

Review



Review of the Recent Development in Metallic Glass and Its Composites

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Abstract: Metallic glasses are known for their mechanical properties but lack plasticity. This could be prevented by combining them with other materials or by inducing a second phase to form a composite. These composites have enhanced thermo-physical properties. The review paper aims to outline a summary of the current research done on metallic glass and its composites. A background in the history, properties, and their applications is discussed. Recent developments in biocompatible metallic glass composites, fiber-reinforced metallic glass, ex situ and in situ, are discussed.

Keywords: metallic glass; composite; biocompatible metallic glass composite; in situ; ex situ composite

1. Introduction

Metallic glass is known for its advanced engineering properties. They are amorphous. In 1960, Klement et al. from the California Institute of Technology developed the first metallic glass by using gold silicon alloy [1]. It was detected that 25 percent of the gold was amorphous when quenched. In 1966, studies were conducted on the effect of different cooling rates during rapid quenching of metals from spat cooling. This resulted in the formation of metastable phases, such as in amorphous alloys [2]. Binary Pd–Si glass, ternary Pd–Au–Si, and Pd–Cu–Si were prepared at room temperature by quenching at different cooling rates [3]. In 1975, $Fe_{40}Ni_{40}B_{20}$ metallic glass was produced by a melt spinning technique. Inoue et al. showed the large glass-forming ability of the La-Al-Ni amorphous alloys [4]. Phase separation of Au₅₅Pb_{22.5}Sb_{22.5} metallic glass was studied and showed the influence of the surface energy on the metallic glass. It was concluded that surface energy had a contribution to the decomposition process [5]. Drehman et al. showed the preparation of $Pd_{40}Ni_{40}P_{20}$ by the undercooling process. During formation, crystallization occurred uniformly, and the activation energy was calculated [6]. The Pd–Ge and Cu–Zr alloys had higher thermal properties, compared to metallic glass prepared by the melt-spinning technique [7]. $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10,0}$ metallic glass was alloyed by the induction melting process at a cooling rate of less than 10 K/s. It had excellent glass-forming ability and the effect of crystallization was studied [8]. Metallic glass is mainly made up of two types: metal-metalloid and metal-metal combinations. In metal-metalloid [9], the metalloid constituent comprises 10–20% of the composition. The metal constituent is more than 80%. Some of the examples of metal–metalloid metallic glass are $Pd_{77}Cu_6Si_{17}$, Fe₄₀Ni₄₀B₂₀, and Ni₄₉Fe₂₉B₆P₁₄Si₂. In metal-metal, the metal can have any compositional ratio. $Ni_{60}Nb_{40}$, $La_{80}Au_{20}$, and $Fe_{90}Zr_{10}$ are some examples. Some of the commonly used metallic glass are Zr-based [10–13], Fe-based [14–16], Co-based [17,18], Ni-based [19,20], Cu-based [21,22], and Pd-based [23,24] types. Metallic glass is used in biomedical applications [25,26]. Zr-based metallic glass can be used in stents [27]. Fe–B–Nd–Nb metallic glass is used in micro cantilevers [28]. Metallic glass can be used as a micro scanner [29]. They are used in electrical applications [30] and catalysis [31]. Metallic glass is generally prepared by the rapid cooling of the molten liquid [32], melt-spinning [7,33], powder metallurgy [34], liquid squat quenching [35], magnetron sputtering [36], and pulsed laser



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). quenching [37]. Metallic glass is formed from the continuous cooling of the liquid state. It is generally non-crystalline in nature. The major criterion for the formation of metallic glass is its glass-forming ability (GFA). The glass formation ability is dependent on the critical cooling rate (R_c). The critical cooling rate (R_c) is the minimum cooling rate required to keep the molten amorphous, without any formation of the crystal precipitates during solidification. The lower the R_c, the higher the glass-forming ability (Table 1). The main criteria that are used to measure the glass-forming ability are reduced glass transition temperature (T_{rg}) and supercooled region (T_{sr}) . The reduced glass transition temperature (T_{rg}) is defined as the proportion of the glass transition temperature (T_g) to the melting temperature (T_m) of the metallic glass. The supercooled region is the region in between the crystallization temperature (T_x) and the glass transition temperature (T_g). Metallic glass is formed near their eutectic points as compared to the non-eutectic points. The offset liquidus temperature (T_1) showed that T_g/T_1 have a better correlation criterion to have a glass-forming ability than T_g/T_m [38]. The GFA is directly proportional to the thickness of the sample and inversely so to the critical cooling rate (R_c). Mukherjee et al. showed that the volume change in the crystallization is correlated with the viscosity at the melting temperature [39]. The fragility index (m) is related to the glass forming and plasticity of the metallic glass [40]. The glass forming ability was increased with the addition of Co in $Ce_{70x}Al_{10}Cu_{20}Co_x$. It was due to the increase in the Al-site symmetry and is a characteristic of the local structure.

Table 1. Different critical cooling rates (R_c) of metallic glass.

Metallic Glass	R_{c} (K s ⁻¹)	References
Au ₅₅ Cu ₂₅ Si ₂₀	$3.4 imes10^4$	[41]
$Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$	140–190	[42]
$Co_{75}Si_{15}B_{10}$	$3.8 imes10^8$	[43]
Fe ₇₉ Si ₁₀ B ₁₁	$3.7 imes10^8$	[43]
Ni ₇₅ Si ₈ B ₁₇	$2.4 imes10^8$	[43]
Pd _{77.5} Cu ₆ Si _{16.5}	$1.5 imes 10^8$	[43]
$Pd_{40}Ni_{40}P_{20}$	$1.4 imes10^7$	[43]
Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni _{10.0} Be _{22.5}	≤ 10	[44]
Al ₅₁ Ge ₃₅ Ni ₁₄	10^{4}	[45]
Fe ₇₆ Si ₉ B ₁₀ P ₅	\leq 550	[46]
Pd ₄₀ Cu ₃₀ Ni ₁₀ P ₂₀	$2.08 imes10^{-5}$	[47]
Au49Ag5.5Pd2.3Cu26.9Si16.3	600	[48]
Zr _{52.5} Ti ₅ Al ₁₀ Ni _{14.6} Cu _{17.9}	$10^3 - 10^5$	[49]
$Fe_{67}Mo_{4.5}Cr_{2.3}Al_2Si_3C_7P_{8.7}B_{5.5}$	$9.3 imes10^4$	[50]
$Al_{86}Ni_6Y_{4.5}Co_2La_{1.5}$	3.01×10^3	[51]

Metallic glass is known for its mechanical properties [52,53] and has corrosion resistance [54]. The amorphous metals (Figure 1) have a better elastic limit and Young's modulus, compared to (the mechanical properties of) the traditional alloys. The defects and grain boundaries in the crystalline solution make crystalline alloys susceptible to stress corrosion cracking and intergranular corrosion. Peter et al. showed the corrosion resistance of the metallic glass in an aqueous solution as compared to the crystalline materials [55]. They have higher wear resistance [56] and elastic behavior [57] compared to crystalline alloys.

Metallic glass exhibits physical-thermal properties in the supercooled region. They soften in the supercooled region and can be easily transformed into the desired form [58]. Mechanical properties of Zr–10Al–5Ti–17.9Cu–14.6Ni in the supercooled region had excellent mechanical properties. This was due to the formation of nano-crystallites in the supercooled region [59]. The $Ti_{46}Zr_{20}V_{12}Cu_5Be_{17}$ metallic glass matrix composite showed an increase in the tensile ductility and necking in the supercooled region [60].



Figure 1. The elastic limit (MPa) plotted against Young's modulus (GPa) for different materials. In total, 1507 metals, metal–matrix composites, alloys, and metallic glasses (at%) are compared. (σ_y/E) contour represents elastic strain limit and (σ_y^2/E) as resilience. Reproduced from the permission of ref. [53]. Copyright 2009 Elsevier Ltd.

Metallic glass has no crystal defect, and has high strength, hardness, and yield strength. It has certain shortcomings, such as a brittle nature and low plasticity [61]. This is due to the absence of crystal defects and grain boundaries. The lack of ductility causes a deterioration in the mechanical properties of the metallic glass. The mechanical properties of the metallic glass in a non-equilibrium state are shifted toward the metastable equilibrium. This physical process is known as structural relaxation [62]. This causes modification in the physical properties, such as viscoelastic properties, elasticity, anelastic, magnetic, and corrosion, and other properties that are influenced by structural relaxation [63]. There are two kinds of structural relaxations: α -relaxation and β -relaxation. α -relaxation causes glass transition phenomena and vitrification [64]. It generally disappears below glass transition temperature [64]. The beta-relaxation occurs at high temperatures, affects the mechanical properties of the metallic glass, and influences the plasticity mechanism [65]. The brittleness of the metallic glass can be overcome by the activation of shear zones [66]. It is defined as an irreversible shear strain that occurs when stress is applied to a localized deformed noncrystalline solid. This, in other words, can be called the formation of the shear bands [67]. When stress is induced, plastic deformation occurs by the shearing of the material relative to its resting part. This causes a change in the shape of the material. The localized cluster is plastically deformed, causing it to become softer than its undeformed surroundings. This causes more flow of plastic strain into thin bands. They can occur by external and internal factors. Maass et al. showed that the strength of Zr_{52.2}Ti₅Cu_{17.9}Ni_{14.6}Al₁₀ increases with a decrease in temperature. Shear band activity is increased with an inhomogeneous flow through a single shear band at cryogenic temperatures [68]. The shear band density, bending strain, and other mechanical properties of Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5} and Zr₃₅Ti₃₀Cu_{8.25}Be_{26.75} metallic glasses were decreased with an increase in the temperature. When the same strain was applied, the shear band at lower temperature produced multiple bands with smaller lengths, leading to increased properties [69].

