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Fabrication and Mechanical Properties of Porous Fe Skeleton-Reinforced Mg-Zn-Ca-Sr Bulk Metallic Glass Composites

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Abstract

Mg-Zn-Ca bulk metallic glasses (BMGs) have attracted significant attention in the field of biodegradable metallic biomaterials due to their desirable in vivo degradability and high strength. However, their relatively high brittleness limits further practical applications. In this work, porous Fe skeleton-reinforced Mg-Zn-Ca bulk metallic glass composites (BMGCs) were fabricated by pressure infiltration using porous Fe skeleton as the toughening phase and $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ alloy as the matrix. It was found that electroless copper plating improved the interfacial wettability between molten Mg and Fe, as well as the infiltration-forming capability of the BMGCs. Quasi-static compression tests showed that the BMGC exhibited a compressive strength of 500 MPa, a plastic strain of 0.2%, and a yield strength of 420 MPa, representing a significant improvement over the matrix BMG alloy. The fracture surface displayed a vein-like pattern, indicating a noticeable transition from brittle to ductile fracture behavior. Thus, the porous Fe skeleton-reinforced Mg-Zn-Ca BMGC shows promise as a potential biodegradable biomedical material. Moreover, the preparation route presented here offers a new perspective for developing degradable Mg-Zn-Ca-based BMGCs.

Keywords: bulk metallic glass composite; porous Fe skeleton; Mg-Zn-Ca alloy; mechanical property

1. Introduction

Mg-Zn-Ca bulk metallic glasses (BMGs) have attracted extensive attention across multiple fields such as materials science and biomedical engineering, owing to their outstanding specific strength, favorable biocompatibility, degradability, and unique glass-forming ability (GFA) [1–3]. In contrast to conventional crystalline magnesium alloys, metallic glasses (MGs) possess a long-range disordered and short-range ordered atomic arrangement [4]. This distinctive structure avoids crystalline defects such as grain boundaries and dislocations, thereby endowing them with near-theoretical-limit strength, higher elastic limit, good corrosion resistance and lower elastic modulus—properties that more closely match the mechanical behavior of human bones. As a result, Mg-Zn-Ca BMGs demonstrate significant potential for applications in lightweight structural materials and biodegradable implants [5–8].

The Mg-Zn-Ca ternary alloy exhibits optimal GFA near its deep eutectic composition, such as $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_4$. Using copper mold casting, a maximum critical diameter of 4–6.5 mm can be achieved for fully glassy rods [1,5,9]. The addition of strontium (Sr) to



Academic Editor: Chun-Liang Yeh

Received: 25 January 2026

Revised: 11 February 2026

Accepted: 16 February 2026

Published: 21 February 2026

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form the Mg-Zn-Ca-Sr quaternary system significantly enhances both GFA and plasticity. With a minor Sr addition (≤ 2 at.%), the supercooled liquid region expands, allowing the critical diameter to increase to about 6 mm [10]. Moreover, the introduction of gallium (Ga) leads to obvious improvement in GFA [11], with reported critical diameters reaching up to 7 mm [12]. Consequently, the GFA of the Mg-Zn-Ca system remains inherently limited, making further enhancement of its critical diameter both essential and scientifically challenging.

Mg-Zn-Ca-based BMG alloys demonstrate high strength and a relatively low elastic modulus [1,9]. However, its room-temperature plasticity is generally limited to below 0.5%, accompanied by brittle fracture behavior [9], similarly to other members of the Mg-based BMG family. Alloying is also recognized as an important strategy for improving the plasticity of Mg-Zn-Ca-based BMG alloys [13–15]. According to reports, the addition of elements such as Pd [16], Ag [17], Cu [18,19], Mn [20,21], Nd [22], Y [23,24], Yb [15,25], and Zr [14] is beneficial for improving its plastic behavior to some extent. In particular, Yb alloying can even enable the bending of ribbon samples [15]. However, to date, no study has reported a dramatic enhancement in plasticity sufficient to induce a brittle-to-ductile transition in these systems.

To address the inherent limitations of Mg-Zn-Ca BMGs, the introduction of extrinsic reinforcing phases has become a significant and active research direction. Early research primarily focused on incorporating hard, high-modulus ceramic particles as reinforcements. For instance, Shanthi et al. demonstrated that adding Al_2O_3 particles into an Mg-Zn-Ca MG matrix can serve as stress concentration sites, promoting the initiation of multiple secondary shear bands [26]. This mechanism helps distribute plastic deformation to some extent, thereby enhancing the compressive plasticity of the composite. However, the limitations of this method are also evident: the interfacial bonding between ceramic particles and the MG matrix is generally weak. Excessive addition not only leads to interfacial debonding, which can act as crack initiation sites, but also significantly reduces the overall strength and fracture toughness of the material [27]. Subsequently, researchers have shifted their focus toward ductile metallic reinforcements, aiming to further enhance the plasticity and toughness of the materials through the inherent deformability of these phases. Representative metallic reinforcements include Fe particles [28,29], porous Mo particles [30], Ti particles [31], Ni-Ti shape-memory alloy particles [32], as well as SnZn intermetallic phases [33,34]. These metallic phases are expected not only to dissipate energy effectively via their own plastic deformation but also to establish favorable mechanical coupling with the MG matrix. Such coupling can promote shear-band bridging and retard crack propagation during deformation, thereby contributing to more pronounced toughening.

The ex situ Mg-Zn-Ca-based BMGCs face multiple challenges including interfacial bonding, particle distribution uniformity, and matrix stability. First, interfacial reactions between the reinforcement and the matrix tend to weaken interfacial bonding. The Mg-Zn-Ca MG matrix is chemically active and prone to react with reinforcements during high-temperature processing such as melt casting or powder metallurgy. For example, Ti particles may react with the Mg-based melt to form brittle Ti-Zn intermetallic compounds [35]. Such reaction layers can consume alloying elements from the matrix, potentially altering the local composition and impairing GFA. Second, inhomogeneous distribution of reinforcing particles limits their toughening effectiveness [36]. Finally, the inherently limited GFA of the Mg-Zn-Ca system means that the addition of reinforcements may further promote matrix crystallization. The resulting crystalline phases are typically brittle, leading to reduced strength and increased brittleness of the composite. Consequently, reinforcements such as porous Mo particle [37,38], Fe particle [39–42], and Ti particle [43–47], which have demonstrated effective toughening in systems like Mg-Cu-Ag-Gd, have not achieved

comparable performance enhancement in the Mg-Zn-Ca system. Therefore, controlling interfacial reactions, achieving uniform particle dispersion, and maintaining the stability of the matrix remain critical issues that must be addressed for Mg-Zn-Ca-based BMGCs.

To address the critical issue of inhomogeneous reinforcement distribution, a simple strategy is to pre-form the reinforcement into a uniformly distributed three-dimensional continuous network preform, which is then infiltrated with an MG matrix. Kim et al. fabricated BMGCs by infiltrating carbon fibers into a Zr-based alloy melt, achieving a homogeneous distribution of fibers [48]. However, severe interfacial reactions between the carbon fibers and the reactive metallic melt limited the ductility improvement [49,50]. Yin et al. employed pressure infiltration to inject the amorphous alloy melt into a Cu-coated carbon-fiber preform placed in a Cu mold [51,52]. The Cu coating suppressed interfacial reactions, inducing an obvious improvement in plasticity. Wang et al. used porous SiC foam as a preform to produce Zr-based BMGCs via pressure infiltration [53]. The three-dimensional continuous ceramic skeleton not only effectively impeded shear bands and promoted their multiplication, but also carried substantial load, leading to a marked increase in compressive strength and plasticity. Wang et al. fabricated Ti-based BMGCs reinforced with a continuous porous Cu preform, which significantly enhanced the energy-absorption capacity and plastic deformability of the composite [54]. Similar improvement effects are observed when porous Cu is replaced with porous Ni [55]. Ma and Gao et al. introduced stainless-steel wire-mesh/capillary-tube preforms, successfully imparting notable ductility and work-hardening capability to the BMGCs [56,57]. Zhang et al. developed dual-continuous reinforced BMGCs using porous W, achieving considerable strengthening [58,59]. These studies confirm that the use of continuous metallic preforms can effectively toughen BMGCs.

It is known that Fe is a biodegradable, non-toxic metal element with a high melting point and good plasticity, making it an ideal reinforcement choice for improving the plasticity and toughness of Mg-Zn-Ca BMGCs. In light of this, this study employs continuous porous iron (Fe foam) to enhance the mechanical properties of the $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ amorphous alloy. The influence of electroless Cu plating treatment on improving the Fe-Mg wettability and the formability of the composite is investigated, while the mechanical properties of the composite are tested, and its deformation-fracture behavior is analyzed.

