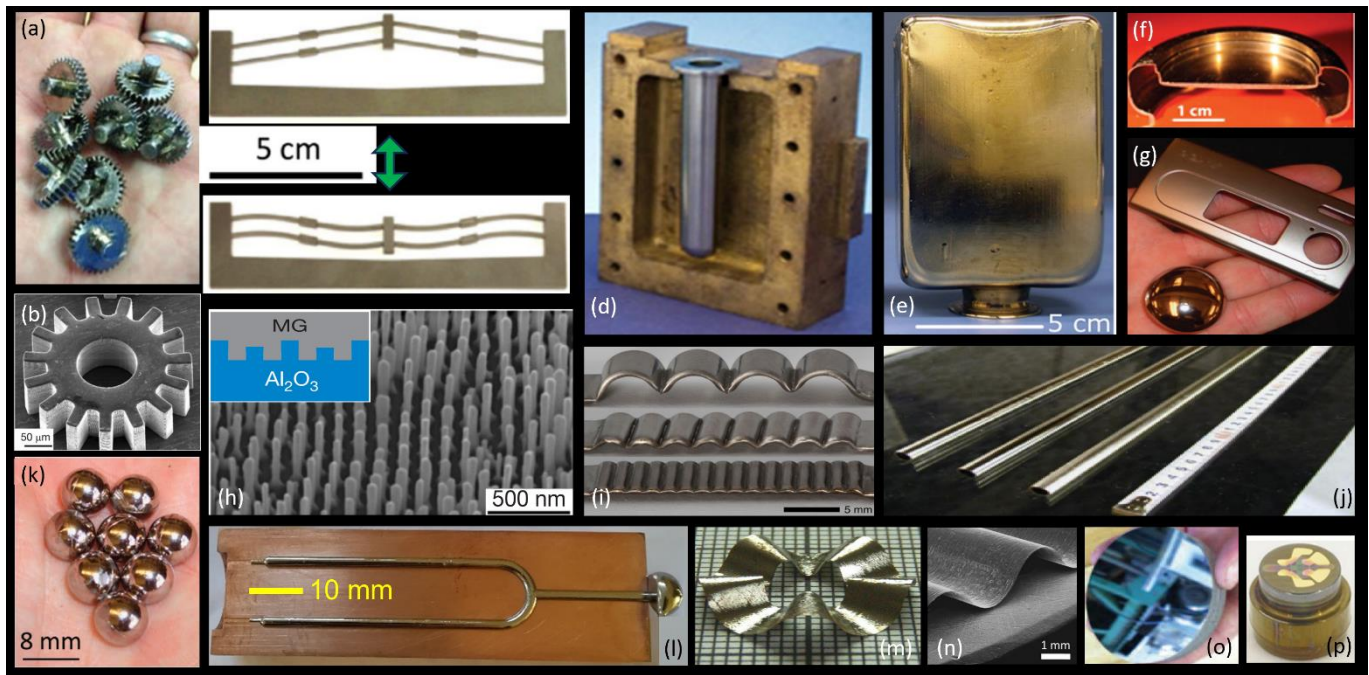


Fig. 4. Examples for different ways of processing and applications of MG. (a) Near net-shape cast (Ti-based) [19] and (b) nano-moulded (Pt-based) gears [40], (c) two states of an MG (Zr-based) compliant mechanism [41], (d), (e) and (f) blow-moulded MG shapes (Zr-based) [42], (g) die-cast part and MG (Zr-based) feedstock [43], (h) nano-moulded MG (Pt-based) by embossing into an alumina mould [40], (i) MG (Zr-based) shaped by electromagnetic pulsing [22], (j) MG (Pd-based) tubes [1], (k) MG ball bearings [43], (l) suction cast MG (Zr-based) part inside copper mould (Cranfield University), (m) and (n) novel wave springs made from a planar-flow cast MG (Fe-based) foil [44], (o) MG mirror [37] and (p) pressure sensor with MG (Zr-based) diaphragm [1].

