Postprint: Fabrication and Properties of 304 Stainless Steel Capillary-Tube-Toughened Zr53.5Cu26.5Ni5Al12Ag3 Bulk Metallic Glass

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Abstract

Using the infiltration method, a novel Zr53.5Cu26.5Ni5Al12Ag3 bulk metallic glass composite containing numerous metallic glass wires was successfully fabricated by incorporating 304 stainless steel capillaries with various volume fractions. The compressive properties were analyzed using a universal mechanical testing machine, while the surface and fracture morphologies were examined via white light interferometry, X-ray three-dimensional imaging, and SEM. The results demonstrate that the plasticity of the composite is significantly enhanced; specifically, when the capillary volume fraction reaches 34%, the compressive strain of the composite attains 22%. Additionally, work hardening occurs during deformation, with the degree of work hardening being dependent on the capillary content. The fracture exhibits near-45° shear failure with a relatively flat surface, where capillary tearing and interface debonding constitute the crack path. The capillaries undergo severe deformation, and the number of shear bands increases with increasing capillary volume fraction; the matrix encapsulated within capillaries experiences shear lag relative to the matrix external to the capillaries. Research on capillary-toughened bulk metallic glass composites holds significant importance for elucidating the toughening mechanisms of bulk metallic glass composites and for advancing the application of bulk metallic glass alloys in engineering structural materials.

Full Text

Study on Fabrication and Properties of 304 Stainless Steel Capillary Tube/Zr53.5Cu26.5Ni5Al12Ag3 Bulk Metallic Glass Composites

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Abstract

Different volume fractions of 304 stainless steel capillary tube/Zr53.5Cu26.5Ni5Al12Ag3 metallic glass composites were prepared using infiltration method. Their properties and deformation behaviors were investigated systematically. The mechanical properties were performed on materials test machine. Surfaces and fracture morphologies were examined using white light interferometer, X-ray 3D imaging and SEM techniques. The results show that the ductility of composites was improved. Its compressive strain reaches 22% when the volume fraction is 34%. The deformation involves obvious work hardening. The amount of work hardening depends on the content of tubes. The composite fails in the shear mode along 45°. The split and debonding of tubes and interfaces act as the propagation way of crack. The amount of shear bands increase as the volume fraction increases. The shear deformation of amorphous in tubes falls behind that out tubes. The work will enrich the ductility mechanisms of amorphous and promotes the application of amorphous.

KEY WORDS Zr53.5Cu26.5Ni5Al12Ag3 bulk metallic glass, 304 stainless steel capillary tube, shear band, work hardening

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Zr-Cu-Ni-Al amorphous alloys exhibit strong glass-forming ability and a wide supercooled liquid region, enabling the fabrication of large-scale bulk metallic glasses with excellent properties [1~4]. The addition of small amounts of Ag to Zr-Cu-Ni-Al alloys can substantially improve their glass-forming capacity, allowing the production of amorphous rods up to 20 mm in diameter [5]. Such bulk metallic glasses with exceptional glass-forming ability possess high strength, hardness, fracture toughness, wear resistance, and corrosion resistance [6~10], making them promising candidates for practical applications.

However, bulk metallic glasses tend to develop highly localized shear bands under external loading at room temperature, which propagate rapidly and lead to catastrophic fracture. This severely limits their application as structural materials. Consequently, improving the room-temperature plasticity of amorphous alloys has become a critical research topic. Numerous studies [11~16] have demonstrated that the formation of dispersed second-phase dendrites or micro/nano-scale particles in situ within the amorphous matrix can enhance plasticity. For instance, Hui et al. [17] achieved a compressive plastic strain of 18% in Mg-based amorphous alloys by obtaining uniformly distributed micron-sized -Mg phases. Hofmann et al. [18] prepared Zr-based amorphous composites with tensile plasticity reaching 13%.

