Thermal stability of mechanically alloyed boride/Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_{4}$Sn$_{6}$ glassy alloy composites

L.C. Zhang, Z.Q. Shen, J. Xu *

Shenyang National Laboratory for Materials Science, Institute of Metal Research, CAS, 72 Wenhua Road, Shenyang 110016, China

Received 17 June 2004; received in revised form 23 April 2005

Abstract

The Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_{4}$Sn$_{6}$ multicomponent alloy was chosen as base alloy due to a complete glass formation under ball milling and a sizable supercooled liquid region, $\Delta T_x = 66$ K. The mixtures of prealloyed Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_{4}$Sn$_{6}$ fragments with CrB or TiB$_2$ particles up to 30 vol.% were mechanically milled to fabricate the boride/Ti-based glassy alloy composites. The structural features of the as-milled products were characterized using X-ray diffraction, transmission electron microscopy and differential scanning calorimetry. In the ball-milled composites, the CrB or TiB$_2$ particles with sizes ranging around 10–200 nm are dispersed in the Ti-based glassy alloy matrix. Similar to the Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_{4}$Sn$_{6}$ glassy alloy without any borides, a well-defined glass transition temperature, $T_g$, and a wide supercooled liquid region, $\Delta T_x$, are observed also for the boride-containing composites. Furthermore, the glass transition and thermal stability of supercooled liquid for the matrix alloy in the composites are dependent on the fraction of boride addition. In the case of CrB addition, the $\Delta T_x$ value of glassy phase matrix was reduced due to a strong fraction dependence of the $T_g$ than that of the $T_x$, remaining at about 60 K for boride fractions less than 15 vol.%. In contrast, both the $T_g$ and $T_x$ of the TiB$_2$-containing composites were raised with increasing TiB$_2$ fraction up to 30 vol.%, resulting in no significant change for the $\Delta T_x$.

© 2005 Elsevier B.V. All rights reserved.
PACS: 81.20.E; 68.60.D; 61.43.D; 81.05.J

1. Introduction

Bulky amorphous alloys (or bulk metallic glasses) and their derivative composites have gained considerable attention in recent years [1,2]. A significant interest arises from their unique mechanical properties such as large elastic limits and high strengths. However, it remains a challenge problem that the single-phase metallic glasses typically display limited plastic flow in compression and none in tension at room temperature. To improve the ductility or plasticity of such materials, metallic glass matrix composites were developed. The glasses were reinforced by second-phase particulates [3–7], fibers [8,9], or in situ formed ductile phase precipitates [10–12]. It has been shown that these reinforcements in the glasses play a key role to hinder propagation of shear bands and to encourage the formation of multiple shear bands [10,13].

On the other hand, it is an attractive route to synthesize large-size bulk glasses through powder processing and subsequent warm consolidation in the supercooled liquid region [14–20]. This is especially important for the alloy systems with insufficient glass-forming ability to obtain large samples by melt casting, such as Al-, Ti-, Ni-based alloys. It is therefore a crucial issue if the alloy in its supercooled liquid state has adequate thermal stability in order to provide a temperature–time window for consolidation. Usually, such a thermal stability is characterized in a calorimetric scan by a wide supercooled liquid region, defined as the temperature...
interval ($\Delta T_g$) between the glass transition temperature ($T_g$) and the onset temperature of crystallization ($T_x$).

Mechanical alloying (MA) has been found to be a convenient method to produce the glassy alloy powder precursors for subsequent consolidation in many multi-component alloy systems with a sizable supercooled liquid region [21–25]. Furthermore, it is of interest to note that MA has an advantage for the processing of glassy alloy composites, as the vitrification of the matrix alloy and the dispersion of reinforcement agent can be realized simultaneously. Based on this strategy, several composite systems comprised of glassy alloys with a wide supercooled liquid region and insoluble ceramic particulates as dispersoids have been investigated, including SiC/Zr$_{65}$Al$_{17.5}$Ni$_{19}$Cu$_{17.5}$ [26], oxides/Zr$_{65}$Al$_{17.5}$Ni$_{19}$Cu$_{17.5}$ [27], nitrides/Zr$_{65}$Al$_{17.5}$Ni$_{19}$Cu$_{17.5}$ [28], ZrC/Zr$_{52}$Cu$_{30}$Al$_{10}$Ni$_{5}$ [29], and oxides/Mg$_{25}$Cu$_{30}$Y$_{15}$ [30]. It was indicated that, due to partial dissolution of the added dispersoids under mechanically forcing, the thermal stability of matrix glassy alloy, with respect to the glassy alloy without ceramic particulates, was affected in the course of composite formation. The supercooled liquid region was either enlarged or reduced, depending on the solid-state interaction between matrix alloy and ceramic agent, and on the fraction of addition.