Due to the catastrophic failure and brittle nature of metallic glass, researchers have developed composites with excellent thermo-physical properties.

The aim of the present work is to provide a brief overview of the recent development in metallic glass with a stress on the progress in the last 10 years. *Please note that bulk metallic glass is considered and written as metallic glass in this review.*

2. Biocompatible Metallic Glass and Their Composites

Metallic glasses are new in the field of biomedical applications with superior toughness, strength, and ductility, compared to crystalline alloys. Earlier, metallic glasses were used for structural engineering, due to their high mechanical properties. Metallic glasses are nowadays used as biomaterial implants.

Metallic crystalline materials, such as titanium alloys, Zr alloys, and stainless steel, are used in cardiovascular stents, hip joints, and bone implants (orthopedic joints) [70].

These crystalline metals have low strength, low wear, and corrosion resistance. Complex implants can be made from metallic glass because of their atomic structure, promising chemistry, and surface configurations. These properties can construct a biological response (Figure 2) with excellent properties over the present metallic biomaterials. Figure 2 also explains that the combination of amorphous structures with metallic constituents produces bio-metallic glasses. Biomedical metallic glasses have a high elastic modulus at 2%, compared to human bone (1%) and under stress, they have a unique ability to flex with the natural bending bone. This concludes that stress will be uniformly distributed, reducing the stress shielding effect, and the healing rate will be achieved faster [71].



Figure 2. The bio-metallic glass is formed by bioglass and crystalline bio-metallic alloys. This also shows the relationship between bioglass, bio-metallic alloys, and bio-metallic glass. Reproduced with permission from ref. [71]. Copyright 2016 Elsevier Ltd.

Metallic glass is used in medical–surgical equipment [72], cardiovascular stents [73] and orthopedic implants [74].

2.1. Ti-Based Biomaterial Metallic Glass

Titanium-based metallic glass is used in implant applications and has better corrosion properties, higher fracture strength, and a lower Young's modulus than crystalline materials. $Ti_{45}Zr_{10}Cu_{31}Pd_{10}Sn_4$ [75] was prepared by gas atomization and porous $Ti_{45}Zr_{10}Cu_{31}Pd_{10}Sn_4$ by Spark Plasma sintering (SPS). Porous metallic glass has better functionality than the commercially used Ti and Ti–6Al–4V implantable biomaterials. The decrease in the porosity in the metallic glasses causes an increase in Young's modulus and the compressive strength and a decrease in the corrosion resistance. It showed better biocompatibility than the commercial implantable biomedical materials. Similar work was done by Xie et al. [76] in which $Ti_{45}Zr_{10}Cu_{31}Pd_{10}Sn_4$ metallic glass was made by the combination of gas atomization and NaCl powder and SPS. NaCl powder was used to keep the porosity under control. The composite exhibited three times higher yield strength than human bone and could be used for surgical implants. $Ti_{51}Zr_5Cu_{41}Sn_3$ [77] showed better wear resistance and tribological properties than the pure Ti in the SBF (simulated

body fluid). It also showed good biocompatibility in vitro than the $Ti_{45}Zr_5Cu_{41}Ni_9$ and $Ti_{45}Zr_5Cu_{41}Ni_6Sn_3$. A thin-film metallic glass [78] of different ratios, Ti–Cu–Pd–Zr and Ti–Cu–Pd–Zr: B were fabricated by pulsed laser deposition (PLD). Boron-added metallic glass (Ti–Cu–Pd–Zr: B) showed good biocompatibility and corrosion resistance. The glass transition temperature was increased with an increase in the boron percentage. There was non-agglomeration of the RBC (red blood cell) in TFMGs after 30 minutes. The morphology of the TiB-2 cell (Figure 3) shows the disturbed nature with the addition of EDTA to the cell.



Figure 3. Hemocompatibility tests for different TFMGs (Ti-based thin film metallic glasses). (**a**) Control uncoated TFMGs, (**b**) TiB-0 (without Boron), (**c**) TiB-1 (4% B), (**d**) TiB-2 (8% B) and (**e**) TiB-3(14% B). Reproduced with permission from ref. [78]. Copyright 2021 Elsevier B.V.

Ti-based metallic glasses Ti₄₅Zr₄₀Si₁₅ (Cu-free), Ti₄₅Zr₄₀Si₁₀Cu₅ (low-Cu), and Ti₄₅Zr₂₀Cu₃₅ (high-Cu) [79] were prepared by different Cu proportions. It showed that metallic glass with low content of Cu had good biocompatibility and low cytotoxicity, compared to pure Ti. Ti₄₅Zr₂₀Cu₃₅ (high Cu) showed poor in vitro viability, due to the higher content of the Cu. This suggests that the $Ti_{45}Zr_{40}Si_{15}$ (Cu-free), can be used in biomaterials. $Ti_{47}Cu_{38-x}Zr_{7.5}Fe_{2.5}Sn_2Si_1Ag_2Ta_x$ (x = 1–4) [80] were prepared by copper mold casting. The supercooled region of the metallic glass decreased with an increase in Ta content. The material showed good bio-corrosion resistance, mechanical properties, and a large, supercooled region. Laser surface remelting was used from an in situ bonded coating of the Ti₄₇Cu₃₈Zr_{7.5}Fe_{2.5}Sn₂Si₁Nb₂ metallic glass [81]. The additional Nb formed an oxide layer, which prevented corrosion. There was an increase in the hardness and a decrease in the elastic modulus. The non-toxic nature, low elastic modulus, and corrosion resistance (Table 2) can ensure the using of metallic glass as a biocorrosion biomaterial. Nb was added to Ti-Cu-Zr–Fe–Sn–Si–Ag [82] metallic glass, and $Ti_{47}Cu_{38-x}Zr_{7.5}Fe_{2.5}Sn_2Si_1Ag_2Nb_x$ (x = 0, 1, 2; at %) was prepared. The addition of Nb showed a decrease in the glass transition temperature, superior bio-corrosion resistance, good in vitro compatibility, and excellent mechanical properties. Ti₄₀Zr₁₀Cu₃₆Pd₁₄ [83] metallic glass was compared with conventional Ti–6Al– 4V and could be used in dental implantology. It showed high thermal stability, cytocompatibility, resistance to sterilization, and good corrosion resistance. These properties ensure that the material can be considered biomaterial. A glassy matrix Ti₇₅Zr₁₀Si₁₅ with embedded $Ti_{60}Zr_{10}Nb_{15}Si_{15}$ [84] was prepared by melt spinning with the formation of single β -type nanocrystals. Stable surface passivity was due to the homogeneous distribution of the constituents. Nb improved the glass-forming ability, mechanical properties, and resistance toward the pitting corrosion. Hydroxyapatite was formed in the metallic glass in SBF (simulated body fluid). Ti₆₀Zr₁₀Nb₁₅Si₁₅ showed wear and bio-corrosion resistance. The oxide layer was formed in Ti_{41.5}Zr_{2.5}Hf₅Cu_{37.5}Ni_{7.5}Si₁Sn₅ [85] and showed good corrosion resistance, and hardness. Pitting corrosion was higher in the artificial saliva solution than in SBF (simulated body fluid). Ti_{41.5}Zr_{2.5}Hf₅Cu_{37.5}Ni_{7.5}Si₁Sn₅ has lower cell viability L929

and NIH3T3 cells. This shows that metallic glass can be used in bone tissue and has excellent osseointegration. Ti-based nano glass composite with sub-micro-nanometer-sized hierarchical glassy structure was prepared by magnetron sputtering. Enhancement in cell proliferation, better biocompatibility, and bioactivity was attained by the formation of button-like clumps [86].

