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New compositional design for creating tough metallic glass composites with excellent work hardening

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Abstract—The extrinsic size of both crystalline alloys and amorphous metallic alloys strongly affects their mechanical properties at the submicron scale or nanometre scale. For example, Zr-based metallic glass nanopillars exhibit ceramic-like strengths (2.25 GPa) and metal-like ductility (25%) simultaneously when the pillar dimension is reduced to <100 nm. Here, we report a new compositional design approach to create tough metallic glass composites consisting of micrometre-scale dendrites and nanometre-scale amorphous matrices that exhibit high strength and ductility in the normally brittle MgZnCa metallic glass system. When the thickness of the amorphous matrix is reduced to the nanometre scale, a low density ($\rho \approx 1.99$ g cm^{-3}) $Mg_{91.5}Zn_{7.5}Ca_1$ alloy exhibits room temperature tensile ductility exceeding 15.6%, a yield strength of 215 MPa and a fracture strength of 478 MPa. Transmission electron microscopy analysis demonstrates that the alloy consists of micrometre-scale α-Mg solid solution dendrites and nanometre-scale amorphous matrix (80–530 nm in thickness). The homogeneous deformation of nanometre scale amorphous matrices is believed to be responsible for the high toughness and excellent work-hardening behaviour.

Keywords: Mg-based metallic glass composite; Composition design; Work hardening; Homogeneous deformation

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1. Introduction

The achievement of both high strength and extended deformability is vital for most structural materials, but these two attributes are generally mutually exclusive [1,2]. Bulk metallic glasses (BMGs) are a new class of engineering materials which exhibit excellent properties such as high elastic limit, high strength, high hardness and improved wear resistance [3–7]. However, most BMGs have low ductility and fail in a brittle manner due to highly localized deformation processes, such as shear banding, which propagates unhindered since there are no microstructural features in a monolithic metallic glass to impede them [8–10]. Since the discovery of Mg–Ni–Ce BMG by Inoue et al. [11], Mg-based BMGs have become especially attractive in the BMG family due to their excellent glass-forming ability, high strength, low density and relatively low cost [12]. In comparison with Zr (or Cu and Pd)-based BMG, Mg-based BMGs are more brittle and flaw-sensitive [13]. BMG matrix composites (BMGMCs) are currently well recognized as leading-edge new materials, because they maintain the useful properties of monolithic metallic glass such as high strength and large elastic strain limit but exhibit high ductility as well [14–16]. Currently, most of the ductile BMGMCs are developed from the Ti/Zr–Be-based systems [14–18]. The Ti/Zr–Be-based composites are optimal for BMGMC formation due to the lack of stable compounds between the constituents and Be, which prevents heterogeneous nucleation at the dendrites during quenching [17]. Although both in situ [12,19–21] and ex situ [22,23] Mg-based BMGMCs have been developed in several alloy systems, only improvement in compressive ductility has been observed in these Mg-based BMGMCs.

Hofmann et al. [14] suggest that the large plastic strain and toughness of these Ti/Zr–Be-based composites are based on the following two principles: (i) introducing dendrites with lower shear modulus compared with the amorphous matrix to initiate local shear banding; and (ii) matching the microstructural length scale such as the interdendritic spacing, λ, with the radius of the plastic zone (R_p) to impede the shear band extension. However, the method to design a Be-free metallic glass composite that exactly satisfies the above two principles is currently not clear and subject to debate. Moreover, the Zr/Ti–Be-based BMGMCs exhibit a macroscopic strain-softening phenomenon with an early onset of necking [16,24], which would limit their usefulness as engineering materials [24]. The early macroscopic softening is believed to be associated with the micrometer-scale glass matrix that usually exhibits softening after yielding [16], suggesting that mitigation could be achieved by using this feature size as a design parameter, decreasing the thickness of the glass matrices to the nanometre scale. When the sample size is reduced

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to a critical value (30–100 nm for Zr-based BMG) [2], the stress required to propagate a pre-existing shear band is higher than the stress required for homogeneous plastic deformation, so any formed embryonic shear band remains stable while homogenous deformation prevails [2].

In the current work, new Mg-based BMGMCs with high tensile ductility and excellent work hardening are developed from a normally brittle MgZnCa ternary BMG by a new composition design method. These alloys were designed in the following three steps:

(i) Identify a Mg-based BMG alloy with robust glass-forming ability and restricted solubility of the alloying elements in the equilibrium system. The MgZnCa ternary system was chosen because it exhibits high glass-forming ability and Zn and Ca have restricted solubility, even at the high temperature of the equilibrium close-packed hexagonal (cph) Mg [13,25].

(ii) Target the composition with highest glass-forming ability of the BMG system and use this atomic ratio of alloying elements in the composition. According to Zhao et al. [13], $Mg_{66}Zn_{30}Ca_4$ exhibits the highest glass-forming ability (with a critical diameter of 5 mm), so this defined the atomic ratio of Zn/Ca as 7.5.