2. Materials and Methods

2.1. Preparation of Composites

Commercial porous Fe skeletons (Fe foam, fabricated via the electroforming-Fe-on-polyurethane-sponge process, Dingyuan Metal Materials Co. Ltd., Qingdao, China) were cut into cylindrical rods (6 cm in height, 1.5–3 mm in diameter) and thin sheets (2 mm × 15 mm × 60 mm) using wire electrical discharge machining (Dalong DK7732, Taizhou, China) to serve as preforms for the BMGCs. Prior to pressure infiltration, the porous Fe preforms were first ultrasonically cleaned in acetone for 15 min to remove oils, then immersed in a dilute aqueous HCl solution (3 vol%) for 5 min to eliminate surface oxides, iron rust and dust deposits, followed by activation in an activation solution (0.1 g/L PdCl_2 (Macklin Biochemical Co. Ltd., Shanghai, China) 10 mL/L HCl in water (Guangdong Xinchengyuan Technology Co. Ltd., Huizhou, China)) for 15 min. Finally, electroless copper plating was carried out using a plating bath whose composition is listed in Table 1. Before plating, the pH value of the plating solution is adjusted to approximately 12.5 using a 20% (by volume) aqueous sodium hydroxide solution. The temperature of the plating solution is maintained at 25–30 °C using a water bath heating device.

Table 1. The Chemical Composition of the Bath Used in Electroless Copper Plating.

Chemical Reagent	Molecular Formula	Concentration
Copper(II) Sulfate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	5.31 g/L
Formaldehyde Solution	CH_2O	9.36 mL/L
Sodium Chloride	NaCl	6.38 g/L
Disodium EDTA	$\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8$	15.89 g/L
Potassium Sodium Tartrate	$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	6.03 g/L
Potassium Ferrocyanide	$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	2.13 mg/L
2,2'-Bipyridine	$\text{C}_{10}\text{H}_8\text{N}_2$	4.26 mg/L

All the chemicals were purchased from Fuchen Chemical Reagent Co. Ltd., Tianjin City, China.

A master alloy with the nominal composition $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ [10] was prepared from commercial high-purity Mg (99.99 wt%, Shanxi Yinguang Huasheng Magnesium Industry Co. Ltd., Yuncheng, China), Zn (99.999 wt%, Chihong Zinc and Germanium Co. Ltd., Qujing, China), and Mg-20 wt% Ca (Yueyang Yuhang New Materials Co. Ltd., Yueyang, China) and Mg-20 wt% Sr (Yueyang Yuhang New Materials Co. Ltd., Yueyang, China) master alloys. The raw materials were weighed by precision analytical balance (Mettler, ME204E, Columbus, OH, USA) and melted together by induction melting (Shanghai MTINST, VIMS-1000, Shanghai, China) under an argon atmosphere to obtain an ingot of the master alloy. Subsequently, the composite samples were fabricated by pressure-assisted infiltration of the molten alloy into the porous-Fe preforms placed in a copper mold. The master alloy was melted inside a quartz tube via induction heating. The temperature of the melt was monitored using an infrared two-color laser pyrometer and maintained at approximately 800 °C. The molten alloy was subsequently injected into a copper mold through a small pore located at the bottom of the quartz tube, driven by high-purity argon gas at a pressure of approximately 1 MPa. The detailed procedure follows that described in the literature [51]. The composite fabricated with uncoated porous iron is designated as BMGC1, while the composite produced with copper-coated porous iron is designated as BMGC2.

2.2. Structural Characterization

The phase structure of the BMGC materials was analyzed by X-ray diffraction (XRD, Tongda TDM-20, Cu $K\alpha$ radiation, Dandong, China). In order to examine whether the composite samples possess an amorphous matrix, XRD measurements were conducted at a scanning speed of 8°/min over a 2 θ range of 10–90°.

The microstructures of the porous Fe before and after Cu plating were observed using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800, Tokyo, Japan). The interfacial microstructure and chemical composition of the composites were further characterized by combining the same SEM with its attached energy-dispersive X-ray spectroscopy (EDS) system.

Low-magnification morphology of the composite samples was examined by optical microscopy (OM, Zeiss Axio Imager M2m, Jena, Germany), and the porosity of the porous Fe in the composites was quantified using Image J software. To observe the distribution of porous Fe in BMGCs, the cross-section of the composite material was ground with 2000-grit sandpaper, and low-magnification optical micrographs were acquired using the aforementioned Zeiss OM. The images were then converted into black-and-white binary format using AxioVision SE64 software to facilitate measurement. Since porous Fe extends in 3D space, it is difficult to obtain continuous 2D cross-sectional images for accurate pore size analysis. To address this, the discontinuous pore walls visible in the 2D images were reconstructed into continuous structures using the artificial intelligence (AI) module in

AxioVision SE64 software. Finally, statistical analysis was performed with Image Pro Plus 6.0 software.

Differential scanning calorimetry (DSC) curves of the composites were recorded from room temperature to 750 K at a constant heating rate of 20 K/min with a simultaneous thermal analyzer (STA, Setaram Thermo ONE, Lyon, France). Various thermodynamic temperature parameters were derived from the DSC curves to identify the glassy structure of the matrix.

2.3. Quasi-Static Compression Mechanical Property Testing

To evaluate the quasi-static compressive mechanical properties of the BMGC material, uniaxial compression tests were performed on cylindrical specimens with a size of $\Phi 2 \text{ mm} \times 4 \text{ mm}$ using an electronic universal material testing machine (Guanteng PA200, Changchun, China). The specimens were sectioned with a low-speed diamond saw (Kejing SYJ150, Shenyang, China). To avoid crystallization induced by temperature rise during cutting, the wheel speed was kept below 120 rpm and lubricating oil was applied for cooling. Compression tests were conducted at room temperature in accordance with ASTM E9 standard [60]. Prior to testing, a thin layer of grease was applied between the specimen ends and the compression platens to reduce end-friction effects. The tests were carried out under displacement-control mode at a constant strain rate of $1 \times 10^{-3} \text{ s}^{-1}$, and loading continued until obvious yielding, predefined deformation, or fracture occurred. During testing, the load–displacement data were automatically recorded by the testing system and subsequently converted into engineering stress–strain curves. Each test condition was repeated at least three times, and the average value of the three tests was taken to ensure reliability.

Fracture surfaces of the compressed specimens were examined using the S-4800 SEM to identify the fracture mode.

3. Results

3.1. Effect of Electroless Cu Plating on the Forming of BMGCs

To successfully fabricate porous iron-reinforced Mg-Zn-Ca BMGCs, it is essential to achieve favorable wettability between the porous iron surface and the molten Mg alloy during pressure infiltration. As reported in the literature [52,61], electroless copper plating can enhance the wettability between the reinforcement and the Mg-based amorphous alloy matrix. Accordingly, we employed this method to modify the surface of the porous iron, with the results presented in Figure 1. The insets in Figure 1a,b compare optical photographs of the porous iron before and after electroless copper plating. After plating, the color of the porous iron changed from gray to reddish-brown, consistent with the characteristic appearance of metallic copper.

Figure 1a presents a scanning electron microscopy (SEM) image of the porous iron substrate prior to plating, clearly showing a porous and loosely structured surface composed of particles with a broad size distribution. These morphological features are typical of electrodeposited metallic layers produced via the template-assisted fabrication method—specifically, electroplating onto a sacrificial polyurethane sponge template that is later removed, leaving behind the open-cell iron network. From Figure 1a, the average pore size within the porous iron structure can be roughly estimated at approximately 800 μm . This relatively large pore dimension is particularly advantageous for subsequent processing, as it facilitates effective pressure infiltration during the fabrication of metal-matrix composites, ensuring uniform reinforcement distribution and good interfacial contact.