Chemical Composition	Preparation Method	Young's Modulus (GPa)	Compressive strength (MPa)	$\begin{array}{c} Corrosion \ Values \\ E_{corr}(V)/I_{corr} \ (A \ m^{-2}) \end{array}$	Reference
$Ti_{45}Zr_{10}Cu_{31}Pd_{10}Sn_{4}$	Gas atomization	100 ± 3.2	2060 ± 85	$E_{corr} = -0.206$	[75]
$Ti_{45}Zr_{10}Cu_{31}Pd_{10}Sn_{4}$	Spark Plasma sintering	10–30	2060	_	[76]
$Ti_{51}Zr_5Cu_{41}Sn_3$	Laser Cladding	-	-	$I_{\rm corr} = 10^{-5}$	[77]
$\mathrm{Ti}_{45}\mathrm{Zr}_5\mathrm{Cu}_{41}\mathrm{Ni}_6\mathrm{Sn}_3$	Pulsed laser deposition	-	-	$I_{corr} = 1.33$	[78]
Ti ₄₅ Zr ₂₀ Cu ₃₅ (high-Cu)	Ti ₄₅ Zr ₂₀ Cu ₃₅ (high-Cu)	77	-	E_{corr} = -0.259 \pm 0.041	[79]
$\begin{array}{c} {\rm Ti}_{47}{\rm Cu}_{38-x}{\rm Zr}_{7.5}{\rm Fe}_{2.5}{\rm Sn}_{2}{\rm Si}_{1}{\rm Ag}_{2}{\rm Ta}_{x}\\ (x=1\!-\!\!4)\end{array}$	Copper mold casting	100	2028 ± 32	_	[80]
$Ti_{47}Cu_{38}Zr_{7.5}Fe_{2.5}Sn_2Si_1Nb_2$	Laser surface remelting	153.6	-	$I_{corr} = 12 \times 10^{-6}$	[81]
$\begin{array}{c} Ti_{47}Cu_{38-x}Zr_{7.5}Fe_{2.5}Sn_{2}Si_{1}Ag_{2}Nb_{x}\\ (x=0,1,2;at\%) \end{array}$	Melt spinning Process	100.4 ± 0.1	2010 ± 66	$I_{\rm corr} = 0.1 \ {\rm Am}^{-2}$	[82]
$Ti_{40}Zr_{10}Cu_{36}Pd_{14}$	Tilt copper mold-casting	96	1930	$I_{corr\text{=}}6\times10^{-9}$	[83]
${\rm Ti}_{60}{\rm Zr}_{10}{\rm Nb}_{15}{\rm Si}_{15}$	Melt spinning	-	_	$E_{corr}=-0.195\pm0.025$	[84]
$Ti_{41.5}Zr_{2.5}Hf_5Cu_{37.5}Ni_{7.5}Si_1Sn_5$	Induction heating	150.4 ± 4.7	2000 ± 78	$I_{\rm corr} = 10^{-5}$	[85]

Table 2. Mechanical and corrosion properties of the Ti-based metallic glass and composite.

2.2. Zr-Based Biomaterial Metallic Glass

Zr-based metallic glass has anticipated properties in orthopedic applications [87]. It is used in arthroplasty, bone screws, and intramedullary nails. The main problem with Zr-based metallic glass is that it does not allow adhesion and tissue growth at the host site. Metallic glass $Zr_{44}Ti_{11}Cu_{10}Ni_{11}Be_{25}$ [88] was converted into ceramic films. Ceramic conversion treatment (CCT) in an oxidizing medium was used in the supercooled region of the metallic glass to convert its surface. Thermal oxidation was performed at 350 °C for 40 h and at 380 °C for 4.5 h to alter the surface properties. There was an increase in the surface hardness and Young's modulus (Table 3), and the coefficient of friction was reduced. SAOS-2 human osteoblast-like cells increased surface coverage for the untreated surface. This shows that metallic glass increased its biocompatibility and tribological properties. The surface quality of the Zr-based metallic glass (Zr₆₇Cu_{10.6}Ni_{9.8}Ti_{8.8}Be_{3.8}) [89] was improved by bioactive hydroxyapatite suspended powder in dielectric fluid from electro-discharge machining (EDM). The surface hardness was increased and a crack-free HA-EDMed surface, with nanopores, was achieved. Tribocorosion was studied for Zr₆₅Cu₁₈Ni₇Al₁₀, and Zr₅₅Cu₃₀Ni₅Al₁₀ found that Zr₆₅Cu₁₈Ni₇Al₁₀ [90] has better plasticity and can be used as a potential load-bearing implant. Abrasive wear was experienced in both metallic glasses. The passive nature of the Zr₆₅Cu₁₈Ni₇Al₁₀ showed a negative effect on tribological corrosion. $Zr_{48}Cu_{36}A_{18}Ag_8$ [91] thin film (at.%) was prepared by a 316L stainless steel substrate by applying magnetron sputtering. The membrane should have good scratch resistance, mechanical properties, and lower Young's modulus. TFMG-coated steels showed good corrosion resistance in SBF (simulated body fluid) and a non-cytotoxic nature in L929 cells. Low energy ion implantation [92] was done on the $(Zr_{0.55}Al_{0.10}Ni_{0.05}Cu_{0.30})_{99}Y_1$ to improve the biocompatibility and activity of the metallic glass. Ca-ion showed an increase in cell adhesion and changed the cell behavior. A higher cell proliferation was observed in Ni-free $Zr_{60 + x}Ti_{2.5}Al_{10}Fe_{12.5 - x}Cu_{10}Ag_5$ (at. %, x = 0, 2.5, 5) [93]. $Zr_{55}Cu_{30}Ni_5Al_{10}$ based metallic glass shows the highest wear rates in the different electrolyte systems (NaCl, phosphate solution with and without protein) as compared to the crystalline structure. The formation of the nanocrystalline (Zr_2Cu) leads to the formation of a passive layer, leading to corrosion

resistance (Figure 4). The author concluded that the Zr-based metallic glass should be mixed with the (Zr₂Cu) nanocrystalline particles to improve the passivation [94].

Table 3. Mechanical and corrosion properties of the Zr-based metallic glass and composite.

Chemical Composition	Preparation Method	Young's Modulus (GPa)	Compressive Strength (MPa)	Corrosion Values E _{corr} (V)/I _{corr} (A m ⁻²)	Reference
$Zr_{44}Ti_{11}Cu_{10}Ni_{11}Be_2$	Ceramic conversion treatments	145.70 ± 3.13	-	$E_{corr} = -0.02 V$	[88]
$Zr_{48}Cu_{36}Al_8Ag_8$	Magnetron sputtering	113.92	-	$I_{corr}=7.24\times10^{-6}$	[91]
$\begin{array}{c} Zr_{60+x}Ti_{2.5}Al_{10}Fe_{12.5-x}Cu_{10}Ag_{5}\\ (at.\%,x=0,2.5,5) \end{array}$	Copper mold casting	70–78	$240-255 \pm 3$	$I_{corr} = 0.86 - 1.23$	[93]



Figure 4. SEM images of tribocorrosion wear of (**a**) c-BMG, (**b**) a-BMG, and (**c**) Zr and alumina counterparts, (**d**) c-BMG, (**e**) a-BMG, and (**f**) Zr. Reproduced with permission from ref. [94]. Copyright © 2021 Elsevier B.V.

Ni-free $Zr_{65}Ti_{2.5}Al_{10}Fe_{7.5}Cu_{10}Ag$ showed good mechanical properties and in vitro biocompatibility [95]. $Zr_{55}Al_{10}Cu_{30}Ni_5$ was alloyed with 1 at.% yttrium for surface roughness and cell behavior. The addition of 1 at.% yttrium did not have any substantial effect on proliferation and cell adhesion, but a decrease in alkaline phosphatase (ALP) activity was seen [96].

2.3. Magnesium-Based Biomedical Metallic Glass

Magnesium alloys degrade over time and do not need surgery to remove them. They have a density similar to bone $(1.8-2.1 \text{ g/cm}^3)$ and can be used as an allograft [97]. In vivo studies of Mg₆₆Zn₃₀Ca₄ and PCL composite [97] were examined and it was found that the composite was biocompatible. The composite properties can withstand 100% elongation when stress is applied and have thermal properties. Scaffolds of PCL/Mg metallic glass and PCL/nHA/Mg metallic glass [98], when immersed in SBF (simulated body fluid), showed their bioactivity. The mechanical properties were affected faster in the early stages of the hydrolysis but were slower later regarding in vitro loss. The composite scaffolds also controlled magnesium release. The scaffolds have better mechanical properties, hemocompatibility and can be used in orthopedic implants. The bio-corrosion and cytotoxicity of two relaxed and crystallized Mg₇₀Zn₂₆Ca₄ ribbons [99] in MTT (tetrazolium-based colorimetric assay) showed that the relaxed metallic glass had better biocorrosion

