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REPORT



Simultaneously enhancing the strength and plasticity of Ti-based bulk metallic glass composites via microalloying with Ta

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ABSTRACT

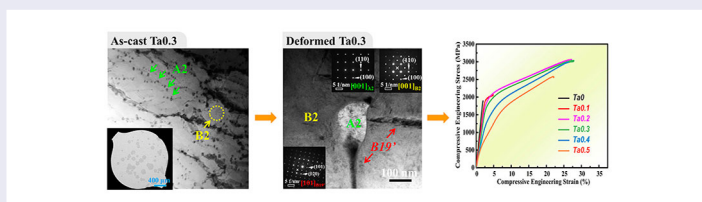
Characteristics of deformation-induced transformation under loading dictate the mechanical performance of TRIP (transformation-induced plasticity)-reinforced bulk metallic glass composites (BMGCs), which have shown great potential as engineering materials. Here, we report that the addition of 0.3 at.% Ta in the $\text{Ti}_{45}\text{Cu}_{41}\text{Ni}_9\text{Zr}_5$ alloy could induce the formation of uniform glassy composite structure with B2-(Ti,Zr)(Ni,Cu) precipitates. More interestingly, nanosized A2-(Ti,Zr)(Ni,Cu) particles also formed inside B2 grains which effectively impede rapid propagation of martensite plates and lead to the formation of multi-oriented martensites, eventually homogenizing the involved plastic flow during deformation-induced transformation. Consequently, high fracture strength (~ 3000 MPa), large plasticity ($\sim 25\%$) and pronounced work-hardening ability were achieved.

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Metallic glass composites; microalloying; transformation-induced plasticity; martensitic transformation; strengthening



IMPACT STATEMENT

Microalloying of Ta not only homogenizes the B2 distribution, but also facilitates formation of multi-orientated martensites during deformation, resulting in simultaneously enhanced strength and plasticity of a Be-free Ti-based BMGC.

1. Introduction

Ti-based bulk metallic glasses (BMGs) have attracted enduring scientific and commercial interests because of their large elastic limit and exceptionally high specific strength, resulting from the low density of titanium [1,2]. However, the highly localized shear banding deformation mechanism always leads to catastrophic fracture with extremely low plasticity, seriously limiting their practical usages [1,3]. One of the most effective ways for addressing this issue is to fabricate BMG composites (BMGCs) by introducing crystalline phases into the

amorphous matrix [4–9]. Among these, the concept of transformation-induced plasticity (TRIP) turns out to be one of the most promising strategies, which was firstly employed in Zr-based BMGs [6–8,10–14]. During deformation, TRIP BMGCs underwent martensitic transformation, which gives rise to the large tensile ductility and striking work-hardening ability.

Based on the crystalline structure of reinforcing media, TRIP-reinforced Ti-based BMGCs can be categorized into two groups, i.e. β -type and B2-type. For the former category, the transformation from β -Ti to α'' -Ti

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occurs during deformation, which indeed enhances the plasticity. Nevertheless, both the yield and fracture strength appreciably decreased for this type of BMGCs due to the existence of a large volume fraction (usually above 50%) of soft crystalline β phase [8,15]. Meantime, the β -type TRIP-reinforced Ti-based BMGCs always contain a high amount of the poisonous element Be. Therefore, researchers have shifted their focuses towards the development of the B2-type TRIP-reinforced Ti-based BMGCs which are free of Be [6,7,10,16]. However, B2 particles formed during solidification are prone to coarse and thus distribute inhomogeneously, which inevitably deteriorate the TRIP effect [16,17]. Moreover, the involved deformation-induced martensitic transformation takes place swiftly and the rapid propagation of large martensite plates tends to initiate microcracks at the interface, thus diminishes the TRIP reinforcement in the Ti-based BMGCs. To further improve the mechanical properties of the B2-type TRIP-reinforced Ti-based BMGCs, therefore, the characteristics of deformation-induced martensitic transformation need to be further modulated.