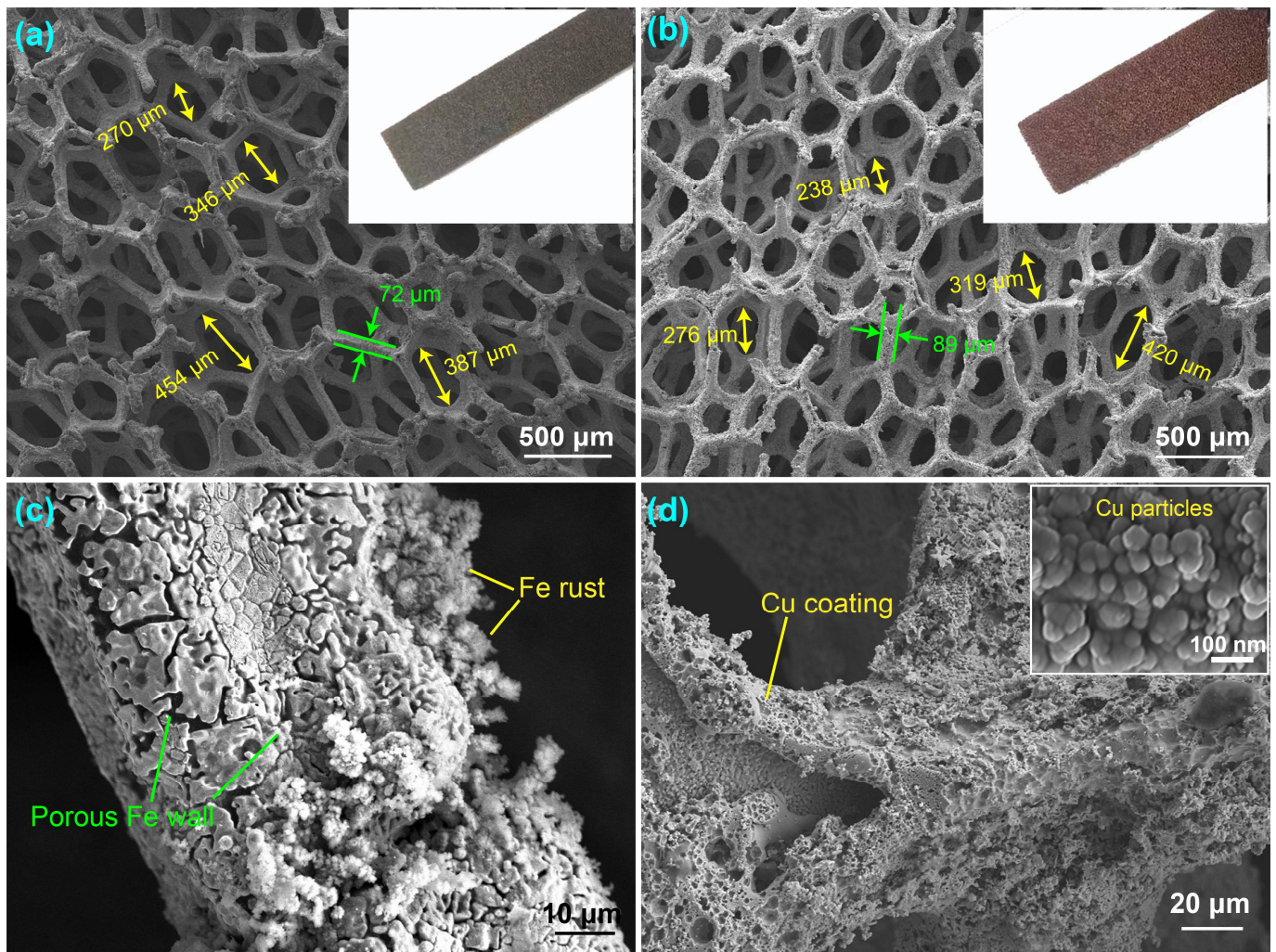


Figure 1. SEM micrographs of porous iron (a,c) before and (b,d) after electroless copper plating. The insets in (a,b) show corresponding optical photographs of the porous iron before and after plating, respectively.

After electroplating, as observed in Figure 1b, the pore diameter exhibits a slight reduction due to the deposition of the copper coating, although the change remains minimal and the overall porous architecture is well preserved. Moreover, the plated surface demonstrates a continuous and relatively smooth copper layer consisting of fine grains or particles. This deposited layer effectively fills the original interparticle gaps and surface voids on the porous iron substrate (pore walls), thereby enhancing surface uniformity and potentially improving mechanical interlocking as well as electrical conductivity in the resulting composite structure.

Figure 2 shows optical images of cylindrical porous-iron preforms in both un-plated and copper-plated states, together with the corresponding Mg-Zn-Ca BMGC samples reinforced with these porous-iron structures. As can be seen in Figure 2a, the un-plated porous-iron rod, with dimensions of 2 mm in diameter and 40 mm in length, yielded an infiltration depth of only about 5 mm in the resulting composite. In sharp contrast, when using the copper-plated porous-iron rod—measuring 1.5 mm in diameter and 35 mm in length, as shown in Figure 2c—the infiltration length surpassed 30 mm, clearly indicating that the electroless copper deposition markedly enhances the pressure-infiltration performance of the composite system. This substantial improvement in infiltration not only highlights the effectiveness of the copper coating in facilitating melt flow and pore filling,

but also verifies that the coating substantially promotes wettability between the porous-iron reinforcement and the molten Mg-Zn-Ca alloy. The improved interfacial wetting contributes to stronger bonding, more uniform reinforcement distribution, and ultimately better mechanical properties in the final composite material.

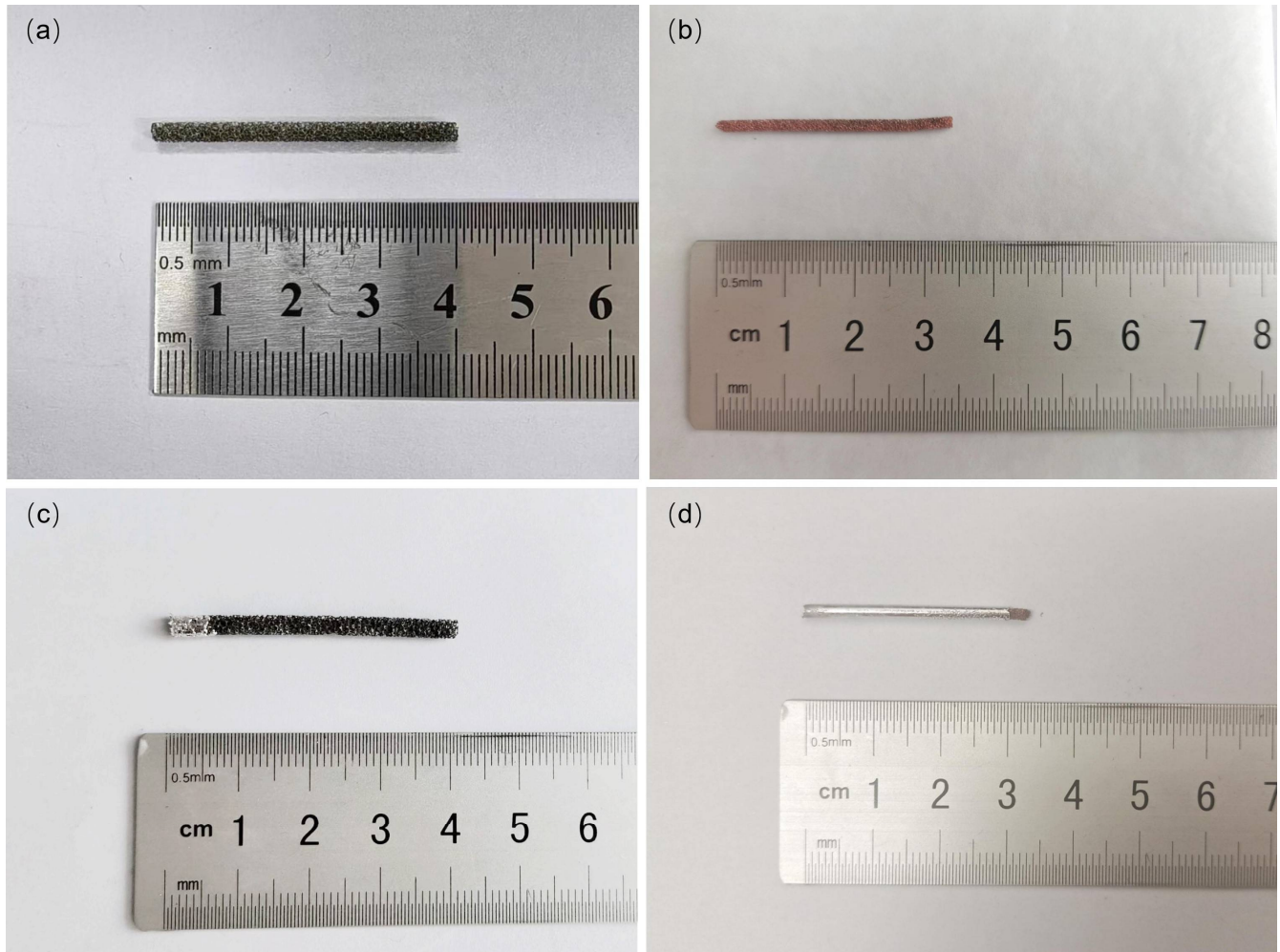


Figure 2. Optical images of the porous-iron preforms and their corresponding composite samples: (a) un-plated porous-iron rod, (b) copper-plated porous-iron rod, (c) composite sample fabricated from un-plated porous iron, and (d) composite sample fabricated from copper-plated porous iron.

3.2. Microstructure of BMGCs

Figure 3 presents representative optical micrographs of the infiltration region on the surface and within the interior of the composite. Due to direct contact with the mold surface, the outer layer remained non-infiltrated by molten Mg, resulting in exposure of the porous iron scaffold, as depicted in Figure 3a,b. A reddish-brown phase, attributed to the electroless copper coating, is discernible on the pore walls of the porous iron. Metallographic observations of the composite cross-section, shown in Figure 3c,d, indicate satisfactory interfacial bonding between the matrix and the continuous porous iron reinforcement. It is noteworthy that although the infiltration depth varies between composites reinforced with uncoated and copper-coated porous iron preforms, their microstructural characteristics exhibit similarity and remain consistent with the morphology illustrated in Figure 3a,c.