The in situ method for fabricating endogenous phase-toughened amorphous alloys offers the advantage of a simple process flow, but controlling the type, content, size, and distribution of the endogenous phases is challenging, hindering widespread practical application. Alternatively, introducing controllable second phases directly into amorphous alloys—such as unidirectional wires or fibers, frameworks, or partially crystalline particles—can effectively block shear band propagation and improve room-temperature plasticity [19~22], with certain successes achieved in this approach. Nevertheless, issues remain regarding the uniform distribution of metal particles and the excessively high volume fraction of metal wires (exceeding 50%) [22~27]. Except for W wire-reinforced composites with compressive strains over 10%, composites reinforced with more economical Fe or Mo wires exhibit relatively low compressive strains. Recently, Deng et al. [28,29] reported the use of a novel toughening material—stainless steel capillary tubes—to prepare Zr-based amorphous composites, achieving favorable toughening effects. With a unidirectional continuous capillary tube volume fraction of 38%, the composite' s compressive plasticity reached 14%. However, unidirectional continuous fiber-reinforced metal matrix composites exhibit high strength and modulus only along the fiber direction, presenting certain limitations. Therefore, this work systematically investigated the effects of stainless steel capillary tube volume fraction on the properties and deformation behavior of amorphous composites by varying the aspect ratio of capillary tubes to change their volume fraction, introducing variations in continuous interfaces within the composites. Random distribution was employed to achieve dense packing, realizing composite isotropy, and the toughening mechanism was elucidated.

The amorphous matrix selected was Zr53.5Cu26.5Ni5Al12Ag3 with high glass-forming ability. High-purity (99.9%) Zr, Cu, Ni, Al, and Ag were weighed according to atomic fractions and arc-melted under high-purity Ar (99.99%)

protection. The alloy ingot was remelted four times to obtain a homogeneous Zr53.5Cu26.5Ni5Al12Ag3 master alloy. Differential scanning calorimetry (DSC) using a Netzsch 404C instrument revealed a melting point of 1132 K for the master alloy. The 304 stainless steel (0Cr18Ni9) capillary tubes used in the experiments had an outer diameter of 0.5 mm and wall thickness of 0.1 mm, which were cut into tubes with aspect ratios (l/d) of 1, 2, 4, and 6 using wire electrical discharge machining. The processed capillary tubes were then placed in boiling NaOH solution to remove oil contamination from their inner and outer walls, followed by repeated boiling in deionized water to remove residual NaOH, and final ultrasonic cleaning in anhydrous ethanol. The cleaned capillary tubes were randomly placed in a crucible with an inner diameter of 8 mm according to a predetermined mass. Zr53.5Cu26.5Ni5Al12Ag3 alloy was placed on top of the capillary tubes, and the crucible was inserted into a resistance furnace. After evacuating to 3×10^{3} Pa, the system was heated to 1293 K. Once the alloy melted, molten Zr53.5Cu26.5Ni5Al12Ag3 alloy was fully infiltrated into the stainless steel capillary tubes under 0.1 MPa pressure, followed by water quenching to produce 304 stainless steel capillary tube/Zr53.5Cu26.5Ni5Al12Ag3 amorphous composites. The composite rods were ground to a diameter of 4.5 mm using centerless grinding, cut into 10 mm cylinders, and the end faces were polished to ensure parallelism, resulting in compression specimens measuring 4.5 mm in diameter and 9 mm in length.

The composite interfaces, fracture morphologies of compression specimens, and shear band characteristics on side surfaces were examined using a MicroXAM white light interferometer, VersaXRM-500 transmission X-ray 3D imaging system, and S-3400N scanning electron microscope (SEM). For transmission electron microscopy (TEM) analysis, samples with a diameter of 4.5 mm and thickness of 1 mm were sectioned from the ends of compression specimens and prepared as TEM samples. Selected area electron diffraction (SAED) analysis of the composite matrix was performed using a Tecnai G2 20 TEM. Compression tests were conducted on an Instron 5582 universal testing machine at a strain rate of 1×10 s^{1}. Some compression specimens were ground to create a small platform approximately 2 mm wide on the side surface, which was polished to facilitate SEM observation of shear band formation and crack initiation and propagation.