In this work, we reported that the deformation-induced martensitic transformation in B2-type TRIP-reinforced Ti-based BMGCs could be tailored by forming disordered A2-(Ti,Zr)(Ni,Cu) phase inside the transformable B2 phase. Microalloying with Ta not only promotes homogeneous distribution of micrometer-sized B2 phase, but also facilitates precipitation of nanosized A2 phase inside the B2 particles, which enhances the TRIP effect and eventually optimizes overall mechanical properties of the Ti-based BMGCs.

2. Experimental methods

Master alloys with nominal compositions of $\text{Ti}_{45-x}\text{Cu}_{41}\text{Ni}_9\text{Zr}_5\text{Ta}_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5 at.%, denoted as Ta_x alloys hereafter) were prepared by arc-melting mixtures of constituent elements with a purity of above 99.9% in a Ti-gettered argon atmosphere. To ensure chemical homogeneity, Zr and Ta, which have relatively a high melting point and large solid solubility at high temperatures, were arc-melted to form an intermediate binary Zr-Ta alloy before being re-melted with Ti, Cu and Ni. Cylinder samples with a diameter of 2 mm were fabricated by suction casting. The structure and morphology of these alloys were characterized by X-ray diffraction (XRD, Philips PW1050, Cu $K\alpha$), scanning electron microscopy (SEM, Zeiss Supra 55) equipped with energy-dispersive spectrometry and transmission electron microscopy (TEM, Tecnai G2 F30) with a field-emission gun and an energy dispersive X-ray detector (EDX). Uniaxial compression tests were carried out on

2 mm diameter samples with an aspect ratio of 2:1 at a strain rate of $2 \times 10^{-4} \text{ s}^{-1}$, using a universal CMT 4305 testing machine. Both the surface and ends of the compression specimens were carefully ground and polished. Tensile tests were conducted with a WDW-200D machine with a maximum load of 200 kN at a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ on samples with a gauge dimension of $\Phi 1.4 \text{ mm} \times 5 \text{ mm}$ machined and polished from the 2 mm diameter rods. At least three samples were tested for each BMGC with a specific amount of Ta.

3. Results and discussion

3.1. Effect of Ta addition on the microstructure of $\text{Ti}_{45-x}\text{Cu}_{41}\text{Ni}_9\text{Zr}_5\text{Ta}_x$ alloys

Figure 1 shows the representative cross-sectional SEM micrographs and the corresponding XRD patterns of the as-cast 2 mm rods of the Ta_x alloys. Ta_0 shows a fully amorphous structure (Figure 1(a)). However, a small amount of spherical particles with a diameter of 50–100 μm are formed in the amorphous matrix of $\text{Ta}_{0.1}$ (Figure 1(b)). Because of its minute amount, these crystals were not detected in the XRD result (Figure 1(g)). For $\text{Ta}_{0.2}$ and $\text{Ta}_{0.3}$ alloys (see Figure 1(c,d)), spherical crystallites with a diameter of 50–200 μm , which were identified as B2-(Ti,Zr)(Ni,Cu), are homogeneously distributed in the featureless amorphous matrix. With the further increase of Ta, the dark gray spherical crystals grew significantly and interconnected with each other (Figure 1(e,f)), suggesting that excessive Ta addition dramatically deteriorates the glass formation ability (GFA). As indicated by the XRD result, B2 and Ti_2Cu phases coexist in $\text{Ta}_{0.4}$ and $\text{Ta}_{0.5}$ alloys. The volume fraction of the crystalline phases (V_c) is estimated to be 0%, $3 \pm 2\%$, $15 \pm 3\%$, $25 \pm 5\%$, $40 \pm 5\%$ and $70 \pm 10\%$ for Ta_0 , $\text{Ta}_{0.1}$, $\text{Ta}_{0.2}$, $\text{Ta}_{0.3}$, $\text{Ta}_{0.4}$ and $\text{Ta}_{0.5}$ alloys, respectively. It is reported that the desirable volume fraction of the B2 phase with a spherical shape in BMGCs was estimated to be 15–45% from a standpoint of enhancing plasticity [7,10,18]. Therefore, refined BMGCs with homogeneously distributed single B2 phase could be obtained by the addition of 0.2–0.3 at.% Ta in the present alloy system.