resistance and biocompatibility. MTT (tetrazolium-based colorimetric assay) assay used with Schwann cells concluded its application in nerve tissue regeneration. Tribological studies of Mg₆₅Zn₃₀Ca₅ [100] in phosphate-buffered saline (PBS) applied on ball-on-disk reciprocating sliding showed that the metallic glass had the highest wear resistance with a comparison with AZ31B alloy and pure Mg. The corrosion potential decreases the tribological contact and increases the corrosion current densities of the Mg-based alloys. The wear resistance suggests that magnesium-based metallic glass can be used in future orthopedic implants. A new composition of metallic glass $Mg_{(85-x)}Ca_{(8+x)}Au_7$ (with x = 0, 2, 4) [101] and $Mg_{(81 - x)}Ca_{10}Au_7Yb_{(2 + x)}$ (with x = 0, 8) showed resistance to the crystallization and has the potential to be used in sterilization procedure in biomedical applications. The absence of non-toxic elements in the metallic also plays a major role in its biomedical usage. In vitro studies of $Mg_{66}Zn_{30}Ca_{4-x}Sr_x$ [102] (x = 0, 1 and 1.5 at.%) metallic glass was studied for the bone-forming MC3T3-E1 pre-osteoblast and for the viability in the orthopedic implant. The results showed that metallic glass had more cell adhesion compared to AZ31B alloy, caused the proliferation of pre-osteoblasts, and no cytotoxicity occurred. These properties suggest that metallic glass is biocompatible and has the potential for biomedical applications. $Mg_{66}Zn_{30-x}Ca_4Ag_x$ [103] (x = 0, 1 and 3 at.%) showed that the addition of Ag improved corrosion and suppressed hydrogen evolution. Properties like corrosion resistance, and Ag alloy's anti-bacterial and cytotoxicity properties make it biocompatible. The Mg-based metallic glass can be used as a biomaterial material. Comparison studies (Figure 5) were performed between $Mg_{66}Zn_{30}Ca_{4x}Sr_x$ [104] (x = 0, 0.5, 1 and 1.5 at.%) and MgZnCaSr. It showed that $Mg_{66}Zn_{30}Ca_{4x}Sr_x$ has the better glass-forming ability, increased corrosion resistance, good mechanical properties, and cytocompatibility. These properties show future potential in biomedical applications.



Figure 5. A comparison of corrosion rates of the Mg-Zn-Ca-Sr (BMGs), biodegradable BMGs, and crystalline Mg alloys in physiological solution. Reproduced with permission from ref. [104]. Copyright 2014 Elsevier Ltd.

The alloying of 2% to 4% of Yb to $Mg_{66}Zn_{30}Ca_4$ [105] increased the ductility of the composite. This is due to the presence of extensive shear bands in $Mg_{66}Zn_{30}Ca_2$ Yb and (Yb₂) $Mg_{66}Zn_{30}$ Yb₄ (Yb₄). Further, in vitro studies showed that the addition of 4% Yb decreases cytotoxicity. It was concluded that the $Mg_{66}Zn_{30}$ Yb₄ amorphous composite can be used in future biomaterial implants. Alloying Mn to $Mg_{69} - {}_xZn_{27}Ca_4Mn_x$ (x = 0, 0.5 and 1 at.%) showed a decrease in the mechanical strength and glass-forming ability of the composite. There was an increase in the bio-corrosion resistance (Table 4) and cell viability of osteoblasts. The strength of the composite is similar to bone implants and can be used as biomaterials. Metallic glasses with different thicknesses [106], $Mg_{67}Zn_{27}Ca_4$ at different cooling rates (30 m/s (M1) and 10 m/s (M2)) were prepared by $Mg_{67}Zn_{28}Ca_5$ metallic glass. It showed that metallic glass with a lower cooling rate had a lesser corrosion rate in the saline solution and was susceptible to pitting corrosion.

Chemical Composition	Preparation Method	Compressive Strength (MPa)	Corrosion Rates E _{corr} (V)/R _{corr} (w/sqt)	Reference
Relaxed Mg ₇₀ Zn ₂₆ Ca ₄ ribbon/Crystallized Mg ₇₀ Zn ₂₆ Ca ₄ ribbon	Melt spinning	_	$\begin{array}{c} {\rm E_{corr}=(-1.21\pm0.065)/}\\ (-1.38\pm0.087) \end{array}$	[99]
Mg ₆₅ Zn ₃₀ Ca ₅	Melt pinning/ ball-on-disk reciprocating sliding	715–854	$E_{corr} = -1.23$	[100]
$Mg_{66}Zn_{30}Ca_{4x}Sr_x(x = 0, 0.5, 1, and 1.5 at.\%)$	Induction-melting	$787\pm22847\pm24$	$R_{corr}=8.76\times10^4$	[104]
Mg ₆₇ Zn ₂₇ Ca ₄	Induction-melting	545–364	-1.116	[106]

Table 4. Mechanical and corrosion properties of the Mg-based metallic glass and composite.

2.4. Fe- and Sr-Based Metallic Glass Biomedical Metallic Glass

Fe-based biomaterials are known for their load-bearing implants and are used in hip prostheses, dental implants, and bone fixators in the hip and knee. A thin layer of metallic glass (Fe₃₇Cr₁₅Mo₂B₂₆C₇Nb₃Si₃Al₆Mn₁ (%at)) was [107] formed with a 316L stainless steel substrate by using the ESD method. The layer was biocompatible, uniform, dense, and showed high adhesion. J-quenching and flux treatment were used to prepared a $Fe_{80-x-y}Cr_xMo_yP_{13}C_7$ (x = 10, y = 10; x = 20, y = 5; x = 20, y = 10, all in at.%) [108]. This metallic glass has higher corrosion resistance than the 316L stainless steel and TC4 and is biocompatible. Micrographs also showed that the Fe-based metallic glass was filled with NIH 3T3 cells, shown on the left side of Figure 6. This shows the biocompatibility of Febased metallic glass. Fe73.5Nb3Cu1Si13.5B9 [109] was ball milled for 48 h and three kinds of magnetic fluid, Fe_{73,5}Nb₃Cu₁Si_{13,5}B₉MR fluid, CoFe₂O₄ FF, and Fe₃O₄ FF (ferrofluid), were prepared. The metallic glass showed the potential for use in hyperthermia in tumor therapy. The addition of Nb in $Fe_{55} - {}_{x}Cr_{18}Mo_7B_{16}C_4Nb_x$ (x = 0, 3, and 4 at.%) [110] improved the corrosion resistance in the ringer solution and can be used as a biomaterial. $Sr_{60}Mg_{18}Zn_{22}$ based metallic glass has a low glass transition temperature and has homogenous flow in the supercooled region. The chemical and physical properties of $Sr_{60}Mg_{18}Zn_{22}$ suggest that it can be used as a biomaterial [111].

2.5. Summary

Bio-metallic glass materials and composites are known for their high mechanical properties and corrosion resistance. Zr-based metallic glasses have adhesion and host site limitations. Mg-based metallic glasses cause hydrogen gas to release and can cause degradation of the material. This can be prevented by adding ceramic coatings and metallic materials to the metallic glass matrix. It was shown that metallic glasses show better properties than traditional alloys.



Figure 6. Cont.



Figure 6. Morphologies of NIH 3T3 cells (Swiss mouse embryo fibroblasts 3-day transfer, inoculum 3×105 cells) cultured on (a) 316L SS, (b) TC₄, (c) Cr₁₀Mo₁₀, (d) Cr₂₀Mo₅ and (e) Cr₂₀Mo₅ for 2 days. On the right side are enlarged micrographs of the counterparts. Reproduced with permission from ref. [108]. Copyright 2015 Elsevier B.V.

3. Fiber-Reinforced Metallic Glasses Composites

Fiber-reinforced metal matrix composites are used for their mechanical properties and industrial applications, due to their low-cost production and performance. They are used in the aerospace and automobile industries. The formation of the oxide or carbide layer on the fiber can degrade its physical properties [112]. Metallic glass is known for its mechanical properties but lacks plasticity; a combination of fiber-reinforced metallic glass can produce a composite with good mechanical properties. In recent research, the vacuum pressure infiltration processing method was used to produce a carbon fiber/Ti_{37.3}Zr_{22.7}Be_{25.5}Fe_{5.5}Cu₉ (at.%) composite [113]. Microstructure control, good bonding, and strain percentage were increased, due to the interaction between carbon fiber and shear bands in the metallic glass. Mechanical strength (Table 5) of the tungsten fiber/Zr_{41.2}Ti_{13.8}Cu₁₀Ni_{12.5}Be_{22.5} [114] was increased. This can be attributed to an increase in fiber volume fraction (V_f). Similar studies of tungsten fiber/ $(Zr_{40.08}Ti_{13.30}Cu_{11.84}Ni_{10.07}Be_{24.71})_{99}Nb_1$ [115] increased the mechanical properties of the composite. Nb was added to increase the properties and interference of the composite. The yield stress of the composite gradually decreased with the shear softening. TiNi fibers [116] in metallic glass matrix generated the propagation of multiple shear bands and induced the TRIP effect, resulting in superior mechanical properties. The more the fiber volume fraction (V_f) , the better the mechanical properties of the composite. Tungsten fiber [117] of various dimensions was reinforced in Zr-based metallic glass. The mechanical properties of the composites increase with a decrease in the size of the tungsten fiber. Inhibition of shear bands and different fracture modes caused the superior compressive properties. The maximum compressive strength for the composite was 3079 MPa. A composite was produced by a different volume fraction of the tungsten strings/Zr-based metallic glass [118]. The 68% volume fraction tungsten composite showed the highest mechanical properties among the different composites. The enhanced mechanical properties are attributed to the spatial geometry, which modifies the stress pattern, resulting in the formation of multiple shear bands in the composite. A laminate structure of carbon