2.1 Composite Structure

Figure 1a [Figure 1: see original paper]-d show SEM images of cross-sections of 304 stainless steel capillary tube/Zr53.5Cu26.5Ni5Al12Ag3 amorphous composites with different aspect ratios. The images reveal that the 304 stainless steel capillary tubes are uniformly distributed within the amorphous matrix, with no apparent defects such as voids or gaps at the tube/matrix interfaces. High-magnification images (Figures 1e and f) demonstrate good bonding between the 304 stainless steel capillary tubes and matrix, with continuous and uniform interfaces. Using the area method combined with the mass of added capillary tubes, the volume fractions of capillary tubes in composites with aspect ratios (l/d) of 1, 2, 4, and 6 were calculated to be 34%, 30%, 24%, and 18%, respectively. Evidently, the volume fraction of stainless steel capillary tubes decreases with increasing aspect ratio, resulting in fewer introduced interfaces. However, longer capillary tubes introduce longer continuous interfaces in the specimens, which affects the mechanical behavior of the composites. With the same number of interfaces, shorter continuous interfaces yield better composite plasticity [30].

2.2 Compression Properties

Figure 2 [Figure 2: see original paper] presents the room-temperature compressive stress-strain curves of 304 stainless steel capillary tube/Zr53.5Cu26.5Ni5Al12Ag3 amorphous composites. The deformation process primarily consists of two stages: Stage I—elastic deformation; and Stage II—plastic deformation accompanied by obvious work hardening. Table 1 lists the mechanical properties of the amorphous composites. The results show that the yield strength decreases with increasing capillary tube volume fraction, while both compressive fracture strength and plastic deformation increase. When the capillary tube volume fraction reaches 34%, the material exhibits maximum plastic deformation with a total strain of approximately 20%. This performance surpasses that reported by Deng et al. [28] for unidirectional stainless steel capillary tube amorphous composites (with a reinforcement volume fraction lower than the reported 38%, while compressive deformation increased from the reported 14% to approximately 20%, representing a 57% improvement). Analysis reveals that the enhanced plasticity primarily results from the random arrangement of capillary tubes, which increases shear band quantity and promotes multi-directional, branching, and tortuous shear bands (as shown in Figure 3a [Figure 3: see original paper]). Due to the presence of capillary tubes, numerous fine "amorphous wires" form within the tubes. Amorphous materials exhibit a clear size effect, where smaller dimensions yield better comprehensive properties [31~33]. These "amorphous wires" contribute to composite performance improvement to some extent. Higher volume fractions produce more amorphous wires, yielding greater performance enhancement. In contrast, unidirectional long 304 stainless steel capillary tube/Zr53.5Cu26.5Ni5Al12Ag3 amorphous composites generate shear bands with a single orientation (as shown in Figure 3b), and the long continuous interfaces facilitate crack propagation once interfacial cracking occurs, causing material splitting (as shown in Figure 3c). Randomly distributed capillary tube/Zr-based amorphous composites feature shorter continuous interfaces that more effectively obstruct crack propagation.

2.3 Influence of Capillary Tubes on Composite Deformation

Figure 4 [Figure 4: see original paper] shows SEM images of side surfaces of 304 stainless steel capillary tube/Zr53.5Cu26.5Ni5Al12Ag3 matrix amorphous composites with different volume fractions after 5% compressive deformation at room temperature. The images reveal that shear band quantity increases with capillary tube volume fraction, as does the degree of capillary tube deformation. Shear bands first appear in the matrix outside the capillary tubes and gradually transition to the amorphous material inside the tubes as deformation proceeds, indicating that shear deformation of the amorphous matrix within capillary tubes lags behind that of the external matrix.