Detailed microstructure analyses of the as-cast $\text{Ta}_{0.3}$ and $\text{Ta}_{0.5}$ are present in Figure 2. Figure 2(a) shows a representative TEM image of a B2-(Ti,Zr)(Ni,Cu) particle ($pm\text{-}3m$, $a = 3.12 \text{ \AA}$) in $\text{Ta}_{0.3}$. Interestingly, plenty of nanosized precipitates are observed inside the B2 particles. As listed in the inset of Figure 2(b), the Ta content in the nanoprecipitates (0.8 ± 0.2 at.%) is much higher than that of the B2 phase (0.2 ± 0.1 at.%), suggesting that Ta addition facilitates the formation of massive Ta-rich nanosized precipitates in B2. These

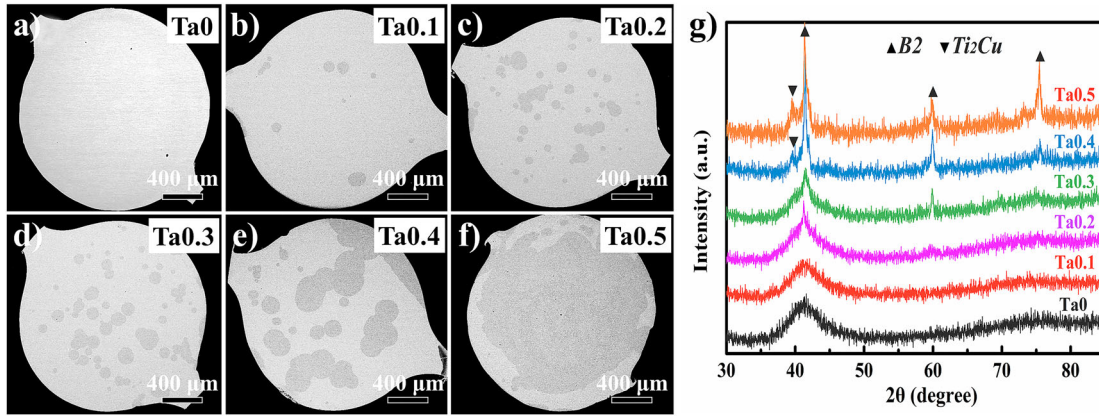


Figure 1. Representative cross-sectional morphology of the as-cast (a) Ta0, (b) Ta0.1, (c) Ta0.2, (d) Ta0.3, (e) Ta0.4 and (f) Ta0.5 alloys. (g) XRD patterns of the as-cast 2mm rods of the Ta_x alloys.