fiber-reinforced epoxy and $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ showed an increase in the adhesion of the composite [119]. A composite [120] based on volume fraction tungsten fiber reinforced with metallic glass at different temperatures showed that the higher the volume fraction of the tungsten, the better the mechanical properties. Both the quasistatic strength and the dynamic strength decrease with an increase in the temperature. Mg-based metallic glass reinforced with carbon fiber has engineering applications [121]. Al matrix composites reinforced with Fe₇₄Mo₄P₁₀C7.5B_{2.5}Si₂ (at.%) [122] metallic glass fibers were prepared by ball milling and hot pressing. The plastic deformation and strength were increased due to the presence of shear slip planes and the axial orientation of the fiber. The addition of the Nb in the W/Zr-based metallic glass composite can increase the interaction between the composite [123]. Chen et al. showed that for W/Zr-based composite, splitting of the composite and the critical energy dissipations for the shear banding are obtained as a function of the strain rate and tungsten volume fiber fraction [124]. It was found that the transition mode in the failure in the W/Zr composite is controlled by the shear to normal strength ratio [125]. B. Zhang et al. studied the effect of tungsten fiber orientation in a tungsten/Zr-based metallic glass composite. It was concluded that with the increase in orientation angle θ_f , the tensile strength decreased and no plasticity was present [126]. Deformation in W/Zr-based metallic glass occurs in two phases. In uniaxial compression, the metallic glass matrix deforms homogenously, but buckling of the tungsten fiber occurs first. After further deformation, shear band propagation occurs in the composite, and the splitting of tungsten fiber with shear bands takes place in the fracture of the composite [127]. A comparison between different composite W/Zr and W/Cu metallic glass showed that the W/Cu-based composite has higher cohesion strength and compression stress and strain. The fracture mechanism of the composites was related to the distinct glass-forming ability of the monolithic metallic glasses [128]. Shear bands in the 61.4 vol% (Figure 7) tungsten wires/ Zr-based metallic glass cause good mechanical properties and cohesion in the composite [129]. Wang et al. [130] showed that at a strain rate below 3000 s⁻¹, the compressive strength of the composite W_f/Zr based metallic glass (60%) increased. A ballistic test on the W/Zr-based metallic glass composite showed that the penetration depth of the composite is 50% more than the tungsten heavy alloy rods (95W rod) [131]. The mechanical properties of the W_f/Zr -based metallic glass composite are increased with an increase in the Nb content. Nb increases the interfacial strength in between the tungsten fiber and metallic glass [132]. Stainless steel capillaries reinforced in Zr-based metallic glass showed an increase in plastic strain by 14% [133].

Summary

Fiberglass and metallic glass composites are low-cost in production. Tungsten b fiberglass reinforced with metallic glass produces high yield strength and plastic strain. The addition of Nb increases the interfacial strength between the metallic glass and fiber. The free volume also determines the properties of the fiber glass and metallic glass composites.

Chemical Composition	Chemical Composition Preparation Method		Fracture Strength (MPa)	Plastic Strain (%)	Reference
Carbon fiber/Ti _{37.3} Zr _{22.7} Be _{25.5} Fe _{5.5} Cu ₉	Vacuum pressure infiltration processing	1880 ± 80	-	$4.8\pm1.0\%$	[113]
Tungsten fiber/Zr _{41.2} Ti1 _{3.8} Cu ₁₀ Ni _{12.5} Be _{22.5}	Forward melt infiltrating method	_	1600	11.7%	[114]
Tungsten fiber/(Zr _{40.08} Ti _{13.30} Cu _{11.84} Ni _{10.07} Be _{24.71}) ₉₉ Nb ₁	Quasi-static compression	2200-2500	-	26%	[115]
TiNi fiber/ Zr_{47} Ti $_{13}$ Cu $_{11}$ Ni $_{10}$ -Be $_{16}$ Nb $_{3}$	Pressure infiltration casting	2100	-	14%	[116]
Tungsten fiber/ $Zr_{41.2}$ Ti $1_{3.8}$ Ni $_{10.0}$ Cu $_{12.5}$ Be $_{22.5}$	Infiltration and rapid solidification	_	_	37%	[117]

Table 5. Mechanical properties of fiber-reinforced metallic glass composite.

Chemical Composition	Preparation Method	Yield Strength (MPa)	Fracture Strength (MPa)	Plastic Strain (%)	Reference
Tungsten strings/(Zr _{40.08} Ti _{13.30} Ni _{11.84} Cu _{10.07Be24.71})99Nb	Infiltration and rapid solidification method	1680	2505	27.1%	[118]
Tungsten fiber/Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni _{10.0} Be _{22.5}	Resistive furnace and quenching	2100	-	20%	[120]
Al matrix composites/Fe ₇₄ Mo ₄ P ₁₀ C7.5B _{2.5} Si ₂ (at.%) metallic glass fibers	Ball milling/ Hot pressing	115 ± 8	4200	40%	[122]
Tungsten fiber/ $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	Infiltration and rapid solidification	_	-	23%	[124]
Tungsten fiber/Zr _{41.2} Ti _{13.8} Ni _{12.5} Cu ₁₀ Be _{22.5}	Infiltration and rapid solidification method	433	-	12.6%	[127]
Tungsten fiber/Zr _{41.25} Ti _{13.75} Cu _{12.5} Ni ₁₀ Be _{22.5}	n fiber/Zr _{41.25} Ti _{13.75} Cu _{12.5} Ni ₁₀ Be _{22.5} Continuous infiltration process		-	0.75%	[128]
$W_{\rm f}(60\%{\rm vol})/{\rm Zr}_{41.25}{ m Ti}_{13.75}{ m Cu}_{12.5}{ m Ni}_{10}{ m Be}_{22.5}$	Melt infiltration casting	2300	-	24%	[130]
$Wf/(Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5})_{100-x}Nb_x$ composites with x = 1, 3, 5 and 7.	Melt infiltration casting	2450	-	20%	[132]

Figure 7. A representation of the (**a**) new continuous infiltration process, (**b**) a bunch of BMG MC (bulk metallic glass matrix composites), (**c**,**d**) SEM images of the cross section of BMG MC bunch having 61.4 vol% tungsten wires and (**e**) TEM image of the interaction between the tungsten and the $Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit 1, at%) shown in the inset of (**d**). Reproduced with permission from ref. [129]. Copyright 2012 Elsevier B.V.

4. Metallic Glass/Polymer Composites

A high magnetoelectric voltage coefficient showed that the P(VDF-TrFE) polymer film laminated on metallic glass ($Fe_{67}Co_{18}B_{14}Si_1$) with an epoxy resin adhesive composite can be used for magnetoelectric energy harvesting [134]. Mg-based metallic glass/PCL composite shows biodegradable properties and can be used in biomedical applications [97]. Al-based metallic glass/PET composite was prepared by ball milling and subsequent spark plasma sintering. The author concluded that a change in the chemical composition took place due to the partial crystallization of the composite [135]. Similar work was done by producing a metallic glass/polymer composite by mechanical alloying and sparks

Table 5. Cont.

plasma sintering. The composite showed that it can be used as an antifriction material and in tribology [136]. M.Y. Zadorozhnyy et al. found that the adhesion of the metallic glass/polymer composite can be increased by adding 10 mass% of triethoxyvinylsilane. The composite (HDPE/Mg_{67,5}Ca₅Zn_{27,5}) also showed high thermal conductivity and elastic modulus [137]. A composite based on Zr₆₅Cu_{17.5}Ni10Al_{7.5} and PTFE polymer showed the formation of Zr₂Cu and Zr₂Ni intermetallic, and the addition of metallic glass increased the thermal conductivity in the composite [138]. A silicone polymer was used as a binder to form a metallic glass-polymer nanocrystalline structure (Fe-based composite). It was also concluded that the composite showed improvement in soft magnetic properties [139]. Zr-based metallic glass/polyacrylonitrile (PAN) composite can be used to produce nitrogen selective applications [140]. Metallic glass-polyisoprene nanolaminate causes an increase in the plastic flow and can be used in structural and nanodevices. The composite also shows corrosion and wear resistance [141]. A similar study was conducted by producing Fe₆₄Co₁₇Si₇B₁₂ metallic glass and polyvinylidene fluoride (PVDF) using an epoxy resin, which has a piezoelectric response and can be used in miniature electronic devices and ultra-low power applications [142].

Summary

Metallic glasses have high strength but lack plasticity. The polymer has low strength and high plasticity. The combination of both can produce a composite with good thermophysical properties. The lack of interaction between the polymer and metallic glass is a major drawback and can be avoided by using binders. M.Y. Zadorozhnyy [137] showed that silane can be used as a binder between metallic glass and polymer.