(iii) Partially replace the Zn and Ca at the fixed atomic ratio of 7.5 with Mg. By introducing more Mg at the expense of the solute constituents (Zn and Ca), the current Mg alloys $Mg_{91.5}Zn_{7.5}Ca_1$ and $Mg_{87.25}Zn_{11.25}Ca_{1.5}$ indicated as C1 and C2 in Fig. 1a) are substantially hypoeutectic in chemical composition. As a result, α-Mg solid solution will solidify first from the melt.

The formation of α-Mg solid solution is extremely difficult to suppress, even with a high cooling rate, since there is a strong thermodynamic driving force and rapid formation kinetics in the hypoeutectic compositions [12]. Zn and Ca have restricted solubility, even at high temperature in the equilibrium cph Mg and thus are expected to partition preferentially to the remaining liquid during the initial stage of solidification, such that the remaining supercooled liquid becomes enriched in Zn and Ca with an atomic ratio close to 7.5. When the remaining supercooled liquid is close enough to the (near) eutectic bulk glass-forming composition, as shown in Fig. 1b, the formation of the eutectic structure can be fully suppressed and an amorphous phase could be formed in the remaining liquid. Therefore, according to Fig. 1b, the volume fraction and size of both dendrite and amorphous matrix can be tuned by varying the composition.

2. Experimental procedures

High-purity elements (99.8% magnesium, 99.5% calcium and 99.99% zinc) were used to fabricate the ingots of MgZnCa alloys in an inductively heated boron nitride crucible under flowing argon. Cylinder samples with a diameter of 2 mm were fabricated by injection casting using a copper mould. Tensile samples with gauge dimensions of 0.8 mm (diameter) × 4 mm were machined and polished from the as-cast rods. Tensile tests were conducted on a Hounsfield testing device at a constant strain rate of $1.0 \times 10^{-4}\ s^{-1}$ and a digital camera was used to calibrate and measure the strain during loading. At least five samples of each composition were tested to ensure reproducibility of the results. The average tensile mechanical properties, such as 0.2% proof stress ($R_{P0.2}$), ultimate tensile stress (UTS) and total strain to failure (ε_{tot}) were determined and are listed in Table 1. Hot extruded pure Mg samples with gauge dimensions of 6 mm (diameter) × 33 mm were also tested on the Hounsfield testing device at a strain rate of $1.0 \times 10^{-1}\ s^{-1}$ for comparison.

A Hysitron Nanomechanical tester (coupled to a scanning probe microscope) fitted with a Berkovitch diamond tip was used to indent the dendrite and amorphous matrix of $Mg_{91.5}Zn_{7.5}Ca_1$. For each phase, at least five different regions were probed at a load of 5 mN. Indentation was performed in the centre of relatively large phase regions, so as to minimize the contribution to the resulting data from surrounding phases. The load, hold and unload regions of the loading schedule each had segment times of 5 s.

The bulk density of the as-cast samples was determined by the Archimedes method using a balance (New Classic MF MS104S/01) with an accuracy of ±0.0001 g. A Perkin Elmer Diamond DSC was used for differential scanning calorimetry (DSC), in standard aluminium pans with a heating rate of $20\ K\ min^{-1}$ up to 700 K. The phases of the alloys were analysed by X-ray diffraction (XRD) in a Sie-

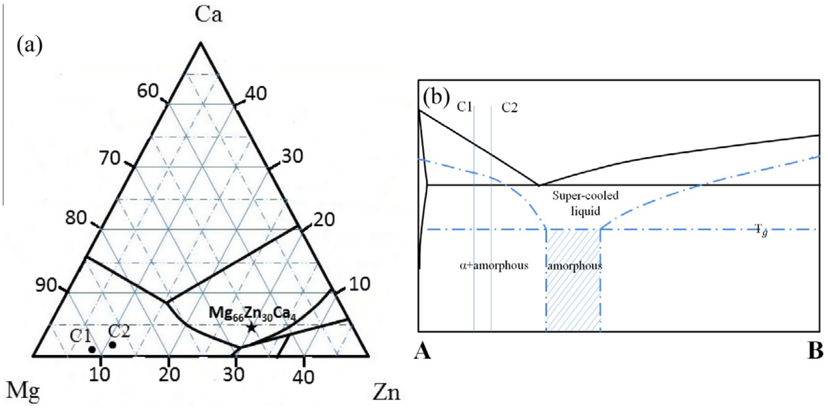

Fig. 1. (a) Pseudo-ternary MgZnCa diagram showing the alloy compositions studied (indicated by solid circles) and the position of $Mg_{66}Zn_{30}Ca_4$ (indicated by stars); black lines in (a) represent the eutectic reaction of ternary MgZnCa alloy in the Mg-rich corner. (b) Schematic diagram showing the solidification process of current hypoeutectic alloys (dashed line in (b) represents the non-equilibrium solidification state occurring in the current work).