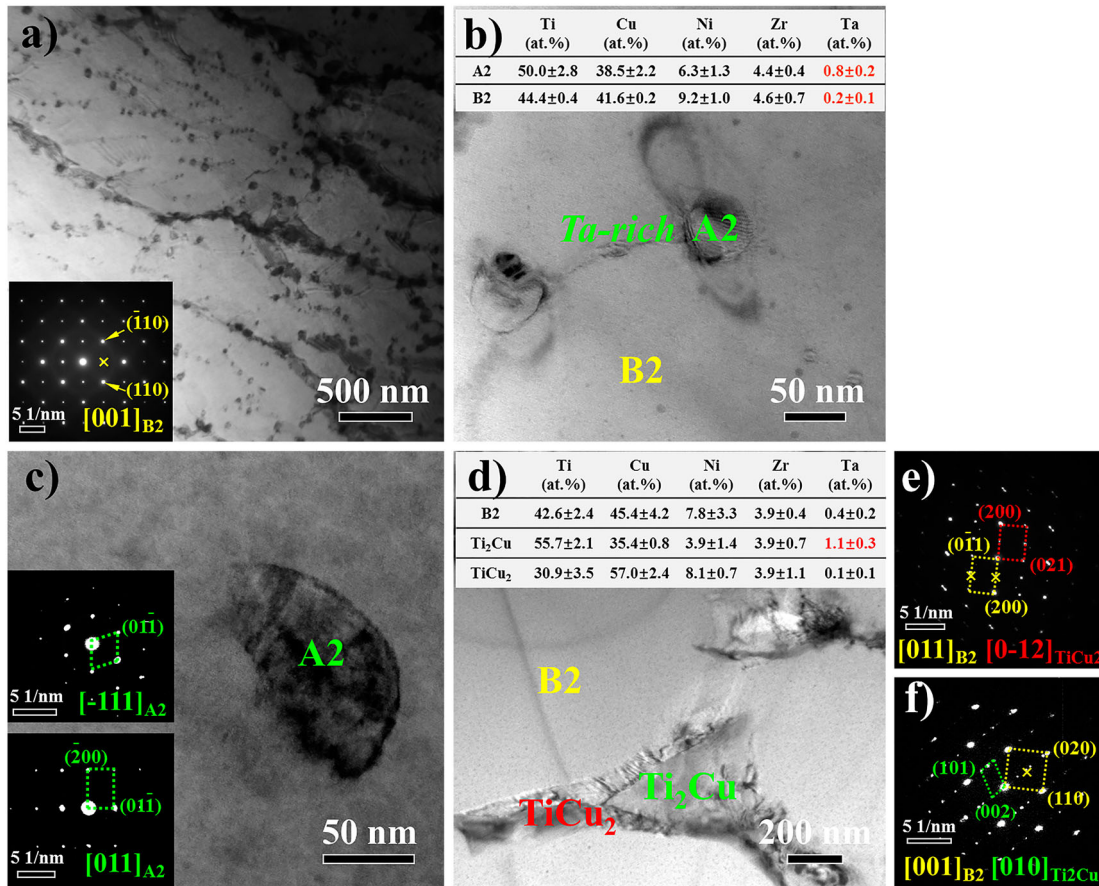


Figure 2. (a) Typical TEM morphology of a B2 particle in as-cast Ta0.3, and the corresponding SAED pattern is shown in the inset. (b) The enlarged image of (a), and the inset shows the EDX data of A2 and B2 phases. (c) The enlarged morphology of a nanosized A2 particle in Ta0.3, and its corresponding SAED patterns are shown in the insets. (d) TEM image of the precipitates embedded in the B2 particles of the as-cast Ta0.5. (e) and (f) are the SAED patterns under the zone axis of $[011]_{B2}$ and $[001]_{B2}$, respectively in Ta0.5.

nanosized Ta-rich precipitates have a disordered BCC (body-centered cubic) A2 structure ($a = 3.21$ Å), as shown in Figure 2(c). The discrepancy between the A2 and B2 is estimated to be 2.9%, which is far below than 12% [19]. Such a small value of discrepancy in Ta0.3 suggests that the heterogeneous nucleation of B2 is potent.

Figure 2(d) exhibits that a polycrystalline structure prevails in the crystals of Ta0.5. The crystals consisted of B2-(Ti,Zr)(Ni,Cu), $TiCu_2$ ($Amm2$, $a = 4.363$ Å, $b = 7.977$ Å, $c = 4.478$ Å) and Ti_2Cu ($P63/mmc$, $a = b = 5.1507$ Å, $c = 8.2441$ Å) crystals, based on their corresponding selected area electron diffraction (SAED) patterns

(Figure 2(e,f)) and EDX results (the inset in Figure 2(d)). The TiCu_2 and Ti_2Cu crystals are formed on the boundaries of the B2 crystals. Additionally, the Ta content in the Ti_2Cu crystals (1.1 ± 0.3 at.%) is obviously higher than the nominal Ta content (0.5 at.%), indicating that excessive Ta addition leads to the formation of multiple intermetallic compounds.