In the present work, composite systems containing the Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ glassy alloys and stable boride particulates such as CrB or TiB$_2$ were chosen to investigate the effect of boride addition on the thermal stability in the MA Ti-based glassy alloy composites. As shown in previous work [31], ball-milled Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ glassy alloy exhibits a supercooled liquid region of about 66 K. Meanwhile, CrB and TiB$_2$ as reinforcement agent have been widely employed in the particulate reinforced metal matrix composite [32]. The density and melting temperature for CrB and TiB$_2$ are $6.14 \times 10^{-3}$ kg/m$^3$ and 2373 K, and $4.5 \times 10^{-3}$ kg/m$^3$ and 3173 K, respectively. They are also of interest to be used as reinforcement agents in the Ti-based glassy alloys with high specific strength.

2. Experimental

With elemental pieces having the purity higher than 99.9 wt%, the master alloy with a nominal composition of Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ (in at.%) was prepared by arc melting under a Ti-gettered argon atmosphere. The alloyed button was then crushed into fragments, with sizes less than ~500 μm and in flake shape, and used as starting materials for ball milling. The fragments were identified to be a mixture of several intermetallic phases including NiTi, Ti$_3$Cu and Ti$_5$Sn [31]. The CrB or TiB$_2$ particles with purity higher than 99.9 wt% and particle sizes smaller than 45 μm were blended with the pre-alloyed fragments, up to 30% of volume fraction. The blended powder mixtures together with hardened steel balls were loaded in a hardened steel vial under an argon-filled glove box with less than 1 ppm O$_2$ and H$_2$O. A ball-to-powder weight ratio about 5:1 was employed. The ball milling process was performed in a SPEX 8000 shaker mill cooled by forced flowing air. For all the samples discussed in this paper, the milling time was fixed at 32 h. This time was chosen based on the results of our prior studies of this system [33], to assure that the milling has proceeded sufficiently long for the samples to reach a steady state, but short enough to avoid excessive contamination from the milling media.

Phase formation in the as-milled powders was characterized by X-ray diffraction (XRD) using a Rigaku D/ max 2400 diffractometer with monochromated CuK$_\alpha$ radiation ($\lambda = 0.1542$ nm). Samples for transmission electron microscopy (TEM) observation were prepared by first embedding the powder particles in a nickel foil via electrodeposition for mechanical thinning and subsequently ion-milling to electron transparency. The conventional TEM and high-resolution TEM observations were carried out in a JEOL JEM-2010 electron microscope.

The glass transition and crystallization behavior were analyzed by differential scanning calorimetry (DSC) in a Perkin-Elmer DSC-7 calorimeter under flowing purified argon, with a heating rate of 40 K/min. A second run under identical conditions was used to determine the baseline after each run. To determine the onset temperature of glass transition, $T_g$, the sample was heated to a temperature below $T_x$ to reach a relaxed state for resolving the initial change in the baseline. The $T_g$ of the samples was defined as the intersection of the tangents to the DSC trace above and below the initial change in the baseline slope [24]. To confirm the reproducibility of the experimental results, at least three samples have been measured for each composition. All the $T_g$ and $T_x$ measurements were reproducible within the error of ±1 K. Isothermal measurement was carried out by heating up to desired temperatures at a heating rate of 200 K/min, then holding for 30 min. A second run under identical conditions was used as the baseline.

The iron and oxygen contents in the ball-milled products were found to be 0.50 wt% and 0.15 wt%, respectively, using inductively coupled plasma emission spectroscopy (ICP10P, ARL) and a LECO TC-436 system.