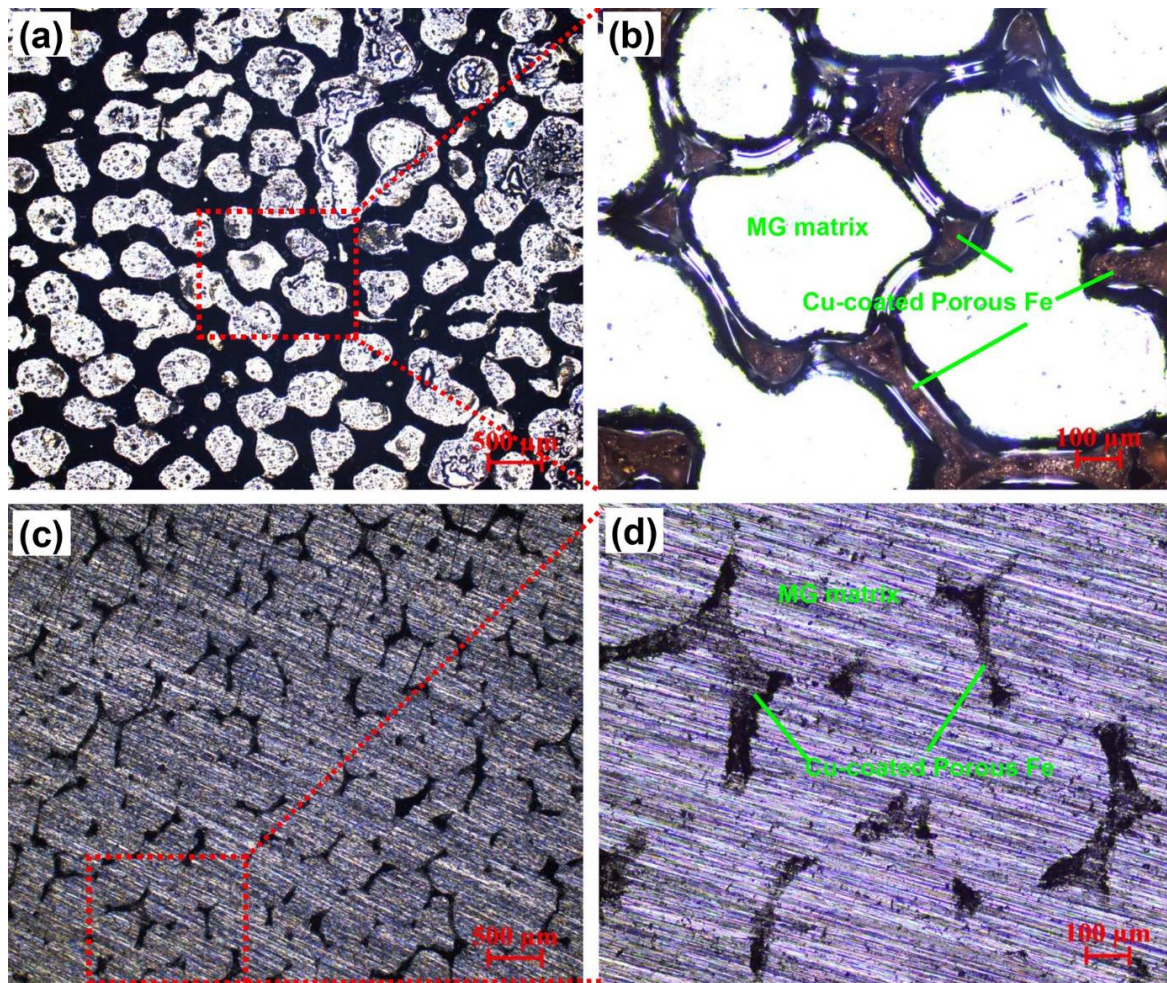


Figure 3. (a,b) Surface view of the infiltrated BMGC2 sample; (c,d) Cross-sectional view of the composite rod.

As a reinforcing phase in BMGCs, the pore structure of porous Fe necessitates a comprehensive quantitative characterization of key geometric parameters such as porosity and pore size. For this purpose, 2D cross-sectional images, similar to those presented in Figure 3c, were used to evaluate both the volume fraction of the iron phase and the pore distribution within the composite, with the quantitative results summarized in Figure 4. Figure 4a,b present the decolorized OM of the BMGC1 and BMGC2 samples, respectively, with the insets showing the corresponding AI-reconstructed images. The measured porosity values for composites reinforced with uncoated porous iron and copper-coated porous iron were 87.2% and 88.1%, corresponding to iron phase volume fractions of 12.8% and 11.9%, respectively. Furthermore, the average pore sizes were found to be $534 \pm 157 \mu\text{m}$ for the uncoated variant and $503 \pm 129 \mu\text{m}$ for the copper-coated one. These results suggest that the electroless copper coating has only a minimal and statistically insignificant impact on the geometric characteristics—specifically, the porosity and average pore size—of the continuous iron reinforcement phase within the composite. Such limited influence implies that the coating process preserves the intrinsic porous architecture of the iron scaffold, which is crucial for maintaining structural continuity, interfacial bonding, and ultimately the mechanical performance of the BMGC.

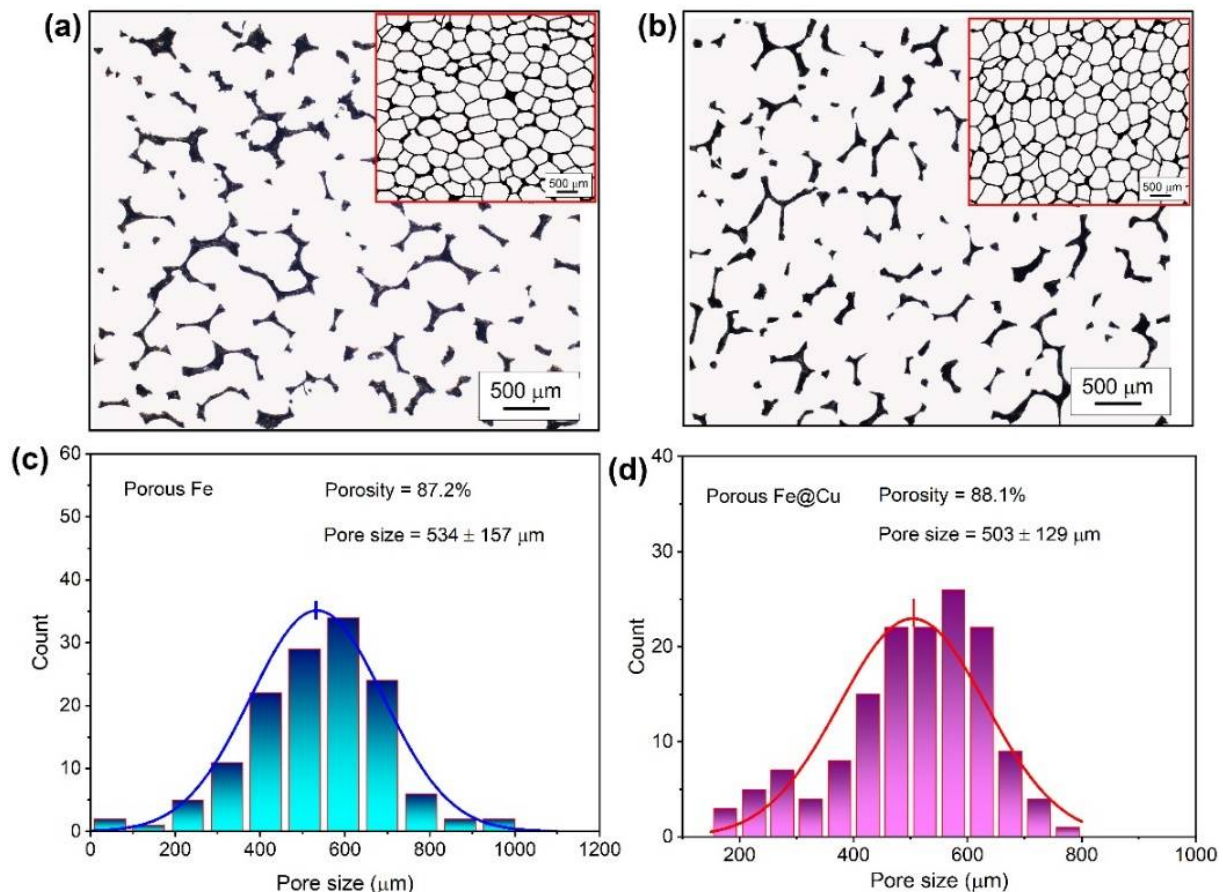


Figure 4. (a,b) Decolorized SEM images of uncoated and Cu-coated porous Fe skeletons, with insets showing reconstructed pore walls; (c,d) Pore-size distribution statistics.

To further elucidate the microstructure of the BMGC, with a specific focus on the influence of the copper coating on interfacial evolution, high-magnification SEM and EDS analyses were performed on the composite prepared with copper-coated porous iron. Figure 5a provides a low-magnification SEM overview of the composite cross-section. Several infiltration-incomplete voids are visible at the boundary between the porous iron reinforcement and the glassy matrix, which can be attributed to the inherently loose and irregular pore-wall morphology of the porous iron substrate. Figure 5b shows a higher-magnification image of the interfacial region. Notably, no distinct secondary phase or reaction layer is observed at the interface separating the matrix and the porous iron reinforcement. Figure 5c presents the EDS spectrum acquired from point C in Figure 5b. The strong characteristic peaks of iron confirm that this region corresponds to the porous iron reinforcement phase. Figure 5d displays the EDS spectrum collected from point D within the matrix region in Figure 5b. In addition to the principal matrix elements—magnesium, zinc, calcium, and strontium—a weak iron signal is also detected, consistent with the nominal composition of the amorphous alloy matrix. Figure 5e shows the EDS spectrum taken from point E, located precisely at the interface in Figure 5b. The simultaneous presence of iron and matrix elements (Mg, Sr, Ca) indicates that limited interfacial diffusion and possible partial mutual solubility have occurred between the iron reinforcement and the amorphous Mg-Zn-Ca-Sr matrix during composite processing. This interdiffusion behavior, although limited in extent, could contribute to improved interfacial bonding and load transfer in the composite system. Nevertheless, the absence of a continuous interfacial reaction layer suggests that the copper coating primarily serves as a wetting promoter without inducing extensive chemical interaction under the present processing conditions.