In the previously reported Ta-containing ZrCu-based BMGCs, it is generally accepted that when the Ta content exceeds its solubility, either pure Ta or Ta-rich particles tend to form [20–23]. Specifically, in the β -type Ti-based BMGCs, Ta generally acts as the β -stabilizer [24]. However, no pure Ta particles were observed in the present BMGCs, implying that Ta has a different role in phase competition during solidification. In the current Tax alloys, above 0.1% Ta addition promotes the formation of the crystalline B2 and A2 phases and demotes GFA. In particular, for the Ta0.2 and Ta0.3 alloys, Ta addition effectively stimulates the nucleation of the main competing phase, i.e. the B2 phase. Meanwhile, the coarsening of B2 particles is likely suppressed by massive Ta-rich A2 particles inside B2. It seems that the Ta concentration in B2 exceeds its solubility and subsequently precipitated out of B2, and, in turn, retards the growth of B2. For Ta0.4 and Ta0.5 alloys, nevertheless, the excessive Ta addition not only promotes formation of B2 phase, but also precipitates new intermetallic compounds, i.e. Ti_2Cu and TiCu_2 phases.

3.2. Effect of Ta addition on the mechanical behavior of $\text{Ti}_{45-x}\text{Cu}_{41}\text{Ni}_9\text{Zr}_5\text{Ta}_x$ alloys

The compressive and tensile engineering stress–strain curves for the Tax alloys are shown in Figure 3. Ta0 BMG shows the catastrophic fracture under both compression

and tension, which is similar to other monolithic BMGs reported previously [1,2]. With Ta addition, the compressive plastic strain and fracture strength were significantly enhanced. Specifically, the Ta0.2 and Ta0.3 alloys exhibit plastic strains of 24.8 ± 1.2 and $25.5 \pm 2.5\%$ and fracture strength of 3064 ± 25 and 3016 ± 16 MPa, respectively, along with the pronounced work-hardening behavior. The work-hardening index, n , can be estimated based on the Hollomon's equation [25]: $\sigma_\varepsilon = K\varepsilon^n$, where σ_ε , K and ε are the true stress, strength factor and true strain, respectively. Correspondingly, the value of n for Ta0.2 and Ta0.3 alloys was determined to be 0.08 and 0.11, respectively, which are obviously higher than that of Ti–6Al–4V alloys widely used in aerospace structure systems (i.e. $n = 0.03$ – 0.06) [26]. Furthermore, different from what was observed in the β -type TRIP-reinforced Ti-based BMGCs, yield strengths of Ta0.2 and Ta0.3 BMGCs are comparable with those of the monolithic Ta0 BMG (i.e. 1842 ± 12 MPa), implying that the ductilization effect of the current BMGCs was obtained at no expense of yield strength. This is mainly attributed to the relatively low volume fraction of B2 phase. However, Ta0.4 and Ta0.5 alloys showed work-hardening behavior (n is 0.23 and 0.42, respectively) but a much reduced compressive yield strength (i.e. 1106 ± 25 and 589 ± 16 MPa, respectively) because of the large amount of crystalline phases. More strikingly, the tensile ductility of about $\sim 1\%$ along with comparable fracture strength was achieved in Ta0.2 and Ta0.3 alloys. The fracture strength for Ta0.2 and Ta0.3 alloys is 1619 ± 8 and 1662 ± 20 MPa, respectively, while the tensile ductility is $0.9 \pm 0.2\%$ and $1.0 \pm 0.2\%$, respectively. Moreover, the tensile stress–strain curve does not show stress drop phenomenon after yielding, implying that the strain-softening phenomenon has been suppressed in