3. Results

Fig. 1(a) and (b) shows the XRD patterns of the ball-milled Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ alloy and its mixtures with CrB or TiB$_2$ particles at different volume fractions, respectively. Also, the patterns of initial powders of each boride are plotted together for comparison. For the ball-
milled Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ alloy without any addition, it can be seen that only a broad diffuse diffraction maximum at $2\theta = 35-55^\circ$ of an amorphous phase was visible, and no diffraction peaks from any crystalline are detected. This indicates that a single amorphous phase formed in the ball-milled Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ powder. Moreover, for the ball-milled mixtures of the alloy with CrB particles, only diffraction peaks from CrB superimposed on the broad diffuse scattering maxima from the amorphous phase, as seen in Fig. 1(a). No considerable amounts of other crystalline phases were detected within the sensitivity limit of X-ray diffraction. It is noticed that the diffraction peaks of CrB phase were broadened with respect of the initial powders, due to the internal strain and grain refinement caused by ball milling. Using a peak-fitting program of Origin with Pearson VII function, the peak position and full width at half maxima (FWHM) were determined for the CrB diffraction peaks and the diffuse maximum of amorphous matrix phase. The average grain size of CrB in the milled powder with 20 vol.% CrB was roughly estimated to be about 20 nm according to the Williamson–Hall method [34]. No significant scatters of the data caused by the strain anisotropy effect were found. Additionally, diffraction peak position of CrB phase remained unchanged whereas the position of diffuse maximum slightly shifted to a lower Bragg angle side, reflecting that the chemical composition of amorphous phase in the CrB-containing powder slightly deviates from the nominal composition of matrix alloy. It is probably caused by the fact that the CrB particles partially dissolved into the amorphous matrix in the composites under ball milling.

Similar to the case of adding CrB particles, the composite containing an amorphous phase and TiB$_2$ nanophase formed also in the ball-milled Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ alloy with TiB$_2$ particles up to 30 vol.%. As shown in Fig. 1(b), diffraction peaks from TiB$_2$ superimposed on the broad diffuse scattering maxima from the amorphous phase. The average grain size of TiB$_2$ in the composites of the 30 vol.% TiB$_2$ was determined to be about 50 nm. In addition, diffraction peaks position of TiB$_2$ remained unchanged, while the position of diffuse maximum shifted to lower Bragg angle side. The scattering vector, defined as $Q_p = 4\pi \sin \theta / \lambda$, of the broad diffuse maxima for the amorphous phase decreased from 26.64 nm$^{-1}$ for the alloy without TiB$_2$ down to 26.48 nm$^{-1}$ for the composites containing 30 vol.% TiB$_2$. It implies that the milling induced the dissolution of a small fraction of TiB$_2$ particles in the amorphous matrix.

The morphology of the as-milled powders for Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ alloy and the mixtures with 20 vol.% CrB and 30 vol.% TiB$_2$ particles was observed using SEM, as shown in Fig. 2(a)–(c). In all cases, the particle shapes are similar, being nearly equiaxial and irregular, and the size distribution of the particles is uniform. However, it was observed that the particle size for the Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ alloy ranged from 10 to 50 nm, the largest among the three samples, whereas the sizes of the particles of the composites with CrB and TiB$_2$ ranged from 10–40 nm to 5–30 nm, respectively. The TiB$_2$-containing powders are the finest.

Fig. 4(a)–(c) displays the TEM bright-field micrographs and corresponding selected area electron diffraction (SAED) patterns (inset) of the ball-milled Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ glassy alloy and the composites containing 20 vol.% CrB and TiB$_2$, respectively. As seen in Fig. 4(a), a featureless structure with a broad diffuse

---

**Fig. 1.** XRD patterns for the ball-milled Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ alloy mixed with (a) CrB and (b) TiB$_2$ at different volume fractions as well as the initial boride particles.
halo in SAED pattern characteristic of amorphous phase was observed in the ball-milled Ti<sub>50</sub>Cu<sub>18</sub>Ni<sub>22</sub>Al<sub>4</sub>Sn<sub>6</sub> alloy without borides. This indicates that a single amorphous phase was homogeneously formed in the ball-milled powder. No unreacted crystalline phase is visible like the situation of ball-milled Ti<sub>50</sub>Cu<sub>18</sub>Ni<sub>22</sub>Al<sub>4</sub>Si<sub>4</sub>B<sub>2</sub> [24] or Ti<sub>16.7</sub>Zr<sub>16.7</sub>Hf<sub>16.7</sub>Ni<sub>13.3</sub>Cu<sub>13.3</sub>Ag<sub>13.3</sub>Al<sub>10</sub> multicomponent alloys [25].

