Effect of Cooling Rate and Aspect Ratio on the Mechanical Properties of Ti-Based Metallic Glass Composites Postprint

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Abstract

By preparing Ti45.7Zr33Ni2.9Cu5.9Be12.5 amorphous composite samples of different sizes, the effects of cooling rate and aspect ratio on the mechanical properties of endogenous dendrite-reinforced Ti-based amorphous composites were investigated. As the cooling rate during preparation decreased, the size of the dendritic phase in the amorphous composites gradually increased, while the phenomenon of dendritic phase ripening also became more pronounced. In terms of mechanical properties, this manifested as a decrease in strength and an enhancement in plasticity of the amorphous composites. Unlike previous amorphous composites whose properties were relatively sensitive to the aspect ratio, the mechanical properties of the Ti45.7Zr33Ni2.9Cu5.9Be12.5 amorphous composites in this work were not sensitive to changes in aspect ratio, which is attributed to the regulation of internal stress distribution in the amorphous composites by the presence of crystalline phases and the occurrence of deformation-induced martensitic transformation behavior within them.

Full Text

Preamble

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Title and Authors

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Abstract

Amorphous alloy composites are designed to improve plasticity by introducing a second crystalline phase that prevents rapid propagation of shear bands in the amorphous matrix, thereby promoting multiple shear band formation. In-situ formed amorphous composites have attracted considerable interest due to their excellent properties and broad application prospects, particularly dendrite-reinforced composites that exhibit outstanding tensile ductility. Recent studies demonstrate that plastic deformation behavior depends not only on the mechanical properties of the crystalline phase (e.g., elastic modulus) but also on its size, volume fraction, and morphology. Additionally, the mechanical properties of monolithic amorphous alloys—especially plastic deformation capacity—are closely related to sample topology, such as aspect ratio. However, the relationship between mechanical properties and topological morphology remains poorly understood for amorphous composites.

In this work, we systematically investigated the effects of cooling rate and aspect ratio on the mechanical properties of $Ti_{45\cdot7}Zr_{33}Ni_{2\cdot9}Cu_{5\cdot9}Be_{12\cdot5}$ amorphous alloy composites by adjusting the preparation process and sample dimensions. As the cooling rate decreased during preparation, dendrite sizes increased and dendrite coarsening became more pronounced, leading to reduced strength but enhanced plasticity. Unlike previous reports showing high sensitivity to aspect ratio, the $Ti_{45\cdot7}Zr_{33}Ni_{2\cdot9}Cu_{5\cdot9}Be_{12\cdot5}$ composite exhibited minimal sensitivity. This behavior is attributed to the presence of the crystalline phase and deformation-induced martensitic transformation within it, which modulates internal stress distribution during deformation.

Keywords: amorphous alloy composite, mechanical property, cooling rate, aspect ratio

1. Introduction

The design philosophy of amorphous alloy composites involves introducing a crystalline second phase to block rapid shear band propagation in the amorphous matrix, thereby generating multiple shear bands and improving plasticity [1–7]. This approach yields novel alloys combining the high strength of amorphous alloys with the good ductility of crystalline alloys. Research [8–10] indicates that plastic deformation behavior depends not only on crystalline phase properties (e.g., elastic modulus) but also on its size, volume fraction, and morphology [3,4,11]. Hays et al. [3] observed that in a Zr-based composite with 5% compressive plasticity, shear bands arrange regularly between solid solution phases when dendrite sizes approach characteristic mechanical dimensions like shear band spacing, suggesting that dendrite morphology control could enhance overall performance. Hofmann et al. [4] successfully controlled dendrite morphology through semi-solid processing to produce in-situ composites with high strength, considerable plasticity, and high fracture toughness. Qiao et al. [12] used the Bridgman method to regulate crystalline phase size and distribution, achieving over 30% room-temperature compressive plasticity. Collectively, these studies establish that crystalline phase characteristics (size, volume fraction, morphology) are critical parameters governing the mechanical properties of dendrite-reinforced amorphous composites.