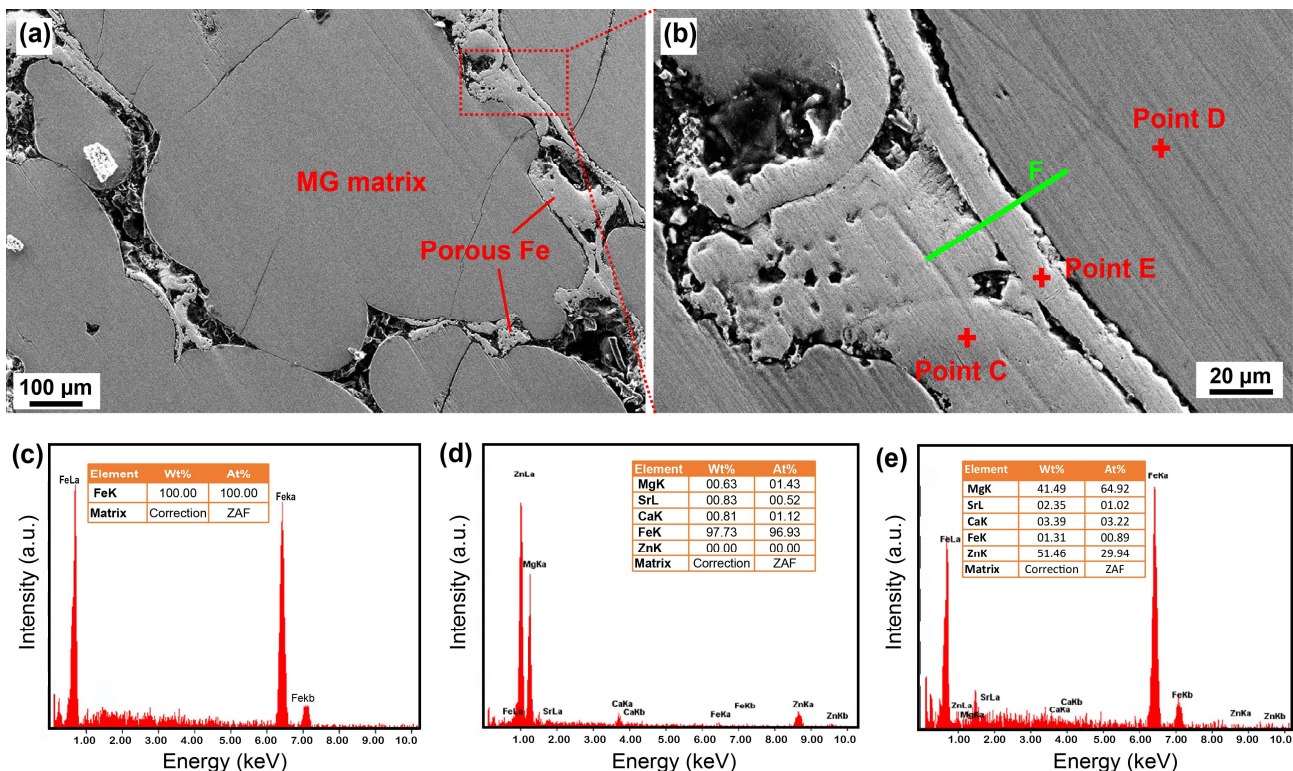


Figure 5. Typical SEM images and corresponding EDS analysis of the composite prepared with Cu-coated porous Fe skeleton. (a) Low magnification SEM image of BMGC2 sample; (b) SEM image with EDS analysis sites: red crosses for the point test and a green line for the line scan; (c–e) EDS spectra taken from points C, D, and E in (b), respectively.

Figure 6 illustrates the results of an energy-dispersive X-ray spectroscopy (EDS) line scan performed along the green trace marked by F in Figure 5b. The compositional profile clearly shows that the characteristic X-ray signal of copper is significantly enhanced at the interfacial region, indicating notable enrichment of copper at the boundary between the porous iron reinforcement and the metallic glass matrix. This observation is consistent with the prior application of electroless copper plating on the porous iron substrate. It is noteworthy that a detectable amount of copper is also present both within the pore-wall structure of the porous iron and inside the adjacent metallic glass matrix. This distribution suggests that during high-temperature pressure infiltration, copper atoms from the coating diffused not only along the interface but also partially migrated into the porous iron skeleton and penetrated into the molten Mg–Zn–Ca–Sr alloy. Such melting-assisted diffusion behavior helps reduce interfacial energy, improves wettability, and thus promotes complete filling of the porous network, which is highly beneficial for achieving sound pressure-infiltration molding, as supported by prior studies [52]. Furthermore, as displayed in Figure 5b, the elements Mg, Zn, and Ca are predominantly located within the amorphous matrix on the right side of the interface, whereas Fe is largely confined to the porous reinforcement on the left side. This distinct elemental partitioning is attributed to the limited mutual solubility and thermodynamic immiscibility between iron and molten magnesium under the present processing conditions. The resulting sharp compositional gradient across the interface reflects the absence of extensive interfacial reaction phases and aligns with the composite’s designed reinforcement-matrix architecture, where the metallic glass matrix and the porous iron reinforcement retain their individual chemical characteristics while being physically integrated through the copper-enhanced interface.

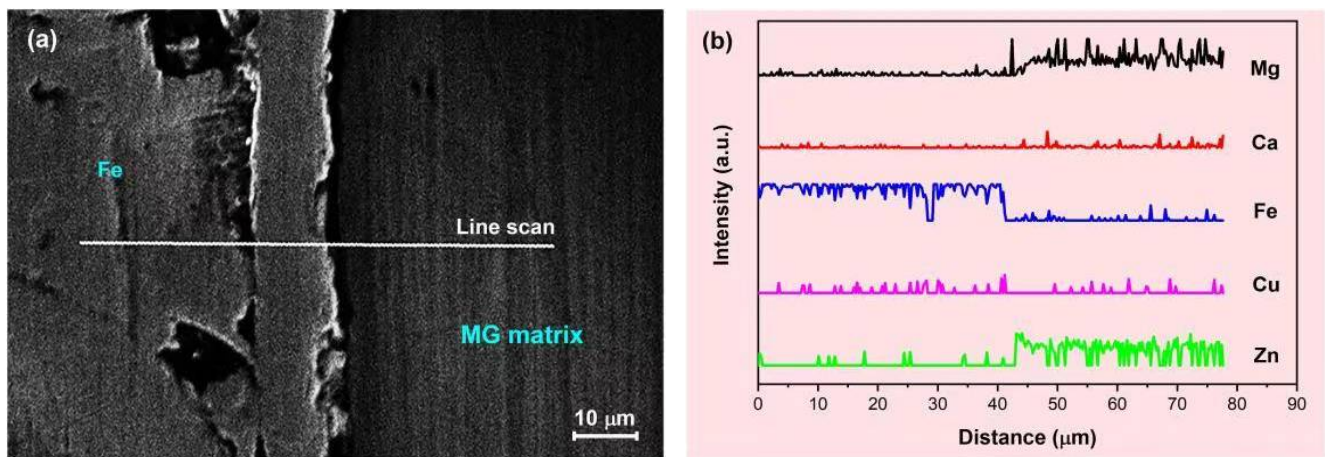


Figure 6. EDS line-scan results at the composite interface. (a) SEM image showing the test line; (b) elemental distribution profiles calculated from the EDS line scan.

Figure 7 shows the XRD patterns of different samples. All samples exhibit a broad diffuse scattering peak within the 2θ range of 30° to 45° , which is characteristic of an amorphous structure. This confirms that the matrix phase in each composite material retains a fully glassy nature. In addition to this amorphous halo, the XRD patterns of the two composite samples display sharp, well-defined diffraction peaks corresponding to the crystalline α -Fe phase. These peaks can be unequivocally attributed to the porous iron reinforcement incorporated into the composites.

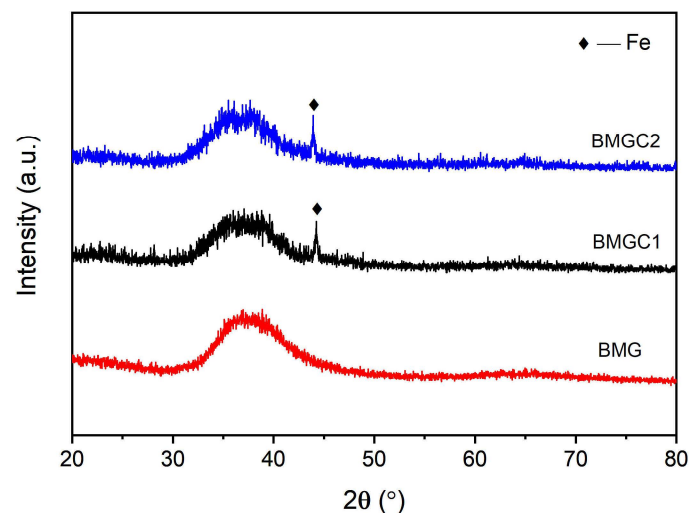


Figure 7. XRD patterns of the BMGC samples compared to the unreinforced $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ BMG.