TEM observations of the boride-containing composites formed by MA revealed that the second-phase boride particles, CrB or TiB<sub>2</sub>, dispersed in the matrix of Ti-based amorphous phase, as seen in Fig. 4(b) and (c). The particles were refined to the sizes ranging around 10–200 nm. The average size of CrB particles is smaller than that of TiB<sub>2</sub> particles. Additionally, the particle sizes of second-phase observed from TEM are larger than the grain size estimated from peak broadening of XRD profiles. It is likely caused by that the large particles of second-phase are polycrystalline containing a number of nanoscale domains. Moreover, for the sample of the composites containing 20 vol.% CrB, the chemical composition of matrix amorphous phase was determined to be Ti<sub>44.2</sub>Cu<sub>20.0</sub>Ni<sub>21.2</sub>Al<sub>4.3</sub>Sn<sub>6.1</sub>Cr<sub>4.2</sub> using the energy dispersive X-ray (EDX) analyzer attached to the TEM. It proved that under the milling, the boride particles partially dissolved in the matrix, resulting in the deviation of the chemical composition of glassy phases in the composites from the nominal composition of the initial alloy, Ti<sub>50</sub>Cu<sub>18</sub>Ni<sub>22</sub>Al<sub>4</sub>Sn<sub>6</sub>. Fig. 5 shows a typical high-resolution TEM micrograph along the [5143] direction of TiB<sub>2</sub> and corresponding electron diffraction patterns (inset) taken from the interface area between the particles and matrix for the ball-milled composite with 20 vol.% TiB<sub>2</sub>. The lattice fringes of TiB<sub>2</sub> particles are clearly visible. No other reacted phase at the interface was observed.

Fig. 6(a) and (b) are the DSC scans of the ball-milled Ti<sub>50</sub>Cu<sub>18</sub>Ni<sub>22</sub>Al<sub>4</sub>Sn<sub>6</sub> alloy and composites with different volume fraction of CrB and TiB<sub>2</sub> particles, respectively. As shown in Fig. 6(a) and (b), crystallization of the amorphous phases proceeds through one single step in all cases, associated with a sharp exothermic peak. The crystallized products were identified to be the cubic NiTi-type phase and an unidentified phase [31].
To the monolithic Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_{4}$Sn$_{6}$ glassy alloy, a distinct glass transition prior to crystallization and a wide supercooled liquid region appear also in two boride-containing composites. The $T_g$, $T_x$ and $\Delta T_x$ of the composites as a function of volume fraction of CrB or TiB$_2$ particles are plotted in Fig. 7. It is observed in the CrB-containing composites that both $T_g$ and $T_x$ were elevated as the CrB fraction increased, as seen in Fig. 6(a). The $T_g$ and $T_x$ increased from 705 K and 771 K for the monolithic glassy alloy up to 747 K and 782 K for the composite with 20 vol.% CrB, respectively. At low CrB volume fractions, the $\Delta T_x$ value of the amorphous phase increased from 66 K for the glassy alloy without CrB up to 69 K for the composite with 10 vol.% CrB. However, with further increasing volume fractions, the $\Delta T_x$ dropped down to 35 K at 20 vol.% CrB, due to a stronger dependence of the $T_g$ on boride fraction than that of the $T_x$, as seen in Fig. 7. Similarly, as the TiB$_2$ fraction in the composites increased, both $T_g$ and $T_x$ gradually shifted to higher temperature. The $T_g$ and $T_x$ increased from 705 K and 771 K for the monolithic glassy alloy to 720 K and 783 K for the composite with 30 vol.% TiB$_2$, respectively, whereas the width of supercooled liquid region remained almost unchanged around 65 K. For comparison purposes, the thermal properties obtained in DSC measurement for the ball-milled Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_{4}$Sn$_{6}$ glassy alloy and boride-containing composites with different volume fractions are also summarized in Table 1, including the $T_g$, $T_x$, peak temperature of crystallization reaction, $T_p$, $\Delta T_x$, and heat release of crystallization, $\Delta H_x$. The change of $T_g$ and $T_x$ for the composites with respect to the monolithic Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_{4}$Sn$_{6}$ glassy alloy implies that the chemical composition of glassy phases in the composites is slightly different from the initial alloy. Meanwhile, the extent of composition derivation is strongly dependent on the addition fraction in the composites.