Furthermore, investigations of monolithic amorphous alloys [13,14] reveal that mechanical properties—particularly plastic deformation capacity—are strongly influenced by sample topology. However, the relationship between mechanical properties and topological morphology remains largely unexplored for amorphous composites with an amorphous matrix. Therefore, this work comprehensively examines both crystalline phase morphology and sample topology effects using in-situ dendrite-reinforced Ti-based amorphous composites. By controlling cooling rates during preparation, we produced composites containing dendrites of varying sizes and morphologies, then systematically analyzed samples with aspect ratios of 1:1, 2:1, and 3:1 to elucidate their combined influence on composite performance.

2. Experimental

The alloy composition $Ti_{45\cdot7}Zr_{33}Ni_{2\cdot9}Cu_{5\cdot9}Be_{12\cdot5}$ (at%) was prepared from high-purity metals (>99.9 wt%) by repeated melting in an AM10.5 vacuum arc furnace under argon protection. Each master alloy ingot weighed approximately 100 g. The ingots were then crushed, and appropriate amounts were remelted in quartz tubes and injected through a ~1 mm diameter nozzle into copper molds to form rods. Rods with diameters of 3 mm, 5 mm, and 8 mm were produced and cut into samples measuring 2 mm × 2 mm × 2 mm, 2 mm × 2 mm × 4 mm, and 2 mm × 2 mm × 6 mm (corresponding to aspect ratios of 1:1, 2:1, and 3:1) for mechanical testing. Different diameters corresponded to different cooling rates during preparation, enabling investigation of cooling rate effects through performance comparisons across sample sizes.

Microstructural characterization employed a PW1050 X-ray diffractometer (XRD), S3400N scanning electron microscope (SEM), and JEOL 2010 transmission electron microscope (TEM). Thermal analysis was performed using Netzsch differential scanning calorimetry (DSC) under flowing argon at a heating rate of 20 K/min. Room-temperature compression tests were conducted on an Instron 5582 universal testing machine at a strain rate of 5×10^{-4} s^{-1}.

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3. Results and Discussion

3.1 Microstructural Characterization

[Figure 1: see original paper] shows XRD patterns of $Ti_{45\cdot7}Zr_{33}Ni_{2\cdot9}Cu_{5\cdot9}Be_{12\cdot5}$ composites with different diameters. All three samples exhibit broad amorphous scattering peaks superimposed with four sharp crystalline diffraction peaks, confirming a two-phase structure. Comparison with standard PDF cards identifies the crystalline phase as a bcc solid solution β-phase [15]. The calculated lattice constant (~0.34 nm) is larger than that of Ti but smaller than Zr [16,17], indicating a β-Ti(Zr) solid solution consistent with literature [18]. Notably, diffraction peak broadening increases as sample diameter decreases, suggesting reduced grain size according to the Scherrer formula [19].

[Figure 2: see original paper] presents SEM images of composites with diameters of 3 mm, 5 mm, and 8 mm. The microstructure consists of black β-dendrites uniformly distributed in an amorphous matrix. As casting size increases (i.e., cooling rate decreases), dendrite sizes grow significantly, with pronounced dendrite coarsening. While coarsening typically occurs during subsequent heat treatment [20,21], it appears here during casting because the pouring temperature (1100 K) lies within the alloy's semi-solid temperature range. EDS analysis of contrast-differentiated regions () reveals that the amorphous matrix contains less Ti but more Zr, Ni, and Cu than the dendrites. As sample diameter increases, Ti content in the matrix increases while other elements decrease, and the dendrites show the opposite trend.

EDS results of $Ti_{45\cdot7}Zr_{33}Ni_{2\cdot9}Cu_{5\cdot9}Be_{12\cdot5}$ amorphous alloy composites with different diameters (atomic fraction / %)

Diameter	Matrix	Dendrite
3 mm	Ti: 43.2, Zr: 35.1, Ni: 3.2, Cu: 6.3, Be: 12.2	Ti: 48.1, Zr: 30.8, Ni: 2.6, Cu: 5.5, Be: 13.0
5 mm	Ti: 44.5, Zr: 34.0, Ni: 3.0, Cu: 6.0, Be: 12.5	Ti: 47.0, Zr: 31.8, Ni: 2.8, Cu: 5.7, Be: 12.7

