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Modulating work-hardening behaviors and tensile plasticity of *in-situ* formed ductile dendrite Ti-based bulk metallic glass composites with tailored dendrite composition

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ABSTRACT

A novel series of *in-situ* dendrite Ti-based bulk metallic glass composites (BMGCs) were obtained. The Mo content of the dendrites monotonically increases from nil to 10.5 at% while the dendrite volume fraction and the composition of the amorphous matrix remain nearly invariant. It was found that the mechanical behaviors varied tremendously simply by changing the Mo content. Thus, the correlation between the composition and the mechanical behaviors under tension has been determined for *in-situ* dendrite Ti-based BMGCs for the first time.

In-situ ductile dendrite bulk metallic glasses composites (BMGCs) have attracted much attention due to the combination of high strength and high toughness [1–7]. However, most *in-situ* dendrite BMGCs exhibit work-softening rather than work-hardening after yielding during tensile tests, which severely hinders their practical applications as structural materials. In order to explore work-hardenable BMGCs, the primary objective is to enhance the work-hardening capability of the crystalline dendrites. Many efforts have been made to introduce strengthening mechanisms in the dendrites. Twinning- and dislocation-strengthening were discovered by minor alloying Nb [1,3,6], V [2,5,8], Ta [6,9] and Sn [10] etc., which are prone to dissolve in the dendrites during solidification, making the dendritic phase plastic and work-hardenable. Martensitic transformation (MT) is another strategy to increase work-hardening capability in titanium alloys [11–13] and some CuZr-based BMGCs [14,15], but its application to *in-situ* dendrite BMGCs is notoriously difficult [4]. Though deformation-induced MT contributing to apparent work-hardening behaviors in compression were reported for some Ti-based BMGCs containing metastable β-phase dendrites [16–18], ductility along with work-hardening capacity induced by MT in tension has been rarely reported so far [6]. To overcome the problem, the key issue is to control the metastability of β-phase dendrites in the composites, which is closely related to their composition. Up to now, it is challenging to tune the dendrite composition in the multicomponent alloys [8].

In this work, a novel series of *in-situ* β-Ti dendrite Ti-based BMGCs with nominal composition of $Ti_{50.32}Zr_{33.92-0.6x}Cu_{4.56}Ni_{2.12}Be_{9.08}Mo_{0.6x}$ (x = 0, 0.5, 1, 2, 4, 6 and 10, denoted as M0–M10) were designed. It is found that the Mo content of the dendrites increased from nil to 10.5 at% monotonically while the dendrite volume fraction remained constant and the composition of the amorphous matrix remained nearly invariant. Variation of the Mo content modulated the metastability of the dendrites, accordingly leading to totally different mechanical behaviors of work-hardening with plasticity induced by MT, and work-softening in the absence of martensitic transformation. To the best of our knowledge, this is the first time that the relationship between the dendrite composition, metastability and mechanical behaviors under tension is revealed for *in-situ* dendrite Ti-based BMGCs. This finding will open up a new perspective for the design of tailored mechanical properties of BMGCs, thus promoting their potential applications.

Pre-alloyed 70 g ingots of each composite were prepared by arc-melting a mixture of Ti, Zr, Cu, Ni, Be and Mo elements under a Ti-gettered high purity argon atmosphere. The Zr and Ti sponge with the purity of approximately 99.4 wt%, and Cu, Ni, Be, and Mo with the purity higher than 99.9 wt% were used as raw materials. Bulk samples with a size of $60 \times 12 \times 6$ mm^3 were produced using copper mold tilting casting technique. Microstructures of both as-cast and fractured samples were characterized by an X-ray diffractometer (XRD; Rigaku D/max-2500PC) with Cu-Kα radiation, a differential scanning calorimeters

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(DSC; Netzsch 204F1), a scanning electron microscope (SEM; ZEISS Supra 55) equipped with an energy disperse spectrometer (EDS) and a transmission electron microscopes (TEM; FEI F20). Uniaxial tension tests were conducted on an Electronic Universal Testing Machine (Instron 5582) with the initial strain rate of 2×10^{-4} s^{-1}. The tensile samples are in dog-bone shape with a gauge length of 15 mm and cross-section dimension of 2×0.8 mm^2. The real-time strain in the gauge section was monitored with an extensometer. At least three samples were tested for each composite to ensure reproducibility. A nanoindenter (Agilent, G200) was utilized to measure the hardness of the dendrite and the glass matrix in the continuous stiffness mode with a depth of 500 nm and a loading rate of 10 nms^{-1}.

The as-cast M0–M10 are all composed of β-Ti and an amorphous phase in the XRD measurements. The corresponding SEM images of M0–M10 are displayed in Fig. 1. A similar microstructure with a dendritic phase and a featureless amorphous phase is presented for all the samples, with slight ripening of the M10 dendrites as the only difference among the samples. The volume fraction and size of the dendrites are similar for all the samples, estimated to be 65 ± 2% and 40–60 μm, respectively.

The average composition of the dendrites and the amorphous phase obtained by EDS analysis (with the uncertainty of less than 1 at%) are listed in Table 1. It clearly shows that the Mo content increases monotonically from nil to 10.5 at% while the Zr content decreases for the dendrites. The corresponding Ti, Cu and Ni contents change in very narrow ranges of 61.2–63.9 at%, 1.5–1.8 at% and 0.5–0.6 at%, respectively. For the amorphous phase, the content of Ti, Zr, Ni and Cu is regarded nearly invariant within the tolerance. It is interesting that Mo was not detected in the amorphous phase for this series of alloys, except for M10 containing a slight amount of 0.3 at%. These results show that the concentration of β phase stabilizing elements increases monotonically from M0 to M10 since Mo is a strong β-stabilizing element while Zr is a weaker one [19].