To confirm the ball-milled products to be truly amorphous phase rather than microcrystalline even though the samples in both cases exhibit broad diffraction halos in XRD or SAED. DSC measurements at 755 K in the isothermal mode were performed for several typical samples, Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_{4}$Sn$_{6}$ glassy alloy and composites with 15 vol.% CrB and 30 vol.% TiB$_2$. Isothermal DSC profiles of the samples are shown in Fig. 8. In all cases, the signal of heat release exhibit a distinct exothermic peak instead of monotonically-decaying heat flow signals. Such a signal is the typical shape for a nucleation and growth process [35]. It further supports the conclusion from the XRD or SAED patterns that the amorphous phase truly formed in all ball-milled Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_{4}$Sn$_{6}$ alloys with or without borides.

Fig. 9 shows a temperature–time-transformation (TTT) diagram for the onset of crystallization of the as-milled Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_{4}$Sn$_{6}$ glassy alloy and composite with 20 vol.% TiB$_2$. The diagram was obtained by performing isothermal DSC runs on the sample at varying temperatures across the supercooled liquid region. This was accomplished by heating the sample at a heating rate of 40 K/min to an annealing temperature above $T_g$, and then holding for sufficiently long times to record the first exothermic peak, which indicates the onset of crystallization. As seen in Fig. 9, for the Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_{4}$Sn$_{6}$ glassy alloy, the supercooled liquid state can be maintained at 20 K higher than $T_g$ for more than 400 s until the crystallization occurs. Such a ‘temperature–time’ window is quite similar to the gas-atomized powders of ZrAlNiCu [14], CuTiZrNiSi [19] and ZrNb-CuNiAl (Vitreloy 106a) [20] glassy alloys. For these
alloys, the fabrication of bulk amorphous materials by consolidation was successful by using the ‘window’. Compared with the Ti50Cu18Ni22Al4Sn6 alloy, the whole window for the composite with TiB2 shifted to higher temperature by about 5 K, and the time to remain the supercooled liquid state at a temperature of $T_g + 20$ K is shorter than 400 s. It implies that the window for thermal processing of the composite is somewhat narrower than that of the TiB2-free alloy.

4. Discussion

As well known, the MA technique has been widely used as a unique means for producing a wide variety of far-from-equilibrium materials [36–39]. In the early work [40–42], it was successfully employed to produce dispersions of insoluble phase such as oxides in the polycrystalline engineering alloys. The goal of dispersed-phase alloys is to strengthen the alloy matrix by impeding the motion of dislocations. Although the mechanical attrition is a complex dynamic process, the shear deformation caused by the ball-powder-ball collisions was considered as the central event. Several models, covering the mechanistic, atomistic, thermodynamic and kinetic aspects, have been proposed to explain the mechanism [43,44]. In the current milling of the Ti-based multicomponent alloy mixed with borides, the boride particles were continuously fragmentized until refined to a nanometer scale and dispersed in the alloy matrix,
while the crystal-to-glass transition took place simultaneously in the matrix alloy. Thus, it can be assumed that the dispersion and refinement process of boride during ball milling is similar to the scenario for oxide dispersion strengthened (ODS) alloys produced by MA [36,40–42]. Considering the milling-induced vitrification in the multicomponent alloy systems, the operative mechanism has been discussed in Ref. [25]. Since the initial state of the alloy employed for ball milling in this work is a mixture of intermetallic phases, we believe that the chemical disordering of the system, induced by shear deformation [44,45], is likely to be responsible for the vitrification of the alloy.