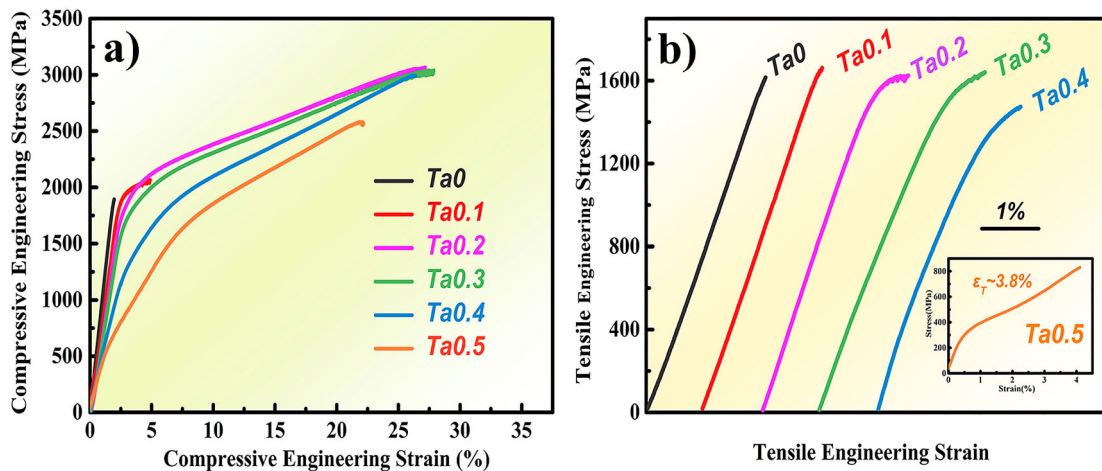
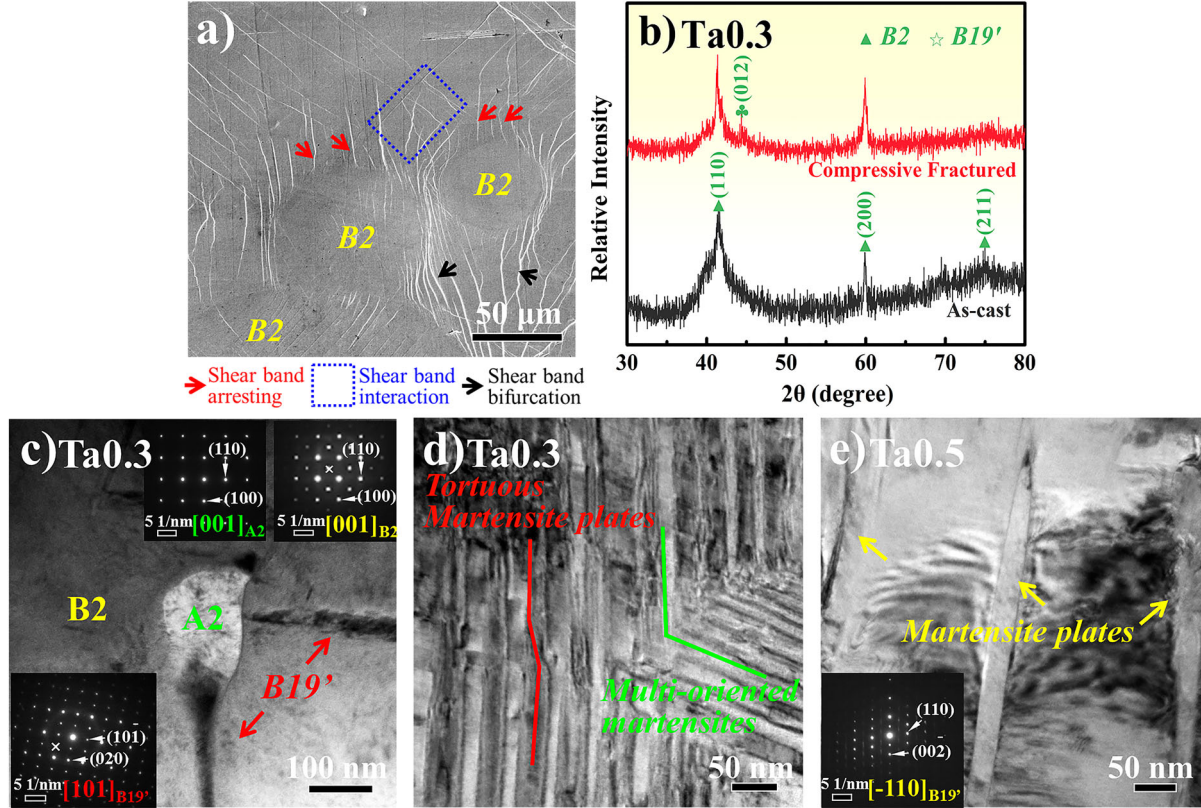


Figure 3. (a) Compressive and (b) tensile engineering stress–strain curves of the Tax alloys.