5. Ex Situ Metallic Glass Composites

Ex situ [143] metallic glass composites are generally formed by mechanical alloying or atomization of the powder. These composites have a glassy phase and reinforcement of second phase particles. The variation in particle size varies from micrometer to nanometer. It can also be formed by introducing a second phase as reinforcement in the glassy matrix. Metallic glass matrix/fiber reinforcement composite are some of its examples. A Ti-based metallic glass composite showed that with an increase in the Zr content, the mechanical properties improved. The solid solution strengthening of ex situ Ti layers hinders the propagation of shear bands and improves the mechanical properties [144]. The addition of Nb in Ti-based metallic glass increases the bond interference and mechanical properties (Table 6) of the composite. The formation of the α -Ti gradient layer helps in restraining the shears bands, which leads to the formation of multiple shear bands and increases the plasticity of the composite [145]. The electroless copper plating forms a stable and protective layer between SiC particles and Mg-based metallic glass. The SiC particles increase the plastic zone size, and the Cu coating helps in the prevention of shear bands, improving the plasticity [146]. The ex situ Mg-based metallic glass composite showed that shear band stability can hinder the motion of shear bands [147]. A work hardening behavior was seen in the composite because of the porous NiTi particle in Mg-based metallic glass. The hindrance of the movement of the single shear bands leads to the increase in the plasticity of the composite [148]. Zr-based metallic glass drill bits can be used in orthopedic drills in medical applications [149]. Ex situ Ta (0–6 vol%) particles were reinforced by pulse laser technique on Zr-based metallic glass, and no harmful crystalline particles were present. There was the formation of sub-zero and nano-size Ta particles in the weld fusion zone. Ta also affected the glass transition temperature and glass-forming ability of the composite [150]. An interfacial reaction occurred when an ex situ composite was welded. There was the formation of an interfacial layer in the reinforced phase (Ta) in PM, WFZ, and HAZ zones. A more stable ZrCu layer was formed in WFZ [151]. The La-based composite showed good mechanical properties but can cause plastic strain, due to the formation of oxide defects [152]. Ti particles in Mg-based composite increase the plasticity of the composite due to the multiple shear bands. The

plasticity of the composite depends on Ti particle size and interparticle spacing [153]. In similar studies, J.B. Li et al. showed that shear band propagation (Figure 8) was restricted by the semi-uniform confinement zones of Ta particles. The plasticity was dependent on the interparticle size and confinement zone [154].

Chemical Composition	Composition Preparation Method		Fracture Strength (MPa)	Plastic Strain (%)	Reference
Ti _{63 - x} Zr _x Ni _{5.3} Cu ₉ Be _{22.7} (at.%, x = 52)	Melt spinning/ Ex situ method	1552 ± 20	1956 ± 20	$8.4\pm0.2\%$	[144]
$(Ti_{0.328}Zr_{0.302}Ni_{0.053}Cu_{0.09}Be_{0.227})_{100-x}Nb_x$	Melt spinning/ Quenching	1078 ± 10	1112 ± 5	5.10 ± 0	[145]
20%TiNi/Mg _{59.5} Cu _{22.9} Gd ₁₁ Ag _{6.6}	Ex situ	-	1173	12.1%	[148]
$La_{55}Al_{25}Cu_{10}Ni_{10}/35$ mesh Ta particles	Melt spinning/Injection cast melting	720	-	40%	[152]
Mg ₅₈ Cu _{28.5} Gd ₁₁ Ag _{2.5} /Ti particles	Injection casting	800	-	25%	[153]
Zr _{47.3} Cu ₃₂ Ag ₈ Al ₈ Ta ₄ Si _{0.7} /ex situ Ta particles Two-step arc melting process and suction casting		1770–1800	1800	44%	[154]
$(Zr_{48}Cu_{36}Al_8Ag_8)_{99.25}Si_{0.75}/Ta particles$	Suction casting	1800	1850	22%	[155]

Table 6. Mechanical properties of ex situ metallic glass composite.



Figure 8. SEM images of fracture area of (**a**) monolithic $Zr_{47.3}Cu_{36}Ag_8Al_8Si_{0.7}$ BMG, (**b**) $Zr_{47.3}Cu_{32}Ag_8Al_8Ta_4Si_{0.7}$ BMGC, (**c**) $Zr_{47.3}Cu_{32}Ag_8Al_8Ta_4Si_{0.7}$ BMGC with ex situ added, 3 vol.% Ta, and (**d**) $Zr_{47.3}Cu_{32}Ag_8Al_8Ta_4Si_{0.7}$ BMGC with ex situ added, 9 vol.% Ta. Reproduced with permission from ref. [154]. Copyright 2012 Elsevier B.V.

Ex situ Ta particles in the Zr-based composite showed an increase in plasticity due to shorter interplanar spacing. The interfacial area was also increased due to the bigger volume fraction particles [155].

6. In Situ Metallic Glass Composites

The plasticity of the metallic glass composite can be increased by introducing a second phase, which can block the propagation of shear bands. The formation of multiple shear bands can increase the plasticity of the metallic glass composite. The crystalline phases occur during the solidification of the melts, which increases the plasticity. These composites are in the form of crystalline phases, nanocrystalline phases, and dendritic phases [156]. Ex situ metallic composites are generally prepared by techniques such as ball milling and the melt infiltration process [142]. Different particles of size ranging from micrometer to nanometer are induced. In situ composites are produced by thermal treatment, high-pressure torsion, and hot extrusion processes. Secondary particles, such as crystalline, semicrystalline, and quasi-crystalline, are formed. By controlling the kinetics and thermo-dynamics of the metallic glass in the supercooled region, the crystallization process can be avoided. The heat treatment process is generally done to control the crystallization process.

6.1. Crystalline/Nanocrystalline Metallic Glass Composites

A dual crystalline phase, α - and β -phase reinforced in Ti-based metallic glass composite showed good mechanical properties. This could be attributed to the hindrance of shear bands by crystalline phases and α -phase toughening in the β -phase [157]. The high torsion method was used to prepare a nanocrystalline composite and a Cu-rich nanocrystal increased the yield and ultimate strength of the metallic glass. The strain hardening and elongation were increased by the increase in the free volume [158]. Nanoporous metallic glass (Fe–Ni–Co) composite can be used in clean energy applications [159]. Martensitic transformation of nanocrystalline Ti₅₀Ni₄₇Fe₃ composite can provide near-ideal strain and strength in a composite [160]. FeCrMoCB metallic glass can be used in joint replacement implants [161]. Uniformity in the eutectic phase and Fe₂B nanocrystalline structure plays an important role in the properties of a material. The nanocrystalline structure of Febased metallic glass enhances the mechanical properties (Table 7) of the composite [162]. The enhancements in the absorption kinetics of Mg-based metallic glass occur due to the formation of nanocrystals by the control agents present in the ball milling process. The dehydrogenation in the Mg₆₀Ce₁₀Ni₂₀Cu₁₀ metallic glass was controlled by the formation of nanocrystal hydrides [163]. Nanocrystals in the Fe-based metallic glass that occurred during partial annealing led to an increase in the ferromagnetic properties of the composite. Crystalline particles present in the composite increased the volume fraction, which resulted in increasing the hardness of the composite [164]. Q. Zhou et al. showed that the addition of Sn to Ti-based metallic glass has wear resistance and can produce the formation of a continuous tribolayer. This tribolayer during sliding shows improved the tribological properties [165]. A. Yao et al. showed that the nanocrystalline metallic glass ($Al_{82}Ni_6Co_3Y_6Cu_3$) can be used as an easy precursor in manufacturing non-porous electrodes [166]. Crystalline Fe_xN in FeSiCrB metallic ribbon provided high electric resistance, magnetic moment, works as a binder, and boosts magnetic properties in the FeSiCrB metallic ribbon. The stacking factor of the magnetic material is near 100% and the composite can be used as a soft magnetic material in electrical and electronics machines [167]. The composite of Zr/nanocrystalline Fe metallic glass has better compressive strength and hardness than the Zr metallic glass [168], but 40% above the volume fraction of Fe-based metallic glass causes cracks and pores formation. X. Ji et al. discussed that microstructure evolution is related to the solidification of the cooling rate, impact-induced temperature rise, plastic flow, oxidation, and interdiffusion of the metal elements [169]. Non-planar thin film (CuO- Cu_2O /ZnO: Al heterojunctions have applications in solar and electronic devices [170]. W. R. Jian et al. studied that the volume fraction of the Cu₆₄Zr₃₆ crystal particles can achieve a balance between hardness, hardness, and ductility [171]. Partial nano-crystallization of Zr-based composite has anticipated vibration and electric transport properties [172]. Microstructure analysis (Figure 9) of the Ti-based composite showed that the crystallization occurred in the amorphous phase in two phases, and the formation of nanocrystals (B2) and precipitation of the γ -TiCu phase occurred afterward [173].





Figure 9. XRD pattern of (**a**) DSC curve, (**b**) SEM-BSE (backscattered electron) image, (**c**) and TEM BF image, (**d**) of as-cast alloy, together with SAED patterns obtained from an amorphous matrix, (**e**,**f**) B2 particle. Reproduced with permission from ref. [173]. Copyright 2016 Elsevier B.V.