Regarding the particle size of final milled powders, it was believed to be associated with the mechanical properties (ductile or brittle) of the materials subject to milling. For comparison, the microhardness, elastic modulus, heat of formation and melting temperature of the present borides together with Ti-based amorphous alloy are compiled in Table 2. Due to lack of the data for CrB in literature, the data for CrB2 were given as a reference. Evidently, the microhardness and elastic modulus of titanium boride are much higher than those of chromium boride. It suggests that the former is more brittle than the later. Consistently, the titanium boride is more chemically stable than chromium boride according to the heat of formation and melting temperature. For the ceramic particles reinforced metallic glass composite [50], it was found that the elastic modulus of the composite as a function of volume fraction of the particles followed the Halpin and Tsai equation (H–T Eq.) [51]:

$$E_c = \frac{E_m (1 + \eta f)}{(1 - \eta f)}$$

(1)

where $E_c$, $E_m$ and $E_p$ are the modulus for the composite, matrix glass and the second phase particles, respectively, $f$ is volume fraction of the second phase particles, and $\eta = (E_p/E_m - 1)/(E_p/E_m + \xi)$ and $\xi$ is a factor to account for the influence of geometry of the reinforcing

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_x$, K</th>
<th>$T_v$, K</th>
<th>$T_p$, K</th>
<th>$\Delta T_x$, K</th>
<th>$\Delta H_x$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti50Cu18Ni22Al4Sn6</td>
<td>705</td>
<td>771</td>
<td>776</td>
<td>66</td>
<td>2.68 ± 0.14</td>
</tr>
<tr>
<td>with 10% CrB</td>
<td>705</td>
<td>774</td>
<td>780</td>
<td>69</td>
<td>2.13 ± 0.17</td>
</tr>
<tr>
<td>with 15% CrB</td>
<td>717</td>
<td>779</td>
<td>785</td>
<td>62</td>
<td>2.10 ± 0.13</td>
</tr>
<tr>
<td>with 20% CrB</td>
<td>747</td>
<td>782</td>
<td>791</td>
<td>35</td>
<td>1.41 ± 0.15</td>
</tr>
<tr>
<td>with 10% TiB2</td>
<td>707</td>
<td>772</td>
<td>777</td>
<td>65</td>
<td>2.40 ± 0.12</td>
</tr>
<tr>
<td>with 20% TiB2</td>
<td>713</td>
<td>778</td>
<td>784</td>
<td>65</td>
<td>2.30 ± 0.12</td>
</tr>
<tr>
<td>with 30% TiB2</td>
<td>720</td>
<td>783</td>
<td>790</td>
<td>63</td>
<td>2.09 ± 0.16</td>
</tr>
</tbody>
</table>
phase, taken as 2 here for spherical particles. Using the H–T Eq. with the data in Table 2, the modulus of the composites containing the 10, 20, 30 vol.% TiB₂ particles were calculated to be 114, 119 and 124 GPa, respectively. The modulus of the composites increased with increasing the fraction of TiB₂ particles. Consequently, it appears that the boride-containing composites are more brittle than monolithic Ti-based glassy alloy. It is well documented that in MA the resultant powder develops through the repeated cold welding and fracture of the powder particles until the microstructural evolution and chemical homogenization reaches a steady state. The particle size of the resultant powder is dominated by a dynamic balance between the cold welding and fracture of the particles. Therefore, the brittle material finally reaches a smaller size than the ductile one. That is a reason why the particle size of the milled powder was finally in the sequence of composite with TiB₂, then that with CrB and monolithic Ti-based glassy alloy.

It should be mentioned that although the CrB and TiB₂ are highly stable and insoluble, the result that a small fraction of the particles dissolved in the matrix alloy under external forcing is unavoidable in the course of ball milling. It leads to the chemical composition of the amorphous phase in the composites containing boride particles to deviate from the nominal composition of Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆ alloy matrix. This is accompanied by a change of the glass transition event and crystallization-resistant ability in the supercooled liquid state, in comparison with the Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆ glassy phase. Similar findings have been observed also in several MA dispersoids/glassy alloy composite systems, such as carbides/Zr-based alloys [26,29], oxides/Zr-based alloy [27], nitrides/Zr-based alloy [28] and oxides/Mg-based alloy [30], as well as in the systems of tungsten/Zr-based alloy [52] and tungsten or tantalum/La-based alloy [53].