Table 1. Compressive and tensile mechanical properties of Tax alloys, including yield strength σ_y , fracture strength σ_f , plastic strain ε_p , fracture strain ε_f and work-hardening index n .

Alloys	Under compression					Under tension			
	σ_y (MPa)	σ_f (MPa)	ε_p (%)	ε_f (%)	n	σ_y (MPa)	σ_f (MPa)	ε_p (%)	ε_f (%)
Ta0	1842 ± 12	1916 ± 23	0.1 ± 0.1	2.2 ± 0.1		1598 ± 10	1608 ± 15	0.1 ± 0.1	2.0 ± 0.1
Ta0.1	1781 ± 32	2076 ± 18	2.6 ± 0.2	5.1 ± 0.3	0.06	1588 ± 14	1653 ± 23	0.1 ± 0.1	2.1 ± 0.1
Ta0.2	1719 ± 36	3064 ± 25	24.8 ± 1.2	27.1 ± 1.8	0.08	1462 ± 21	1619 ± 8	0.9 ± 0.2	2.6 ± 0.2
Ta0.3	1649 ± 28	3016 ± 16	25.5 ± 2.5	27.8 ± 2.2	0.11	1418 ± 18	1662 ± 20	1.0 ± 0.2	2.9 ± 0.2
Ta0.4	1106 ± 25	2991 ± 22	24.2 ± 1.8	26.5 ± 2.5	0.23	1162 ± 36	1475 ± 13	1.0 ± 0.3	2.7 ± 0.2
Ta0.5	589 ± 16	2629 ± 30	20.5 ± 1.3	22.3 ± 1.8	0.42	268 ± 25	831 ± 32	3.8 ± 0.4	4.2 ± 0.4

**Figure 4.** (a) Typical lateral surface of the compressive fractured Ta0.3 sample. (b) XRD patterns of the as-cast and fractured compressive Ta0.3 samples. (c) A typical image shows how martensite plates were impeded by the nanosized A2 precipitates in Ta0.3, and the insets are the corresponding SAED patterns of A2, B2 and transformed B19', respectively. (d) Multi-oriented and tortuous martensite plates were observed in the deformed Ta0.3. (e) The B19' martensite plates in compressive fractured Ta0.5 sample were characterized with similar orientation.

the current BMGCs. The detailed mechanical parameters of the current Tax alloys under different loading are summarized in Table 1.

Apparently, the Tax alloys show notable tension-compression asymmetry in the yield strength, fracture strength and plastic strain. This distinct mechanical behavior is mainly attributed to the divergent interplay between shear banding and martensitic transformation under different loading conditions, which will be interpreted later on.

To unveil the strengthening mechanism responsible for the improved mechanical properties, the structural evolution of representative Ta0.3 after compressive

fracture is present in Figure 4(a–d). As shown in Figure 4(a), the so-called blocking effect [6,21] of crystalline phases can be observed. The shear bands were deflected or arrested by the spherical B2 crystals, eventually facilitate the formation of multiple shear bands and delay the premature rupture of the Ta0.3 samples. More importantly, as shown in Figure 4(b), an extra peak ($2\theta = 44.2^\circ$) corresponding to the martensitic B19' phase appeared in the fractured specimen, confirming the occurrence of the deformation-induced martensitic transformation from B2 to B19', which is mainly responsible for the obtained large plasticity and strong work-hardening behavior. A representative TEM morphology

of an A2 particle in the fractured Ta0.3 sample is displayed in Figure 4(c,d). Obviously, the A2 nanoprecipitate successfully deflects the propagation of martensite plates as the deformation-induced martensitic transformation proceeds (Figure 4(c)). The blocking of A2 particles on the rapid propagation of martensite plates leads to the formation of martensites with multiple orientations, thus homogenizing the martensitic transformation and the involved plastic flow. This phenomenon is similar to that of the Ti-based shape memory alloys in which nanosized precipitates strongly influence the martensitic transformation behavior by manipulating the growth of martensite variants and reorientation of the martensite [27–30]. In addition, some of the deformation-induced martensite plates in Ta0.3 are tortuous (Figure 4(d)), suggesting severe deformation of the sample and existence of large residual stress.