It should be noted that no distinct diffraction peaks corresponding to crystalline Cu are detected in the pattern of the composite fabricated using copper-coated porous iron. This absence suggests that the electroless copper coating melted and dissolved into the matrix or diffused along the interface during the high-temperature pressure-infiltration process, rather than remaining as a separate crystalline phase. Moreover, the XRD patterns show no evidence of diffraction peaks belonging to any other crystalline intermetallic or secondary phases. This indicates that despite the melting and disappearance of the copper interlayer at the reinforcement-matrix interface during composite processing, no crystalline reaction products—such as Fe-Cu, Mg-Cu, or other ternary compounds—formed in the interfacial region or in the adjacent amorphous matrix. The preservation of a purely amorphous matrix, along with the absence of additional crystalline phases, further supports

the role of the copper coating primarily as a wetting and diffusion-promoting agent without inducing significant crystallization or undesirable interfacial reactions under the employed processing conditions.

Figure 8 shows the DSC curves of different BMGC samples and the $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ BMG alloy. As shown in Figure 8a, all DSC curves exhibit distinct glass transition and crystallization features, indicating that all tested samples contain a certain amount of amorphous phase, which is consistent with the XRD results shown in Figure 7. The $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ BMG alloy exhibits five crystallization peaks during heating, while the addition of uncoated porous Fe skeleton reduces the number of peaks to three. This suggests that the crystallization behavior of the matrix phase changes upon the introduction of porous Fe. However, when porous Fe coated with copper is incorporated into the amorphous matrix, the formed BMGC material again shows five crystallization peaks, matching the number observed in the $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ BMG alloy. Furthermore, a comparison of the thermodynamic parameters obtained from the DSC curves (Table 2) reveals that the glass transition temperatures T_g of both composite samples increase by approximately 10 K after composite formation. This indicates that the thermal stability of the composite matrix is higher than that of the monolithic BMG alloy. This phenomenon is likely related to changes in the matrix composition caused by reactions between the rust (Fe oxide) on the pore walls of the porous Fe and the molten Mg.

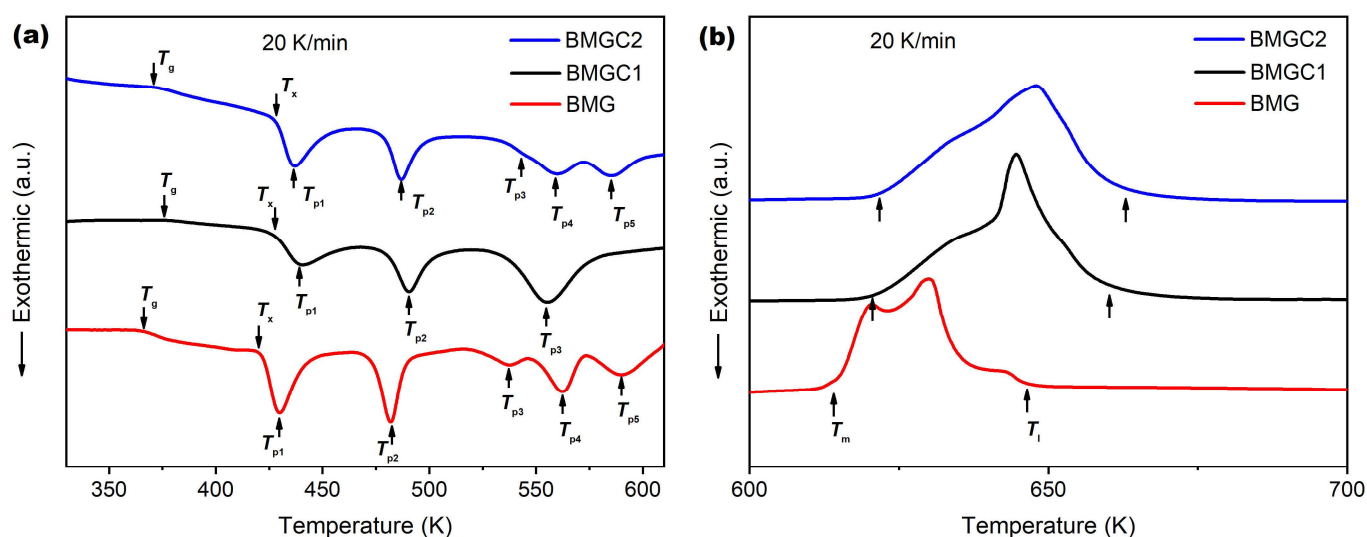


Figure 8. DSC curves of different BMGCs and the monolithic $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ BMG: (a) lower temperature region showing glass transition and crystallization behavior; (b) higher temperature region exhibiting melting events.

Table 2. Thermodynamic parameters measured from the DSC curves.

Sample	T_g (°C)	T_x (°C)	ΔT_x (°C)	T_m (°C)	T_l (°C)	$T_l - T_m$ (°C)	T_{rg}	γ
BMG	364.6	421.9	57.3	614.6	646.5	31.9	0.564	0.417
BMGC1	374.7	427.4	52.7	621.1	659.1	38.0	0.569	0.413
BMGC2	374.1	428.2	54.1	621.7	659.4	37.7	0.567	0.414

Furthermore, as shown in Figure 5b, the melting temperature (T_m) and liquidus temperature (T_l) of the composite samples are slightly higher than those of the $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ BMG alloy. This may be attributed to the introduction of high-melting-point elements Fe or Cu into the composite matrix, which alters its thermodynamic characteristics. An increase in melting point is usually accompanied by changes in other thermodynamic parameters,

thereby significantly affecting the glass-forming ability (GFA) of the alloy. Commonly used criteria for evaluating GFA include the width of the supercooled liquid region ΔT_x ($\Delta T_x = T_x - T_g$) [62], the reduced glass transition temperature T_{rg} ($T_{rg} = T_g/T_l$) [63], and the γ parameter ($\gamma = T_x/(T_g + T_l)$) [64]. Based on DSC data, we calculated the ΔT_x , T_{rg} , and γ values for the three types of samples, and the results are summarized in Table 2. The comparison reveals that the ΔT_x and γ values of the composite samples are generally lower than those of the monolithic amorphous alloy, indicating a certain reduction in the glass-forming ability of the composites. Notably, among the composites, BMGC2 prepared using Cu-coated porous Fe exhibits a relatively smaller decline in GFA, suggesting that its glass stability is less affected by the compositing process.

3.3. Mechanical Properties

Figure 9 shows the quasi-static compressive stress–strain curves of the composite samples and the $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ BMG. The corresponding mechanical properties measured are summarized in Table 3.