Higher capillary tube volume fractions result in more interfaces per unit composite volume, and interfaces serve as the origin for shear band generation. Consequently, more interfaces produce more shear bands, and higher volume fractions yield greater shear band density. Additionally, increased interface numbers more effectively impede shear band propagation, with more shear band tips terminating at capillary tubes. This implies that capillary tubes bear greater stress, which intensifies capillary tube deformation as shear band effects strengthen, thereby releasing stress. Only when capillary tubes deform to a certain extent does deformation of the internal amorphous material occur through interfacial stress transfer. Therefore, the deformation and failure of amorphous material inside capillary tubes occur later than those of the external amorphous matrix.

2.4 Fracture Process and Morphology

Figure 5 [Figure 5: see original paper] presents side surface morphologies of the material at different deformation stages (0, 5%, 10%, and fracture) for a composite with 34% capillary tube volume fraction. As loading increases, shear bands initiate at stress concentration sites such as capillary tube ends and regions of maximum capillary tube deformation. Under the interaction of shear bands, microvoids form at interfaces, and their coalescence leads to interfacial cracking (Figure 5c). Simultaneously, shear bands continue to propagate, encountering capillary tubes via two pathways: either bypassing the tubes (forming interfacial cracks) or passing through them (causing tube tearing). As loading progresses, cracks connect along the maximum shear stress plane to form a main crack traversing the specimen cross-section, resulting in final composite fracture (Figure 5d).

Figure 6a [Figure 6: see original paper] shows a typical room-temperature compressive fracture surface of an amorphous composite with 34% capillary tube content, with the inset displaying a cross-sectional image from 3D transmission X-ray micrography (XRT). The fracture exhibits near-45° shear fracture with a relatively flat surface. XRT imaging reveals no defects such as voids or inclusions within the compressed specimen, and no obvious secondary cracks are observed inside the fracture surface apart from the main crack. The fracture mode resembles that of pure amorphous alloys but differs significantly from unidirectional 304 stainless steel capillary tube/Zr53.5Cu26.5Ni5Al12Ag3 amorphous composites (Figure 3c). Figure 6b shows that the Zr53.5Cu26.5Ni5Al12Ag3 amorphous matrix undergoes brittle fracture, while 304 stainless steel capillary tube tearing and interface debonding form the crack propagation path. The matrix surface lacks obvious vein patterns, and SAED confirms that the matrix remains amorphous (Figure 6c), which differs from the fracture morphology of monolithic amorphous alloys. This is primarily attributed to the elimination of vein patterns in the amorphous phase during large deformation, a phenomenon also reported in dual-continuous phase composites [30]. High densities of slip bands and dislocations are observed within the stainless steel capillary tubes (Figure 6d). White light interferometer analysis of a 304 stainless steel capillary tube/Zr53.5Cu26.5Ni5Al12Ag3 composite compression specimen (with 10% deformation) containing a small platform 贯通 (through) the compression direction reveals that the platform becomes uneven, with severe deformation of the 304 stainless steel capillary tubes (Figure 6e).

3 Conclusions

(1) Stainless steel capillary tube/Zr-based amorphous composites with different aspect ratios (l/d) were successfully fabricated. As the capillary tube aspect ratio decreases (i.e., as capillary tube volume fraction increases), composite plasticity improves progressively. The maximum compressive strain of 22% was achieved at an aspect ratio of 1. This performance enhancement is primarily attributed to the increased number of interfaces in the composites and the greater quantity of high-performance "amorphous wires."

(2) Shear band formation originates at the interface between capillary tube outer walls and the amorphous matrix, with shear band density increasing as capillary tube volume fraction increases.

(3) Deformation of amorphous material inside capillary tubes lags behind that of the external amorphous matrix.

(4) The composites fail via near-45° shear fracture with relatively flat surfaces. The matrix undergoes brittle fracture, while capillary tubes exhibit severe plastic deformation with high slip band densities. Capillary tube tearing and interface debonding form the crack propagation path.

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Note: Figure translations are in progress. See original paper for figures.