Different from the multi-oriented martensite plates in Ta0.3, the martensite plates of the fractured Ta0.5 sample have similar orientations and propagate straightly (see Figure 4(e)). Meanwhile, the B2 particles with an increase size in Ta0.5 are more difficult to undergo martensitic transformation, because the accompanying dimensional variations with the transformation are relatively larger and hence hard to be accommodated via interaction with shear bands. As a result, the deformation-induced martensitic transformation is limited and the beneficial effect from the martensitic transformation is negligible, thus the ‘blocking effect’ of the crystalline phases including B2, Ti_2Cu and TiCu_2 phases became the dominant toughening mechanism in Ta0.5. However, the Ti_2Cu and TiCu_2 phases are brittle and have very limited plastic deformation capability during deformation [16,31].

It should be noted that the similar features of shear band multiplication and multi-oriented martensites can also be observed after the tensile tests, but both the density of shear bands and the fraction of deformation-induced martensites in tension are appreciably lower, as compared with those under compression. As discussed in our prior work of other types of BMGCs [14], the stress field around the B2 phase exhibits large difference in these two loading modes, which, in turn, lead to a different potency of martensitic transformation and consequently different interplay with shear band multiplication of the amorphous matrix. Specifically, under compression, the normal stress exerting on the fracture plane is compressive under compression, but changes to tensile under tension. During compressive loading, the compressive normal stress can retard the nucleation and propagation of shear banding, thus promoting strong interaction between martensitic transformation and shear banding, eventually inducing strong work-hardening behavior. Under tensile loading, however,

the tensile normal stress accelerates the nucleation and propagation of microcracks at the interface and in the amorphous matrix, sharply shortening the time span for the interaction between martensitic transformation and shear banding. In addition, because of the low crystallographic symmetry of the martensitic phase [32], transformation behavior of the parent B2 particles differs considerably under different stress fields, which could also contribute the discrepancies of mechanical properties under different loading conditions.

To sum up, the underlying mechanisms responsible for the enhanced mechanical properties of Tax alloys can be ascribed to the following two aspects; first, the promoted ‘TRIP effect’ from the homogenized deformation-induced martensitic transformation of B2. As the transformation proceeds, specifically for Ta0.3, the A2 nanosized precipitates impede the rapid propagation of single martensite plate and then initiate the multiple orientation of the martensites, eventually promoting deformation-induced martensitic transformation and leading to the transformation-induced plasticity and considerable work-hardening ability. The second is the ‘blocking effect’ of the homogeneously distributed crystalline phases. Uniformly distributed microscale B2 crystals efficiently inhibit shear band propagation and promote the formation and interaction of multiple shear bands, which suppresses crack initiation and also stabilize the plastic flow.

4. Conclusions

In sum, Be-free TRIP-reinforced Ti-based BMGCs within modulated microstructures and tailored martensitic transformation were successfully developed via microalloying with 0.2–0.3 at.% Ta. These BMGC exhibit not only simultaneous increase of fracture strength (~ 3000 MPa) and plasticity ($\sim 25\%$) without sacrificing yield strength under compression, but also appreciable ductility of $\sim 1\%$ under tension. Under loading, the deformation-induced martensitic transformation occurs after yielding. As the transformation proceeds, the nanosized A2 deflects the rapid propagation of martensite plates and leads to the formation of multi-orientated martensites, which, in turn, homogenizes the deformation-induced martensitic transformation and the involved plastic flow. Meanwhile, the homogeneously distributed B2 phase and transformed B19' phase inhibit the propagation of shear bands and result in the shear band multiplication, which also contributes to the plastic flow. As a result, the plastic deformation is greatly promoted. The stress fields around the B2 phase varied with the loading modes, which leads

to different interplay between shear band multiplication and martensitic transformation and subsequently results in the observed tension–compression asymmetry of mechanical behavior. The current study provides a strategy in optimizing the microstructures and martensitic transformation of TRIP-reinforced BMGCs and might be extended to toughen a variety of BMGCs.

Disclosure statement

No potential conflict of interest was reported by the authors.

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