Cu-based metal–intermetallic nanostructured composites have high thermal stability, high ductility, and superior strength because of their distinctive microstructure and irregular deformation mechanism. This composite can have applications in construction, military, automobile, and aerospace [174].

The formation of precipitation of the nano-sized Ni₂SnTi phase occurs during annealing in the metallic glass (Ti₄₅Cu₄₁Ni₆Zr₅Sn₃), and an increase in the wear resistance, microhardness, and wear resistance is induced by the nanocrystals [175]. J.-K. Lee et al. showed that the deformation of W/Ni-based metallic glass composites depends on the layered structure of the nanograined tungsten matrix and its reinforcement [176]. The addition of boron in the Mo–Ni–Si–B metallic glass can increase the glass-forming ability of the composite. Mo-Ni-Si-B metallic glass can be used to form a metallic glass-nitride nanocomposite coating layer and has an application in wear resistance coatings [177]. The porosity structure of $Zr_{70}Cu_{24}A_{14}Nb_2$ metallic glass can be influenced by the SPS procedure. The higher sintering temperatures lead to the formation of nanocrystals in the composite. This composite has an application in functional materials [178]. The coercivity of the Co72B19.2Si4.8Cr4 metallic glass is changed by the intermediate nanocrystalline phase, resulting in an amorphous soft state to a monocrotaline hard magnetic state [179]. Q. Xing et al. showed that pre-compression treatment for $RE_{65}Co_{25}Al_{10}$ metallic glass can induce the formation of the nanocrystalline composite. The pre-compression treatment is good for thermal and mechanical properties [180]. The decrease in the plasticity of Ti-based metallic glass is due to the decimation of the free volume and microcracks, and precipitation of nanocrystals leads to brittle fracture [181]. R. Babilas et al. showed that in $Mg_{60}Cu_{30}Y_{10}$, the homogenous metallic glass has more corrosion resistance than the nanocrystalline particles in the composite [182]. The nanocrystalline Mg rod obstructs the propagation of shear bands in thin-film metallic glass. The more the Mg content in the thin film, the better the ductile behavior. The author concluded that the composite can be used in microelectronic–mechanical biomedical devices [183]. The increase in the fraction β -type phase leads to the degradation and decrease in the mechanical properties in $Ti_{60}Zr_{10}Nb_{15}Si_{15}$ as compared to $Ti_{75}Zr_{10}Si_{15}$. This leads to a high H/E_R ratio and proposes an application in high wear resistance [184]. Ag in Zr₅₆Co₂₂Al₁₆Ag₆, in the local structure of the Zr–Co–Al, is influenced by the positive mixing of Ag and Co in $Zr_{56}Co_{22}Al_{16}Ag_6$. The nucleation rate and growth rate at a maximum temperature are credited to ultrafine nanocrystals [185]. L.M. Zou et al. showed that the addition in the content of Fe in TiNbZrTa increased the glass-forming ability and enthalpy of crystallization and transformed the structure from a nanocrystalline structure in the nanocomposite matrix with nanocrystals in an amorphous matrix [186]. A sintered and porous structure Ti-based metallic glassy/nanocrystalline composite has application in structural and functional applications [187]. The increase in the Cu–Ni content in Ti–Zr–Cu–Ni–Co amorphous alloys showed an increase in the compressive strength and plasticity in the composite [188,189]. Dynamic martensitic transformation and heterophase structure increased the strength and plasticity of the composite in the Ni–Cu–Ti–Zr composite [190]. The addition of Fe in the Ti–Cu amorphous alloy led to the formation of CuTi₂ intermetallic compounds, which degraded the mechanical properties of the composite [191]. I.S Golovin et al. studied the change in the internal friction values; the structural changes occurred due to the martensitic transformation in the Ni₄₀Cu₁₀Ti₃₃Zr₁₇ composite [192]. The addition of Y, Nb, and Al in (Ti–Ni–Cu–Zr) metallic glass induced transformational plasticity and an increase in yield strength [193]. Structural relaxation occurred in the Zr-Cu-Ni-Al metallic glass, storage modulus and internal friction changed due to the amorphous alloy crystallization [194]. The formation of the NiTi₂ phase in the (Ti–Ni)–(Cu–Zr) phase caused degradation in the mechanical properties of the composite [195].

Chemical Composition	Preparation Method	Yield Strength (MPa)	Ultimate Tensile	Plastic Strain	Reference
$Ti_{31.2}Zr_{28.7}Ni_5Cu_{8.5}Be_{21.6}Mo_5$	Melt Spinning/ quenching	1410	1625	3.6%	[157]
$Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$	High-Pressure Torsion	1793	2023	0.4%	[158]
$\mathrm{Ti}_{50}\mathrm{Ni}_{47}\mathrm{Fe}_3$	Arc melting/ annealing	1700	2250	5.5%	[160]
$Zr_{48}Cu_{36}Al_8Ag_8/Fe_{65.4}C_{7.1}Si_{3.3}B_{5.5}P_{8.7}Cr_8Al_2$ (nanocrystalline)	hot-pressing method	-	-	3.4 ± 0.1	[168]
Cu ₈₅ Zr ₁₀ Al ₅	arc melter	1800	2160	1.3	[174]
$W/\mathrm{Ni}_{59}\mathrm{Zr}_{20}\mathrm{Ti}_{16}\mathrm{Si}_{2}\mathrm{Sn}_{3}$	Milling/spark plasma sintering	1730	2409	2.6	[176]
$Ti_{44}Zr_{20}Nb_{12}Cu_5Be_{19}\\$	Arc melting/ annealing	1438	-	8.6	[181]
Mg _x Zr _x Cu _x	Sputtering	1700	-	52%	[183]
Ti-40Nb (Ti _{74.4} Nb _{25.6})	Copper mold casting/melt spinning method	544 ± 66	-	28 ± 7	[184]

Table 7. Mechanical properties of crystalline/nanocrystalline metallic glass composites.

6.2. Dendritic and Quasicrystal Metallic Glass Composite

G.H. Duan et al. showed that the shear bands can be terminated in two ways for dendritic phases. The first is the change in the position of the direction of the shear bands beside the boundaries of dendrites and glass matrix. The second one is the dendrites blocked the shear bands in the glass matrix [196]. Distinct microstructure in FeCrMoBC alloy with different cooling rates can be achieved by laser-directed energy deposition. The varying cooling rates generate the microstructure of soft crystalline dendrites with an amorphous matrix and lead to an intrinsic toughening mechanism [197]. J.I. Lee et al. prepared a metallic glass and alumina composite with the dendritic structure and showed

that the composite at 800 $^{\circ}$ C showed the highest compressive strength of 2490 \pm 65 MPa between the samples [198]. A new deformation method that pulls apart was discovered in in situ dendrites. In this method, dendrites are inserted and then torn apart in the toughened amorphous matrix during the plastic flow [199]. Dendritic B-Ti phase and martensitic transformation increased the strain hardening of the composite. The author also studied the different volume fraction of ß-Ti dendrites and their impact on the composite and concluded that the combination of ß-Ti and 38% volume fraction demonstrates high ductility and strength [200]. The in situ β -Ti dendrite phase in Ti-MG stabilizes the plastic flow, and the generation of nucleation sites of the multiple shear bands leads to enhanced plasticity and strength (Table 8) of the composite [201]. S. Yang et al. concluded that the intermediate glassy phase at the nanoscale that is deformed homogenously could be related to the mechanical behavior of the $Ti_{68}Cu_{13,2}Pd_{5,6}Sn_{1,2}Nb_{12}$ alloy [202]. The deformation-induced martensitic transformation in the B2–ZrCo dendrite in Zr–Co–Al (Z1) displayed high strength and plasticity. High strength and low plasticity were also found in Zr-Co-Al (Z5), due to the presence of a large eutectic inter-dendritic phase in the crystalline phases [203]. N. Hua et al. showed that high-strength ultrafine eutectic-dendrite composites with a high range of ductility and strength can be attained without rapid solidification and an injection mold casting procedure [204]. The Ti_{16.6}Nb₆Co_{5.1}Cu_{6.5}Al alloy has better potential than commercial Ti alloys in biomedical applications [205]. The mechanical properties in Ti-Zr-Nb-Cu-Be were increased and showed structural stability after annealing, due to slight β -thermal relaxation [206]. The addition of Nb in the Ti–Zr– Cu–Pd–Sn metallic glass and formation of the β -Ti phase increased the plasticity (Figure 10) and work- hardening feature [207]. The figure shows the increase in plasticity with the addition of Nb.



Figure 10. Compressive engineering stress–strain ($\sigma - \varepsilon$) curves of the base and Nb-added alloys, Reproduced with permission from ref. [207]. Copyright 2016 Elsevier B.V.