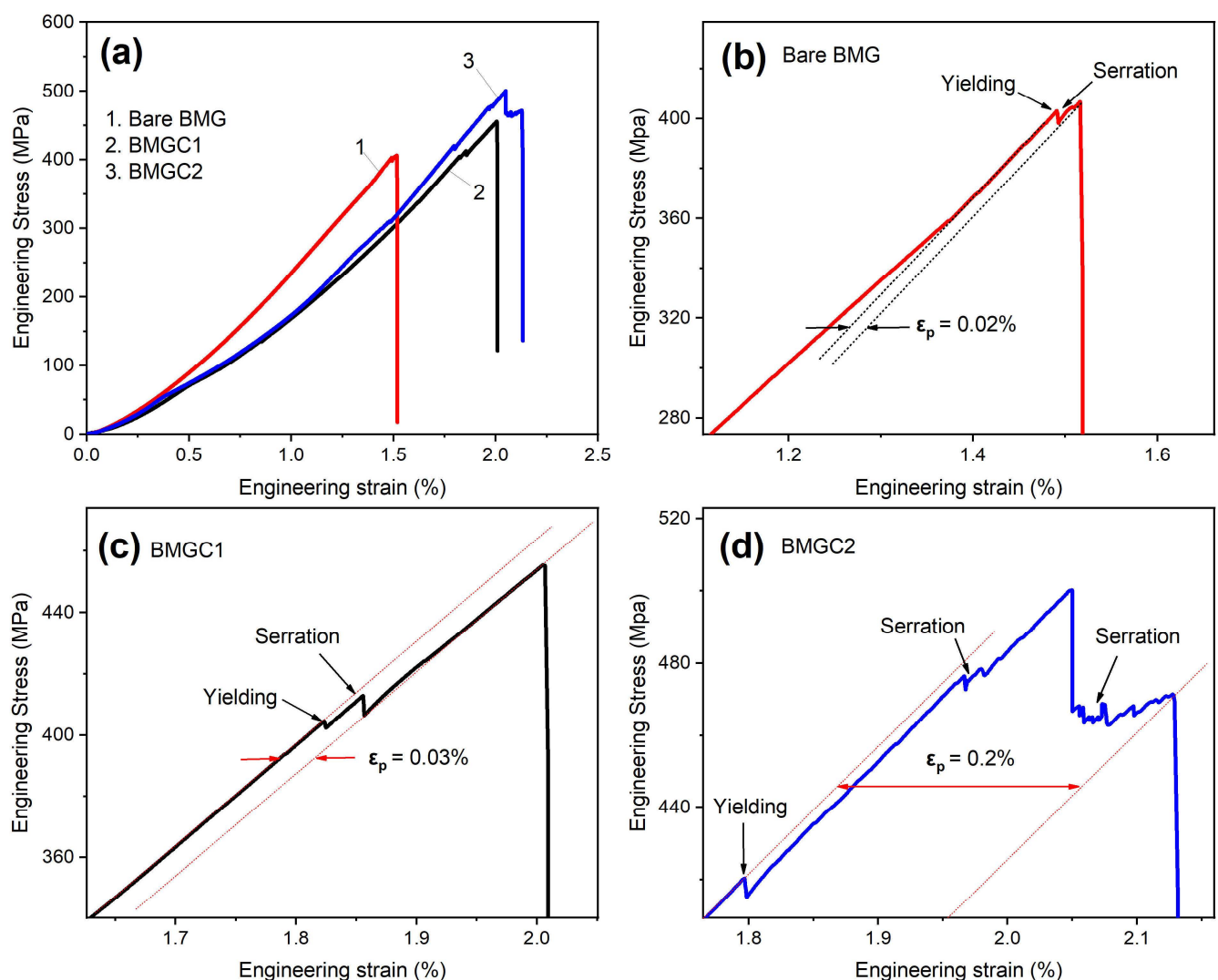


Figure 9. Quasi-static compressive engineering stress–strain curves: (a) Complete curves of $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ BMG and BMGC samples; (b–d) Magnified views of the stress–strain curves in the yielding-to-fracture region for the BMG, BMGC1, and BMGC2 samples, respectively.

Table 3. Mechanical properties of different samples.

Sample	Yield Strength (MPa)	Compression Strength (MPa)	Plasticity (%)	Yang' Moudulus (GPa)
BMG	403 ± 25	407 ± 17	0.02 ± 0.01	38.6 ± 5.4
BMGC1	405 ± 15	456 ± 31	0.03 ± 0.02	33.7 ± 8.2
BMGC2	420 ± 18	500 ± 20	0.2 ± 0.06	35.4 ± 6.1

As shown in Figure 9 and Table 3, the $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ BMG alloy exhibited no significant macroscopic plasticity under compression, with a plastic strain of only 0.02% and a compressive strength of 407 ± 17 MPa. For the composite sample BMGC1, fabricated using uncoated porous Fe, the compressive strength increased slightly to 456 ± 31 MPa, while no notable change was observed in plastic deformation. In contrast, the composite sample BMGC2, prepared with copper-coated porous iron, showed a marked improvement in compressive strength, reaching 500 ± 20 MPa, along with a compressive plastic strain of 0.2%. This indicates that the addition of Cu-coated porous Fe contributed to a certain enhancement in the ductility and toughness of the composite. Moreover, the compressive strength of the BMGC2 sample fabricated using Cu-coated porous Fe in this work slightly exceeds the compressive yield strength range of human bone (~ 230 MPa) [65,66]. Additionally, the Young's modulus of the composite, measured from the stress–strain curve, is 35.4 ± 6.1 GPa, which is close to the Young's modulus of human bone (~ 27 GPa) [67]. When the modulus of an implant matches that of bone, the risk of stress shielding can be effectively reduced. Therefore, the mechanical properties of the composite developed in this study meet the strength and safety requirements for human implantation.

Additionally, by comparing Figure 9b–d, it can be observed that the stress–strain curves of the composite samples exhibit distinct serrated flow behavior. This is a characteristic feature indicating the onset of plastic deformation in BMGs and confirms a tendency towards a brittle-to-ductile transition in the plastic deformation behavior of the composite samples. In our opinion, such a brittle-to-ductile transition is beneficial for enhancing the strength of inherently brittle materials. For instance, measured strength values for BMGs often exhibit significant scatter, which becomes more pronounced with increasing material brittleness [68–72]. The slightly lower compressive strength of the $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ BMG measured in this work compared to some literature values [10,17] can be attributed to this strength scatter associated with brittleness. When ductility is improved, this data scatter correspondingly decreases.

4. Discussion

4.1. Role of Copper Coating

The behavior of the electroless Cu coating in the Mg–Zn–Ca melt plays a critical role in the formation of composites. Analysis of the Mg–Cu binary phase diagram indicates that Mg and Cu form a low-eutectic system at approximately 485 °C [73], which is considerably lower than the melting points of Mg (650 °C) and Cu (1083 °C). The existence of this low-eutectic point implies that, upon contact, solid Cu can undergo a rapid eutectic reaction with the Mg-based melt, resulting in “contact melting” of the Cu surface well below its own melting temperature. This process quickly generates a thin liquid film with a composition close to the eutectic point at the solid–liquid interface, which substantially reduces the interfacial energy and provides favorable thermodynamic conditions for the spreading of the melt over the Cu surface.

The infiltration process of the composite can be regarded as a diffusion-corrosion process of the electroless Cu coating by liquid Zn. It is well known that diffusion coefficients tend to be high at elevated temperatures. According to the study by Christopher et al., the

bulk diffusion coefficient of Zn in Cu at 800–900 °C is on the order of $\sim 10^{-12}$ m²/s [74]. Meanwhile, the electroless Cu coating used in this work exhibits a typical nanocrystalline structure, with grain/particle sizes generally in the range of tens of nanometers, as shown in the inset in Figure 1d. The most prominent structural characteristic of nanocrystalline materials is their exceptionally high grain-boundary density. Grain boundaries, acting as defective regions in the crystal lattice where atomic packing is looser and the activation energy is lower, provide efficient “short-circuit diffusion” pathways for atomic migration. The short-circuit diffusion coefficient along grain boundaries can be 2–3 orders of magnitude higher than the bulk diffusion coefficient, reaching levels of 10^{-10} m²/s or greater. The diffusion depth x of Zn in α -Cu can be roughly estimated using a one-dimensional diffusion model:

$$x = \sqrt{Dt} \quad (1)$$

In Equation (1), D represents the diffusion coefficient of Zn in α -Cu, taken as $\sim 10^{-10}$ m²/s, and t denotes the pressure infiltration time, which is simply estimated as 1 s. With such a high diffusion coefficient, Zn atoms can diffuse over a distance on the micrometer scale along the grain-boundary network within 1 s, far exceeding their diffusion capability in single-crystal or coarse-grained Cu. Consequently, the dense grain-boundary network within the nanocrystalline Cu layer provides a highly favorable kinetic pathway for the rapid transport of Zn atoms from the melt into the Cu layer, as well as for the reverse transport of Cu atoms into the melt. This enables the electroless Cu coating to melt/diffuse and disappear rapidly within the very limited time window available during the pressure infiltration process.

When such a nanocrystalline electroless Cu coating comes into contact with the Mg–Zn–Ca melt, two rapid processes occur simultaneously at the interface. First, an ultrafast reactive inter-diffusion between Zn and Cu takes place, leading to the formation of a compositionally graded and kinetically highly active diffusion-coupled layer within an extremely short period. Second, this diffusion layer forms a eutectic alloy with Mg, and its rapid melting—attributed to the low eutectic point—facilitates thorough mixing with the Mg–Zn–Ca melt. Consequently, neither pure Cu nor distinct interfacial reaction layers can be observed at the composite interface. In our opinion, the melting of the active diffusion-coupled layer plays a decisive role in enhancing the overall wettability.

4.2. Toughening Mechanism

To clarify the role of the porous Fe skeleton in strengthening and toughening the composite, the fracture surface morphology of the BMGC2 sample was examined, as shown in Figure 10. Figure 10a reveals the characteristics of the porous Fe skeleton, which divides the entire fracture surface into distinct regions (pore range). Three primary morphological types are identified in the regions marked as B, C, and D in Figure 10a: vein-like patterns, nanoscale corrugations, and granular fracture morphology. Vein-like patterns are typical of shear-induced deformation and are commonly observed in ductile BMG alloys such as Zr-based [75] and Ti-based [76] BMG systems. In contrast, except for small-sized Mg–Cu–Ag–Gd, Mg–Ni–Ag–Nd and so on, most Mg-based BMG alloys generally exhibit intrinsic brittleness under compression, fracturing into small fragments with nanoscale corrugations [77]. The presence of vein-like patterns in Figure 10b demonstrates that, at least locally, the BMGC sample exhibits ductile fracture behavior.