Diameter	Matrix	Dendrite
8 mm	Ti: 45.0, Zr: 33.5, Ni: 2.9, Cu: 5.9, Be: 12.7	Ti: 46.5, Zr: 32.5, Ni: 2.9, Co: 5.9, Be: 12.2

3.2 Thermal Analysis

[Figure 3: see original paper] shows DSC curves of composites with different diameters. All samples exhibit clear glass transition (Tg), crystallization onset (Tx), and exothermic crystallization peaks, confirming the amorphous phase presence. Thermal parameters derived from DSC () show minimal shift in either crystalline phase transformation peaks or amorphous crystallization peaks with increasing diameter, indicating relatively stable phase composition and structure insensitive to cooling rate variations. A weak exothermic peak appears at 200–300 °C before matrix crystallization, attributed to $\beta \rightarrow \alpha$ phase transformation in the metastable β-phase.

Thermal dynamic parameters of $Ti_{45 \cdot 7}Zr_{33}Ni_{2 \cdot 9}Cu_{5 \cdot 9}Be_{12 \cdot 5}$ amorphous alloy composites with different diameters gained from DSC curves

Diameter	Tg (°C)	Tx (°C)	Crystallization entropy ($J \cdot g^{-1}$)
3 mm	325	385	45.2
5 mm	327	387	44.8
8 mm	326	386	45.0

3.3 Mechanical Properties

[Figure 4: see original paper] shows room-temperature compressive stress-strain curves. All samples initially exhibit linear elastic deformation, then yield at the elastic limit, followed by plastic deformation until fracture. [Figure 5: see original paper] illustrates mechanical property variations with aspect ratio. For aspect ratios of 1:1, 2:1, and 3:1, both fracture strength and yield strength decrease with increasing sample diameter, while plastic strain increases.

The enhanced plasticity with larger crystalline phase size arises from more effective shear band blocking and increased interfacial area. Larger dendrites can accommodate greater plastic deformation due to reduced constraint, while the stress concentration from early dendrite yielding promotes shear band initiation in the amorphous phase, thereby reducing composite strength.

Previous studies [14,22] show that amorphous alloys and their composites are sensitive to sample geometry and loading conditions. For example, Zr-based composites exhibit constant yield strength regardless of aspect ratio, but plastic strain increases significantly as aspect ratio decreases. [Figure 6: see original paper] shows that $Ti_{45\cdot7}Zr_{33}Ni_{2\cdot9}Cu_{5\cdot9}Be_{12\cdot5}$ composites display minimal property variation with aspect ratio. This insensitivity stems from two factors: (1) the crystalline phase alters internal stress states, shifting shear band nucleation and propagation directions; and (2) deformation-induced martensitic transformation occurs during elastic deformation in this alloy [19,23], with a preferred orientation that creates regions favorable for shear band formation, distinguishing its behavior from composites without martensitic transformation.

3.4 Fracture Surface Analysis

[Figure 7: see original paper] shows SEM images of fracture surfaces after compressive failure. Shear bands form on sample surfaces, creating vein patterns on fracture surfaces. Typical viscous flow characteristics appear, similar to monolithic amorphous alloys [24,25]. Both dendrites and matrix undergo rapid fracture with local softening or melting. Vein patterns result from high strain energy release causing localized remelting along primary shear bands, enabling flow and creating characteristic vein-like features.

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4. Conclusions

1. In-situ $Ti_{45\cdot7}Zr_{33}Ni_{2\cdot9}Cu_{5\cdot9}Be_{12\cdot5}$ amorphous composites with varying dendrite sizes and morphologies were prepared by controlling cooling rates. As crystalline phase size increased (i.e., cooling rate decreased), dendrites evolved from fine to coarsened structures, resulting in decreased strength and increased plasticity.
2. Unlike monolithic amorphous alloys and other composites, $Ti_{45\cdot7}Zr_{33}Ni_{2\cdot9}Cu_{5\cdot9}Be_{12\cdot5}$ composites exhibit aspect-ratio-insensitive mechanical properties, attributed to the crystalline phase presence and deformation-induced phase transformation that modulate internal stress distribution.

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