A 2% addition of the Si to Ti metallic glass produced a dendritic, which enhances the mechanical properties of the composite [208]. J. Cui et al. showed that the plasticity of the $Ti_{50}Zr_{20}Nb_{12}Cu_5Be_{13}$ is enhanced by the emergence of the plastic dimple fracture and multiple shear bands [209]. The solid solution strengthening effect is caused by the impurities that are immersed in the ß titanium phase in the $Ti_{48}Zr_{20}Nb_{12}Cu_5Be_{15}$. The author also concluded that the addition of a high amount of oxygen caused degradation in the composite [210]. During solid solution strengthening, the strength and hardness of the dendrites were increased in the Ta-based metallic glass, resulting in the generation of multiple shear bands, which improve the plasticity of the composite [211]. A new approach to form a high-strength Ti-based composite was proposed by inducing a brittle inter-dendritic phase (e.g., Co, Cr, or Cu) until the alloy exhibited β -Ti morphology completely [212]. H. S. Arora et al. showed that the friction stir processing procedure can be used for localized microstructural transformation and homogeneous distribution in the composite [213]. The strain rate of the Zr_{39,6}Ti_{33,9}Nb_{7,6}Cu_{6,4}Be_{12,5} composite is affected by the dispersion of the fracture and shear bands [214]. The withdrawal velocity in Zr-based metallic glass can affect the morphology and mechanical properties. The volume fraction in the crystalline phases is accountable for the improvement in the plasticity of the composite [215]. The formation of dendritic B2 CuZr improves the yield strength and ductility of the Zr metallic glass-based composite [216]. The shear band formation can be reduced by inducing quasicrystals in the amorphous matrix. They also hinder the formation of shear bands and cause the formation of multiple shear bands, increasing the plasticity [217]. The icosahedral quasistatic phase in the Mg matrix increases the plasticity (Table 9) and overall strength of the composite and has a chemical correlation between the quasicrystal phase and the metallic glass matrix [218]. The formation of the I-phase favored by oxygen impurity in the $(Zr_{65}Cu_{15}Al_{10}Ni_{10})_{90}Nb_{10}$ leads to the reducing of the undercooling in the alloy melt, and during cooling, the long-range order of the icosahedral order is easily trapped [219].

Chemical Composition	Preparation Method Yield Strength (MPa)		Ultimate Tensile Strength	Plasticity	Reference
Ti ₄₈ Zr ₂₀ Nb ₁₂ Cu ₅ Be ₁₅ metallic glass	cold crucible levitation melting/copper mold casting	1160	1310	10.7%	[199]
BT80	copper mold casting	1046 ± 17	1326 ± 15	9.1 ± 0.3	[200]
$(Ti_{51}Zr_{38}Nb_{11})_{71}Cu_9Be2_0$	suction casting method	2053	-	8.06	[201]
$Ti_{68}Cu_{13.2}Pd_{5.6}Sn_{1.2}Nb_{12}$	suction casting	1300	-	23.7	[202]
Zr ₅₄ Co ₃₅ Al ₁₁ (Z1)	Suction cast/Quenching	1323 ± 10	-	$28.7{\pm}~0.1$	[203]
Zr ₅₄ Co ₃₅ Al ₁₁ (Z5)	Suction cast/Quenching	1950 ± 10	-	3.0 ± 0.1	[203]
Ni ₉₀ Hf ₁₀	arc-melting	1910	-	34.4	[204]
$Ti_{16.6}Nb_{6}Co_{5.1}Cu_{6.5}Al$	Arc melting/Casting	1230 ± 50	-	$11\pm1\%$	[205]
$Ti_{48}Zr_{20}Nb_{12}Cu_{5}Be_{15}\\$	arc-melting/copper casting	1599	-	34%	[206]
$Ti_{56}Zr_6Cu_{19.8}Pd_{8.4}Sn_{1\cdot8}Nb_8$	Suction casting/ copper molding	1690	2680	20	[207]
$(Ti_{0.425}Cu_{0.425}Ni_{0.075}Zr_0.0_{75})_{1-x}Si_x$	melt-spinning/ suction casting	1497 ± 50	-	10.3 ± 0.1	[208]
Ti _{38.8} Zr _{28.8} Cu _{6.2} Be _{16.2} Nb ₁₀ (Ta _{0.5} (VF))	Melt Spinning/Copper-mold suction casting	1517	2610	20.3	[209]
Ti _{68.8} Nb _{13.6} Cr _{5.1} Co ₆ Al _{6.5}	Melt spinning/ Casting method	1100 ± 20	1290 ± 50	21 ± 3	[212]
$Zr_{60.0}$ Ti _{14.7} Nb _{5.3} Cu _{5.6} -Ni _{4.4} Be _{10.0} (at%)	Arc melting/the semisolid treatment plus Bridgman solidification	1260	2050	16.7	[215]
cast $Cu_{47.5}Zr_{47.5}Al_5$ (series 130)	Arc melter/copper mold suction casting	1311	1628	13.94	[216]

Table 8. Mechanical properties of dendritic of metallic glass composites glass composite.

Table 9. Mechanical properties of quasicrystal of metallic glass composites glass composite.

Chemical Composition	Preparation Method	Yield Strength (MPa)	Fracture Strength (MPa)	Plastic Strain	Reference
Mg ₆₆ Zn ₂₉ Ca ₄ Y	Semi-solid processing	850	870	0.6%	[218]

Summary

Metallic glass composites are generally prepared by either ex situ or in situ processes. In the ex situ process, secondary phases are produced by ball milling or melt infiltration. In situ processes are generally heat treatment for secondary phases. The formation of semi-crystalline, nanocrystalline, and quasi-crystalline particles can produce a metallic glass composite with high properties. Crystalline materials are ductile, and metallic glass lacks plasticity. The combination of both in a crystalline/metallic glass composite enhances the mechanical properties.

7. Conclusions and Prospects for the Future

Metallic glass is amorphous and is known for its mechanical properties, such as high toughness and strength, but lacks plasticity. It can be used in various applications [10–31] and is prepared by techniques such as melt-spinning, liquid squat quenching, powder metallurgy, magnetron sputtering, and pulsed laser quenching. The formation of metallic glass depends on the supercooled region and the critical cooling rate (R_c). Metallic glass has excellent mechanical properties as compared to crystalline materials but has low plasticity. This can be overcome by the introduction of secondary materials to form a metallic glass composite. The main aim of this review is to provide a brief overview; the background on metallic glass, its properties, and its application are discussed. Biocompatible composite and metallic glass based on Ti, Mg, Fe, and Sr are discussed. They have high strength and can be used in bioimplants and stents. The ex situ composites, fiber-reinforced metallic glass composites, are a metallic glass polymer and are also discussed. These composites have increased physical-mechanical properties. Biomaterial composites and metallic glass based on Ti, Mg, and Fe, are discussed. Metallic glass composite could be used as degradable bioimplants. Ti–Zr–Cu–Pd–Sn shows better workability than the commercial Ti and Ti-6Al-4V bioimplants. Biocompatibility and corrosion resistance can be increased by adding boron to Ti-based metallic glass. In general, Ti-based metallic glass and its composite show better cytocompatibility, corrosion resistance, and mechanical properties. Fiber-reinforced metallic glass composites and metallic glass/polymers composites are also discussed. Zr-based metallic glass is used in the musculoskeletal system. Zr-Ti-Cu-Ni–Be metallic glasses are used in ceramic films to increase their biocompatibility and tribological properties. Zr–Cu–Ni–Al composites have better plasticity and are used in load-bearing implants. The formation of the (Zr₂Cu) nanocrystals leads to passivation, and an increase in the Y% increases cell activity. The Mg–Zn–Ca/PCL composite shows biocompatibility. PCL/nHA/Mg (MG) controls the Mg ions release. Mg–Zn–Ca ribbons have better resistance, biocompatibility, and tribological properties. It was also shown that the corrosion resistance of Mg–Zn–Ca is better than the commercial AZ31B and Mg. The addition of the Ag in Mg–Zn–Ca increases the corrosion and controls the hydrogen evolution. The cooling rate of the Mg–Zn–Ca metallic glass also influences the corrosion rate in the saline solution. Fe-based composites have potential in hyperthermia and tumor therapy. The formation of the carbon fiber/Ti-Zr-Be-Fe-Cu and W/(Zr-Ti-Cu-Ni) increases the mechanical properties, and the addition of Be in the Zr-Ti-Ni-Cu increases the adhesion of the composite. The addition of the Nb increases the interfacial strength between the W/MG composite. Recent research was conducted on MG and polymer composites. Some examples are Mg(MG)/PET, Mg(MG)/HDFE, Zr(MG)/PAN, and Cu(MG)/PTFE. They are used in structural and industrial applications. Various binders, such as silane, can be used to improve the interaction between metallic glass and polymer. The addition of the secondary reinforcement and introduction of the secondary phases increases the mechanical properties of the metallic glass composites. These composites are generally prepared by mechanical alloying or heat treatment procedures. The introduction of multiple shear bands and the formation of nano-crystalline, dendritic, and quasicrystal phases increase the plasticity of the metallic glass composite.

There is a great scope for composites based on metallic glass. Both physical and chemical properties can be increased by it. In the future, metallic glass composites have bright prospects in engineering and industrial applications.

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