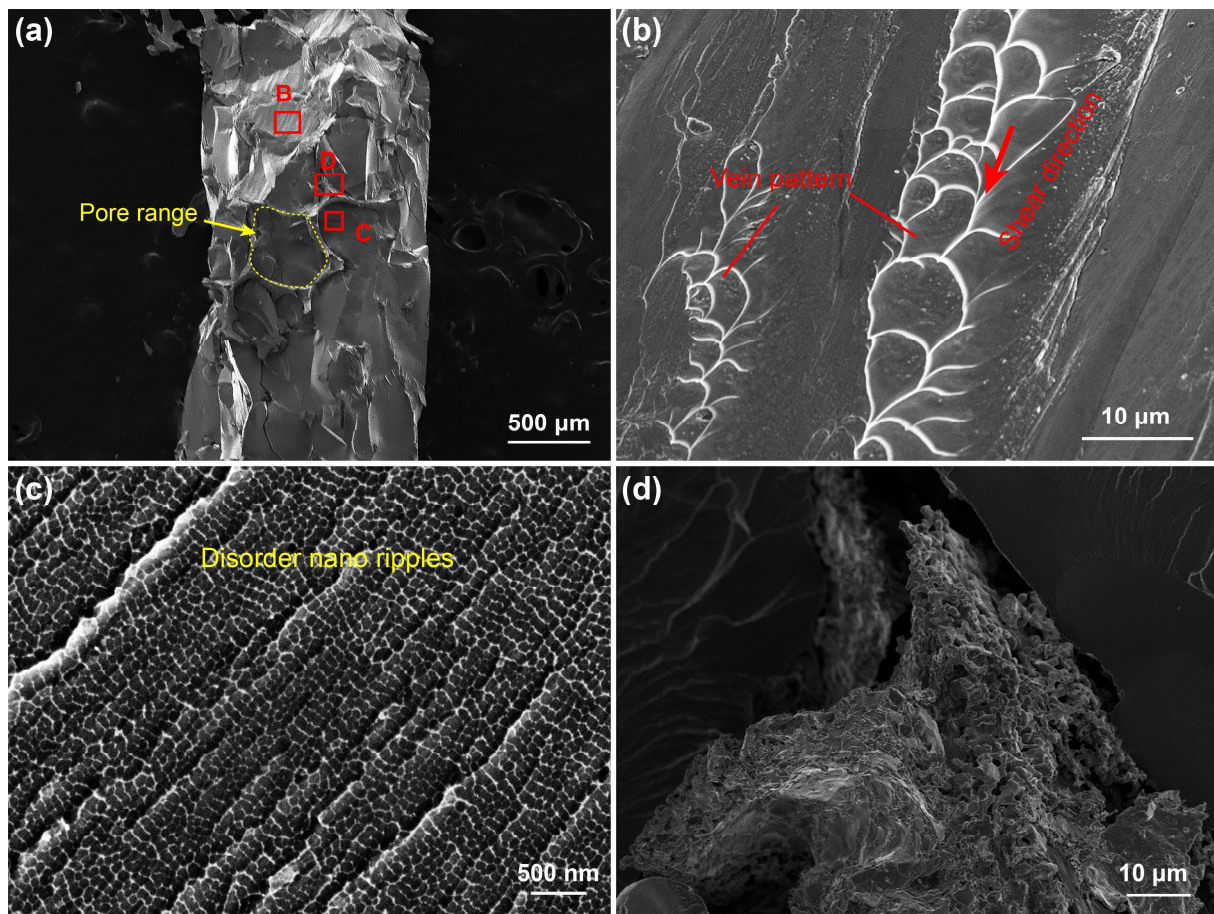


Figure 10. SEM fractography of the BMGC sample prepared using Cu-coated porous Fe: (a) low-magnification overview; (b) enlarged view of rectangular region B in (a); (c) enlarged view of rectangular region C in (a); (d) detailed view of the porous iron area corresponding to rectangular region D in (a).

Nanoscale corrugation pattern is one of the typical fracture surface features in brittle BMGs, such as Mg-based [78], Co-based [79] and Fe-based BMG [80] systems, and often appears within smooth regions of the fracture surface. The formation of this morphology is closely related to the dynamic energy release during fracture: when fracture occurs, the localized release of strain energy excites surface Rayleigh waves along the crack front [80]. The propagation and interference of these stress waves result in periodic nanoscale undulations on the fracture surface—observed as nanoscale corrugations [81]. Notably, the morphology of these corrugations exhibits a distinct spatial variation along the crack propagation direction. In regions farther from the fracture origin, where stress wave propagation stabilizes, the corrugations typically display clear and regular periodic arrangements, classifiable as nano-periodic corrugations. In contrast, closer to the fracture origin, where energy release is more intense and propagation less stable, the corrugations appear more disordered, with reduced periodicity, often resembling dimple-like features formed by the aggregation of numerous nanoscale dimples or micropores [82]. This continuous transition indicates that even in BMGs that exhibit macroscopic brittle fracture, localized plastic deformation and microstructural evolution occur at extremely small scales (e.g., below 10 nm), reflecting the complexity of deformation in BMGs at the nanoscale. From the perspective of material toughening design, controlling the fracture process to suppress the formation of periodic nanoscale corrugations and promote localized energy dissipation is crucial for enhancing the macroscopic toughness of BMGs. This also provides

a theoretical basis for utilizing heterogeneous structures, such as porous Fe skeletons, to regulate the plasticity of the MG matrix.

Figure 10a shows that different pore regions within the porous Fe skeleton are not located on the same continuous smooth fracture surface but rather belong to several independent fracture surfaces. The nanoscale corrugations in these regions all exhibit disordered characteristics, with one typical example shown in Figure 10c. This morphological feature indicates that the fracture origin for each pore region lies within its local vicinity, resulting in shorter crack propagation paths and preventing the formation of long-range ordered corrugation structures along a unified direction. We attribute this phenomenon primarily to the physical segmentation of the MG matrix by the porous Fe skeleton: the 3D network structure of the skeleton hinders continuous crack propagation, confining it to isolated matrix regions. Such spatial constraints deprive the crack front of sufficient continuous medium to support the propagation and interference of stable Rayleigh waves, thereby inhibiting the formation of highly ordered nanoperiodic corrugations. It can thus be inferred that each matrix region segregated by the skeleton may possess independent microcrack origins, which likely initiate near the skeleton pore walls due to stress concentrations caused by structural or compositional variations.

Figure 10d shows the fracture morphology of the pore wall itself, displaying typical brittle fracture characteristics closely associated with the granular deposit-rich structure on the pore wall surface. This observation supports the inference that pore walls act as stress concentrators and primary sites for crack initiation, further confirming the critical role of the skeleton structure in the fracture process.

The porous Fe skeleton significantly alters the crack propagation behavior and fracture morphology evolution in the MG matrix through its spatial segmentation effect. If future research can further optimize the skeleton's properties—such as enhancing its toughness and strength, reducing pore size to improve interfacial bonding, and tailoring the pore wall microstructure—it may be possible to more effectively regulate the deformation behavior of the MG matrix and guide crack propagation along paths more conducive to energy dissipation, thereby improving the overall strengthening and toughening performance of the composite. This understanding not only clarifies the mechanism of porous skeletons in BMG composites but also provides important guidance for the subsequent development of high-performance BMG composites based on structural design and interface engineering.

5. Conclusions

In the present study, a Cu-coated porous Fe skeleton-reinforced $\text{Mg}_{66}\text{Zn}_{30}\text{Ca}_3\text{Sr}_1$ BMGC was successfully fabricated by copper-mold pressure infiltration. Through systematic characterization and mechanical testing, the following main conclusions are drawn:

- (1) Surface Cu coating significantly improved the wettability between the Fe skeleton and the Mg melt. During infiltration, part of the coating dissolved into the matrix, slightly reducing the GFA of the matrix alloy. Nevertheless, owing to the high cooling rate of the copper mold and the small sample size, no crystalline phase was detected in the composite, confirming the fully amorphous nature of the matrix.
- (2) The BMGC exhibited a yield strength of 420 MPa, a compressive strength of 500 MPa, and a plastic strain of 0.2%, showing incensement of 22.8%, 900%, and 100%, compared with the monolithic BMG, respectively. These results indicate that the porous Fe skeleton enhances the plastic deformation capability of the glassy matrix through interfacial coordination.
- (3) The composite showed a mixed fracture mode characterized by “global splitting with local shear.” The fracture surface displayed both typical vein-like patterns and

nanoscale corrugations, suggesting that the crack propagation path was altered by the physical segmentation and interfacial coupling effect of the skeleton.

- (4) Fractographic analysis revealed that the introduction of the porous skeleton modified the crack propagation mechanism in the MG matrix. The pore walls acted as stress concentrators and micro-crack initiation sites, while the spatial confinement provided by the skeleton suppressed the formation of long-range periodic nanoscale corrugations and promoted local energy dissipation.

This work demonstrates the feasibility of using Cu-coated porous Fe as a reinforcing framework for BMGCs and provides a new strategy for tailoring the mechanical performance of BMGCs through heterogeneous skeleton design. Future studies may focus on interface alloying, hierarchical skeleton architectures, and failure mechanisms under dynamic loading, which would facilitate the development of such composites for structural-functional integrated applications.

Author Contributions: Investigation, resources, writing—original draft preparation, T.W.; Investigation, formal analysis, methodology, L.W.; software, validation, L.Z.; writing—review and editing, supervision, project administration, funding acquisition, X.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Central Government-Guided Local Projects in Hebei Province (236Z1018G).

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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