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Mg-based metallic glass matrix composite with in situ porous titanium dispersoids by dealloying in metallic melt

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ABSTRACT

A Mg–Cu–Gd bulk metallic glass matrix composite with porous α-Ti dispersoids was prepared by dealloying in a metallic melt. The in situ formed α-Ti dispersoids had a pore-size of ~500 nm, which was imparted from the Ti_2Cu precipitate in the prealloy. Pore size was therefore controllable through the cooling rate of the prealloy preparation. Plasticity was not improved apparently, however the maximum fracture stress under four point bending mode increased from 217 MPa for the monolithic counterpart to 387 MPa. This was due to the optimal relationship where dispersoid size (L)≈dispersoid interval distance (S)≈process zone size (R_p). This was achieved locally within and around the porous Ti dispersoids, and helped improve the toughness and ductility.

1. Introduction

Mg-based bulk metallic glass (BMG) is a promising structural material, because its specific strength (2.3×10^5 Nm/kg) is higher than that of the Mg-based crystallized alloy AZ91 (1.4×10^5 Nm/kg) and extra super duralumin (2.0×10^5 Nm/kg). However, the fracture toughness of Mg-based BMG is only a few MPa $m^{1/2}$, and comparable with brittle ceramics [1]. Much effort has been given to increasing toughness by developing Mg-based BMG matrix composites (BMGMC). Composites have been prepared by:

(1). direct addition: semi-solid casting of BMG formable liquid with a directly added secondary phase (crystalline particles, fibers and laminated crystals),
(2). in situ precipitation: semi-solid casting of BMG formable liquid with the secondary phase precipitated during melting or cooling,
(3). partial nanocrystallization: annealing the BMG to induce nanocrystalline fillers in a glassy matrix.

Physical properties of Mg-based BMGMC fabricated by direct and in situ precipitation methods are given in Table 1. Values for average particle size, dispersoid volume fraction and mechanical properties (fracture stress and plastic strain under compressive mode) are given [2–6]. The fracture mechanism of metallic glass differs between compressive and tensile modes, due to normal stress working on the shear band [7]. Because of this, improving the mechanical properties under tensile mode is usually more difficult than under compressive mode. High aspect ratio fillers strongly bonding with the matrix glass are required to improve tensile properties. Lee et al. confirmed a plastic strain of 5% under tensile mode by precipitating 40–50 vol% of 4–12 μm length α-La dendrite in a $La_{74}Al_{14}(Cu,Ni)_{12}$ BMG matrix [8]. In the direct addition method, the aspect ratio and filler volume fraction are easily controlled, however surface oxides disturb the strong bonding between the filler and glassy matrix. In the in situ precipitation method, fillers are formed during the fabrication processes and bond strongly to the glassy matrix in the absence of surface oxides. Filler shapes also tend to have a higher aspect ratio (dendritic, ellipsoidal or flaky) and prevent the separation of material at shear planes under tensile mode by a bridging effect. The challenge with in situ precipitation is in designing the fabrication process reaction.

Herein, we report the in situ precipitation to improve the mechanical properties of Mg–Cu–Gd BMG using Ti dispersoids, where the high specific strength of the glassy matrix is not degraded. Submicron porous Ti was recently reported to be fabricated by dealloying Ti from a Ti–Cu alloy in a Mg melt [9]. This process is shown schematically in Fig. 1(a). The in situ porous Ti filler was dispersed in Mg-based BMG by applying the reported dealloying reaction in the composite fabrication, as shown in Fig. 1(b). The purpose of this study is to confirm and control the in situ precipitation of porous α-Ti in the Mg-based BMGMC. The effect of porous α-Ti dispersoids on the mechanical properties of Mg-based BMGMC is also evaluated using the four point

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Table 1
Mg-based BMGMCs prepared by direct addition and in situ precipitation methods. Compressive fracture stress (σ_f), plastic strain (ε_p), size (d) and volume fraction (v_f) of dispersoids.

Filler	σ_f (MPa)	ε_p (%)	d (μm)	v_f	Ref.
By direct addition					
α-Fe	960	7.2	5	20	[2]
TiB_2	900	0.9	10	15	[3]
α-Ti	900	40	< 150	40	[4]
By in situ precipitation					
α-Fe	1000	1.0	50–70	8	[5]
α-Mg	903	2.4	0.5	20	[6]

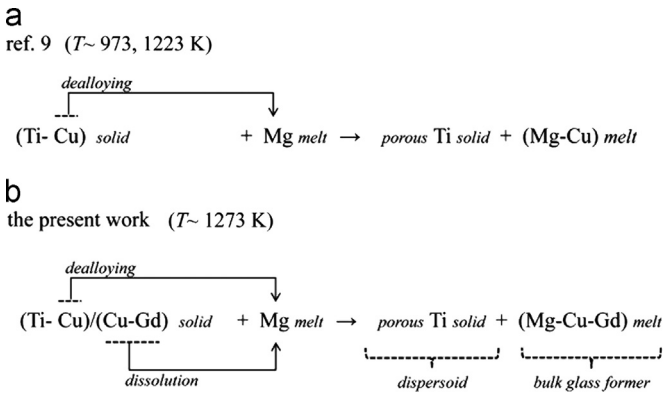

Fig. 1. Schematic showing porous Ti formation by dealloying in the metallic melt (a) reported in Ref. [9], and (b) in Mg–Cu–Gd bulk glass with in situ porous Ti dispersoids. The latter is based on the mechanism shown in (a).