Some further examples of applications that can benefit from the outstanding mechanical properties of MGs in combination with their radiation tolerance are bolts/standoffs with considerably higher tensile strength than that of conventional heat-treated high strength steel bolts, springs or diaphragms for pressure sensors (Fig. 4p) [1]. The high wear resistance of MGs allows for lubrication-free mechanisms [5][19] and can support robotics or other mechanisms in radiative environments. Gears with diameters down to the sub-millimetre range (Fig. 4a,b) [40] have been demonstrated as well as novel springs and actuators (Fig. 4m,n) [44][45], ball bearings (Fig. 4k) and compliant mechanisms (Fig. 4c) [41].

NF-relevant radio-frequency (RF) antennae and waveguides, or parts thereof, can make use of MGs. Although their electrical conductivity is lower compared to crystalline counterparts, their radiation tolerance, low surface roughness, high fracture toughness and advantageous modes of production (e.g. by blow moulding with manufacturability of fine surface details) can make MGs promising candidates in this respect. MGs can also be used as materials for electromagnetic shields or magnetic sensors and actuators [1].

Their elastic properties make MGs appealing as reusable metallic seals for flanges [44], especially, again, in conjunction with their radiation tolerance. Furthermore, exploiting the malleability and superplastic formability of MG alloys in their UCL state they can be used to join (braz) other materials (including crystalline ones) [46][47] helping to alleviate the current size limitations of MGs [21][48][49]. Other methods of joining MGs including laser or electron-beam welding, friction welding, as well as ultrasonic-assisted

joining have been demonstrated [24]. MGs can be the materials of choice for projectiles for impact inertial fusion concepts [50].

The high corrosion resistance of MGs might be exploited in reactor concepts using liquid (breeding) blankets [51]. Surfaces coming in contact with materials like liquid lithium, lithium alloys or molten salts could be coated with MGs or MG pipes (Fig. 4j) could be used for transport of such liquids. MG coatings with higher corrosion resistance than 304 stainless steel have been produced on various metallic substrates using high-velocity powder-spray coating techniques [52].

The free volume of the amorphous atomic structure allows for higher hydrogen solubilities and higher resistance to hydrogen-embrittlement of MGs as well as lower cavity swelling compared to crystalline counterparts, making MGs excellent candidates for high-performance applications in hydrogen environments [53]. The separation of hydrogen isotopes using MG membranes was shown [54][55] but further work in relation to tritium is necessary.

Major alloy development efforts need to be targeted to MGs that will be employed closest to the fusion plasma where not only the radiation levels are extreme but also high temperatures prevail. Here, High-Temperature MGs (HTMGs) and High-Density MGs (HDMGs) are essential. To date, only little is known about these emerging classes of MGs [26][27] [56]. The few compositions developed so far possess advantageous properties like high T_g , T_x , ΔT_x and density but still lack sufficient GFA and contain very expensive chemical elements or those with undesirable high activation properties

[27][56]. Compositions based on tungsten promise to be a valid starting point but further compositional design is mandatory, mainly by adding low-activation elements which simultaneously satisfy the empirical rules for high GFA outlined in Section II. The GFA of these novel materials is expected to increase continuously as it has previously been the case for other families of MGs (Fig. 3c illustrates this for a family of copper-based MGs). Charting the vast design space to find appropriate compositions will be supported by modern experimental and computational methods like high-throughput screening and machine learning as well as thermodynamic calculations. Compositions with high T_g , T_X and ΔT_X are sought to allow for the unique possibilities of manufacturing MG parts which retain their outstanding properties under the extreme conditions in NF.

V. CONCLUSIONS AND OUTLOOK

Dedicated Metallic-Glass research for Nuclear Fusion is still in its infancy. The combination of several outstanding properties of these fascinating materials with high potential for various applications in Nuclear Fusion make their application desirable in this field. While in many cases already developed Metallic Glasses can be directly used in Nuclear Fusion, it will be necessary to optimise their compositions, e.g. with respect to low-activation behaviour, for their broader application in this field. This is enabled by the vast design space and compositional flexibility of these materials. Novel Metallic Glasses based on refractory metals, especially tungsten, with high glass-transition and crystallisation temperatures, wide undercooled liquid regions, high radiation tolerance and shielding capability as well as low-activation behaviour will be in the centre of future design efforts. Furthermore, increasing glass-forming ability and plasticity are important goals for the ongoing research efforts. Metallic Glasses bear the prospect of boosting the viability of future Nuclear Fusion power plants.

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