Fig. 2 shows the DSC curves of the as-cast M0–M10 samples. According to their thermal behaviors, all the alloys can be classified into two groups: M0–M2 and M4–M10. For M4–M10, the samples show similar characteristics that are typical of the amorphous phase including an apparent glass transition (GT) and several exothermic peaks corresponding to the crystallization process. M0–M2 samples exhibit much more complicated characteristics compared to those of M4–M10. Prior to GT, a distinct exothermic peak (referred as Pre-*Tg*) which reflects the precipitation of the ω phase in the metastable β-Ti dendrite [20,21] emerges and shifts to higher temperature from M0 to M2. In addition, an apparent endothermic event in the range of 800–900 K, identified as the α → β phase transformation (initial temperature is marked as $T_{\alpha \rightarrow \beta}$), is observed for M0–M2. It is deduced that the metastable β-Ti phase transformed into α-Ti phase before 800 K during the heating process. The decreasing trend of $T_{\alpha \rightarrow \beta}$ from M0 to M2 indicates that the stability of the metastable β phase increases from M0 to M2. Furthermore, for M4–M10, there is no decomposition of the β phase detected during heating, indicating that the β phase is stable at ambient temperature. These results verify that the stability of the β-phase dendrites is mediated by tuning the concentration of β phase stabilizers, consistent with the Mo distribution behavior.

Fig. 3 shows the tensile properties of M0–M10. It can be seen that M0–M2 show completely different deformation behaviors from those of M4–M10. No obvious yielding point can be observed for M0–M2, which is different from M4–M10 where yielding is exhibited by an evident decline in the stress at the beginning of the plastic deformation. The yielding stress increases considerably from 893 MPa for M0 to

Table 1
Composition of both phases in M0–M10 obtained by EDS (at%).

	Element	M0	M0.5	M1	M2	M4	M6	M10
Dendrite phase	Ti	61.2	61.7	61.4	62	62.5	63.2	63.9
	Ni	0.6	0.6	0.6	0.6	0.5	0.5	0.5
	Cu	1.7	1.8	1.8	1.8	1.6	1.5	1.5
	Zr	36.5	35.4	35.4	34	31.7	28.8	23.6
	Mo	0	0.5	0.8	1.6	3.7	6.0	10.5
Amorphous matrix	Ti	40.2	39.5	39.7	39.4	38.4	38.8	38
	Ni	6.2	6.4	6.4	6.4	6.6	6.4	6.5
	Cu	11.1	11.2	11.3	11.7	11.8	11.7	12
	Zr	42.5	42.9	42.6	42.5	43.2	43.1	43.2
	Mo	0	0	0	0	0	0	0.3

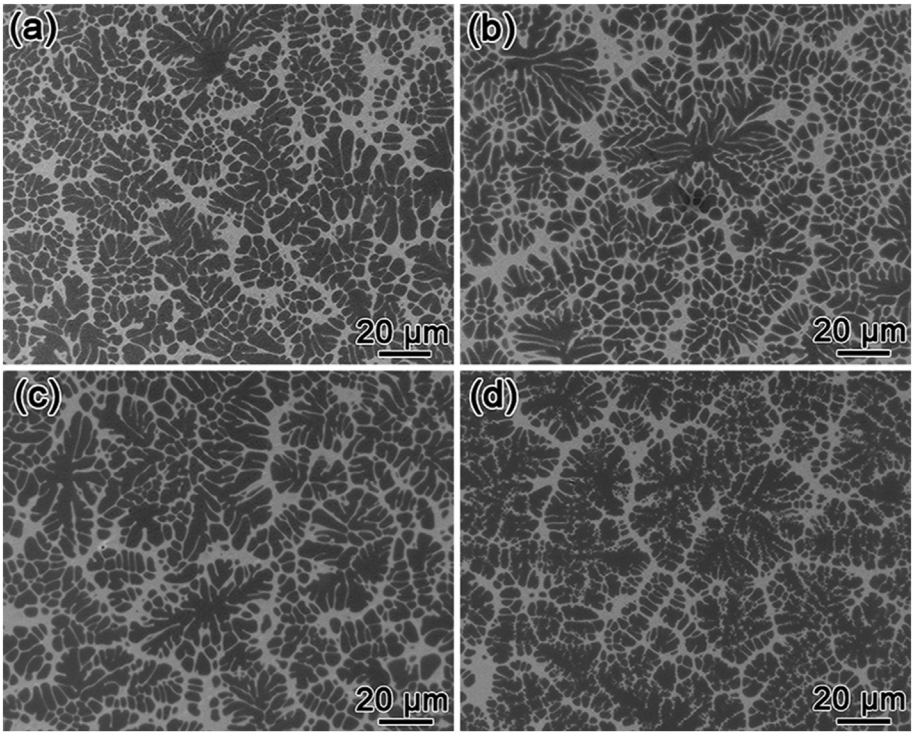

Fig. 1. The SEM images of as-cast M0, M2, M4 and M10 alloys.