Table 2
Enthalpy of mixing $\Delta H^{mix}_{\{AB\}}$ (kJ/mol) of binary liquids at equiatomic constituent compositions, in the Ti–Cu–Gd system prealloy (A) and Mg–Cu–Gd–Ti system mother alloy (B). The mixing enthalpies are taken from Ref. [13].

Element	Ti	Cu	Gd
(A)			
Ti	–	−9	**+15**
Cu	−9	–	−22
Gd	+15	−22	–
(B)			
Mg	**+16**	−3	−6

bending test. During four point bending, shear stress is zero and the bending moment becomes constant in a given area of the specimen. The samples tensile properties can be indirectly evaluated.

2. In situ precipitation by dealloying in metallic melt

Submicron porous Ti has recently been prepared by dealloying Cu from Ti–Cu alloy in a Mg melt. The melt replaces the acidic or alkaline solution used in conventional dealloying [10]. The mechanism can be understood by the mixing enthalpy ($\Delta H^{mix}_{\{AB\}}$) of constituent elements of the precursor and metallic melt, as explained in Ref. [9]. Porous β-Ti, Fe, and Cr, and ferritic stainless steel (Fe–Cr alloy) have all been fabricated using this method [11,12]. Table 2-A shows $\Delta H^{mix}_{\{AB\}}$ values of constituent elements in the Ti–Cu–Gd prealloy [13]. $\Delta H^{mix}_{\{AB\}}$ values of Ti–Cu and Gd–Cu are negative (miscible) while that of Ti–Gd is positive (immiscible). Therefore, Ti–Cu and Gd–Cu phases are expected to form in the prealloy. Table 2(b) shows $\Delta H^{mix}_{\{AB\}}$ values between elements in the prealloy and Mg of the metallic melt. $\Delta H^{mix}_{\{AB\}}$ values of Mg–Cu and Mg–Gd are negative while that of Mg–Ti is positive. The mother alloy preparation is shown schematically in Fig. 2. When the Ti–Cu–Gd prealloy consisting of Cu–Gd and Ti–Cu phases is immersed in the Mg melt, the Cu–Gd phase and Cu dealloyed from the Ti–Cu phase are expected to dissolve. They will form the Mg–Cu–Gd bulk metallic glass formable liquid if the Mg, Cu and Gd proportions are correctly balanced. The remaining elemental Ti from the Ti–Cu phase is thought to form the porous structure by a surface diffusion mechanism [10,14,15] in the Mg–Cu–Gd alloy liquid. Rapid cooling of this semisolid mother alloy yields Mg–Cu–Gd bulk metallic glass with in situ porous Ti dispersoids.

3. Experimental procedures

$Mg_{61}Cu_{28}Gd_{11}$ (at%) was selected as the glassy matrix for Mg-based BMGMC because of its high glass forming ability (GFA); ~12 mm in diameter by the conventional copper mold casting technique in the Mg–Cu–Ln (Ln: lanthanide) ternary system [16]. The composition was $(Mg_{0.61}Cu_{0.28}Gd_{0.11})_{97.5}Ti_{2.5} = Mg_{59.475}Cu_{27.3}Gd_{10.725}Ti_{2.5}$ (at%) for the $Mg_{61}Cu_{28}Gd_{11}$ glassy matrix in situ porous Ti dispersoids, which corresponds to ~2 vol%. Cu, Gd and Ti were mixed using the arc-melting method then solidified on a copper hearth under an Ar atmosphere. This is hereafter termed slow cooled prealloy (SC prealloy). To solidify at a high cooling rate, SC prealloy was melted again then cast into a 10 mm diameter copper mold cavity using the tilt casting technique. Hereafter, this is termed rapid cooled prealloy

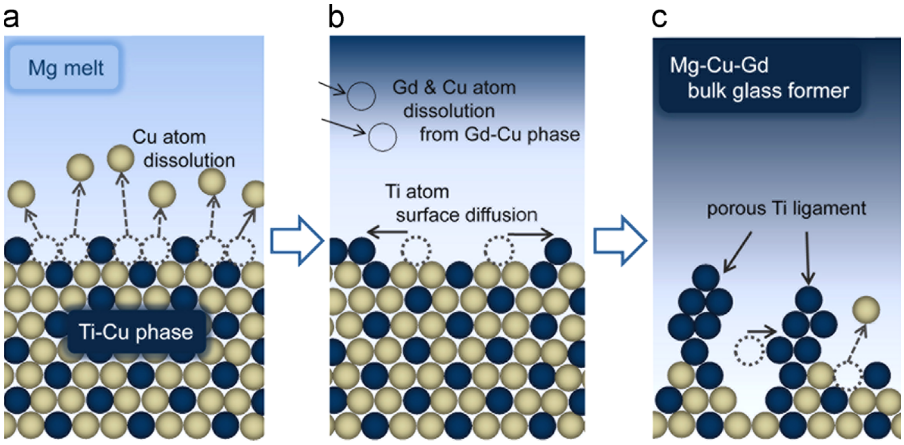

Fig. 2. Schematic showing the preparation of the mother alloy. Mg–Cu–Gd bulk glass forming liquid with porous Ti dispersoids was obtained by immersing the Cu–Gd–Ti prealloy (containing Ti–Cu and Gd–Cu phases) into the Mg melt: (a) Cu atoms dealloyed from Ti–Cu phase surface into the Mg melt; (b) remaining Ti atoms diffused on the surface, and Gd and Cu dissolved from Gd–Cu phases into the melt and (c) Cu dissolution and Ti surface diffusion continued at the inside of the Ti–Cu phase. Ligaments of porous Ti developed in the Mg–Cu–Gd liquid, and the composition remained that of the bulk glass upon reaction completion.