Finally, the CrB addition with large fraction in the MA composites resulted in a more obvious adverse effect: it reduced the width of supercooled liquid region of the original Ti-based glassy alloys. It is probably caused by a fact that the milling-enhanced solubility of the CrB in the matrix is larger than that of the case of TiB₂. As shown in Section 3, the concentration of Cr in the matrix reached about 4 at.% for the 20 vol.% addition. Meanwhile, the atomic size of Cr (r_Cr = 0.130 nm) is smaller than that of the main element in the matrix, Ti (r_Ti = 0.1460 nm). Thus, the CrB addition yields a stronger effect on the ΔTₓ value with respect to adding TiB₂. Furthermore, it is interesting to note that the TiB₂-containing composites not only display a higher thermal stability (the T_g and Tₓ values around 10 K higher than those of the TiB₂-free alloy), but also maintain an extension of supercooled liquid region above 60 K. It is noteworthy that, with such a beneficial feature for subsequent processing, the fraction of TiB₂ as a harder second-phase in the glassy alloy composite can be increased up to 30 vol.%, which is close to the percolation threshold (volume fraction 0.5–0.6) for the composite [54]. As the addition of the nanoparticles leads to a high elastic modulus, it is promising to improve the wear resistance of the Ti-based glassy alloys [55]. Therefore, TiB₂ particles should be a preferable reinforcement agent to optimize the processing widow and mechanical properties for the Ti-based glassy alloys.

5. Conclusion

1. Under high-energy ball milling of mixtures of Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆ alloy together with CrB or TiB₂ particles, composites with the borides dispersed in glassy alloys are obtained in the as-milled products. The crystal-to-glass transition for the matrix alloy and the refinement of insoluble second-phase particulates were achieved via mechanical alloying. For the ball-milled composites containing borides, CrB or TiB₂ particles in the matrix were refined to sizes ranging from 10 to 200 nm. The particles of the resultant
powder are equiaxial and irregular in shape, with the sizes of for the monolithic Ti-based glassy alloy and composites with CrB and TiB$_2$ ranging from 10 to 50, 10 to 40 and 5 to 30 μm, respectively, due to their ductility difference.

2. Similar to the monolithic Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ glassy alloy, a significant calorimetric glass transition signal and a wide supercooled liquid region are observed also in the boride-containing composites. The glass transition temperature, $T_g$, and crystallization temperature, $T_c$, of the glassy phase in the composites increased with increasing boride addition, but the one-step crystallization mode of the glassy matrix remained even for boride fractions up to 30 vol.%. With respect to the monolithic Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ glassy alloy, the width of the supercooled liquid region, $\Delta T_g$, of the glassy phase in the CrB-containing composite was slightly extended at low volume fraction of CrB particles, then reduced with further increasing volume fraction due to a strong fraction dependence of the $T_g$ than that of the $T_c$. In contrast, the TiB$_2$ addition does not yield an adverse effect on the thermal stability of the supercooled liquid. The $\Delta T_g$ value of TiB$_2$-containing composites remained around 65 K. Such a change of the thermal stability of the composite with respect to the boride-free glassy alloy was attributed to the dissolution of small amount of boride particles into the matrix alloy under the shear deformation during ball milling.

3. The temperature–time- transformation (TTT) diagram for the onset of crystallization of the as-milled Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ glassy alloy and composite with 20 vol.% TiB$_2$ is comparable to the gas-atomized powders of ZrAlNiCu, CuTiZrNiSi and ZrNbCuNiAl glassy alloys. It provides a temperature–time window for the consolidation of the powders into bulk materials in the supercooled liquid state.

Acknowledgment

The authors would like to gratefully acknowledge the financial support from the National Natural Science Foundation of China under Contract Nos. 50371084 and 50323009.

References