Mechanically milling-induced amorphization in Sn-containing Ti-based multicomponent alloy systems

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 August 2004; received in revised form 8 November 2004; accepted 16 November 2004

Abstract

Two Sn-containing Ti-based multicomponent alloys, Ti₅₀Cu₃₅Ni₁₂Sn₃ and Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆, were chosen to investigate the amorphization of pre-alloyed fragments under high-energy ball milling. For comparison, the amorphous alloy ribbons with the same compositions were also prepared using melt-spinning method. Amorphous nature of the as-prepared samples was characterized using X-ray diffraction, transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). For the ball-milled (BM) Ti₅₀Cu₃₅Ni₁₂Sn₃ alloy, the glass formation is predominant but a small fraction of the α-Ti nanocrystals still remains unreacted. In contrast, the complete amorphization can be achieved in the ball-milled Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆ alloy. In both cases, thermal properties of the ball-milled glassy alloys are comparable to those of the melt-spun (MS) glasses, exhibiting a distinct glass transition and wide supercooled liquid region about 60 K. The amorphization extent in the final milled products is associated with whether the α-Ti phase exists in the initial microstructure of the alloys as starting materials.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Ball milling; Amorphous alloys; Supercooled liquid region; Crystallization; Ti alloys

1. Introduction

With ultrahigh fracture strength (σf), around 2 GPa [1–5], amorphous Ti-based alloys are promising as a new family of light-weight materials with high specific strength. Unfortunately, unlike other bulk metallic glass-forming alloy systems, it has been difficult to prepare the Ti-based metallic glasses in bulk form from the undercooled melt. The largest thickness achieved so far for Ti-based multicomponent amorphous alloys using conventional casting methods is only of the order of several millimeters [4–9]. Consequently, the powder processing route, with subsequent warm consolidation in the vicinity of glass transition temperature of the glassy alloys, is still an attractive approach to prepare the truly bulky amorphous materials [10–15]. Therefore, it is of interest to synthesize the glassy alloy powders with a high thermal stability at the supercooled liquid state characterized by a sizable supercooled liquid region, defined as the temperature interval (ΔT_x) between the glass transition temperature (T_g) and the onset temperature of crystallization (T_x).

Recently, it has been found that Ti-based glassy alloys with a ΔT_x value about 60 K can be prepared by mechanical alloying (MA) of the Ti–Cu–Ni–Al–Si–B multicomponent alloy system [16]. However, the MA-induced glass formation is incomplete, where the nanoscale particles of α-Ti phase remained in the final ball-milled (BM) products. Such an incomplete amorphization was supposed to be associated with the containing of metalloid elements, Si and B, in the alloys. On the other hand, it was revealed that the Sn addition is effective in improving the thermal stability of the supercooled liquid in the Ti-based glasses [3,17–19]. The supercooled liquid region of the Ti₅₀Cu₃₅Ni₁₂Sn₃ metallic glass was extended to about 78 K [19]. It is, therefore, interesting to understand whether the Sn-containing alloys are more conducive to glass formation under MA processing conditions, with respect to the alloys containing metalloid elements.

In the present work, elements Si and B in the Ti₅₀Cu₁₈Ni₁₂Al₄Sn₆ alloy, which had a large ΔT_x of about 61 K in the MA glassy powders [16], are completely replaced...
with the ductile metal Sn to form a Ti₅₀Cu₃₅Ni₁₂Sn₃ alloy. Moreover, the Ti₅₀Cu₃₁Ni₁₂Sn₃ alloy was chosen due to its large value of ΔTᵣ for the melt-spun (MS) glass. The milling-induced amorphization in the two alloys was investigated. The thermal stability of the BM alloys was compared with that of the MS glasses having the same composition.

2. Experimental

Starting from elemental pieces having a purity higher than 99.9 wt.%, the master alloys with a nominal composition of Ti₅₀Cu₃₅Ni₁₂Sn₃ and Ti₅₀Cu₃₁Ni₁₂Al₄Sn₆ (in at.%) were prepared by arc melting under a Ti-gettered argon atmosphere. The alloyed buttons were then crushed into fragments and used as the starting materials for ball milling. The pre-alloyed fragments together with hardened steel balls were loaded in a hardened steel vial under an argon-filled M-Braun UNI-lab glove box with less than 1 ppm O₂ and H₂O. A ball-to-powder weight ratio of about 5:1 was employed. The ball milling 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 [20], to ensure 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.

The metallic glass ribbons of the two alloys were prepared in an argon atmosphere by induction melting the master alloy ingot in a quartz crucible and ejecting it onto a single-roller using a Bühler melt spinner. The surface speed of the copper roller was 39 m/s. The as-quenched ribbons were approximately 4 mm wide and 20–30 μm thick.

The structure of the BM powders and MS ribbons was analyzed by X-ray diffraction (XRD) using a Rigaku D/max 2400 diffractometer with monochromated Cu Kα radiation (λ = 0.1542 nm). For the BM powders, samples for transmission electron microscopy (TEM) were prepared by first embedding the powder particles in a nickel foil via electrodeposition for mechanically thinning and subsequently ion-milling to electron transparency. The conventional TEM and high-resolution TEM observation were carried out in a JEOL JEM-2010 microscope. The glass transition and crystallization of the glassy alloys were examined by differential scanning calorimetry (DSC) in a Perkin-Elmer DSC7 under flowing purified argon. Isothermal measurement was carried out by heating up to the desired temperature at a heating rate of 20 K/min.

The oxygen and nitrogen contents in the samples were examined using a LECO TC-436 system to be 0.026 wt.% and 0.0024 wt.% for the starting materials and 0.15 wt.% and 0.031 wt.% for the final BM products, respectively. The iron contents in the final BM products were examined using inductively coupled plasma emission spectroscopy (ICP10P, ARL) to be 0.50 wt.%.

Fig. 1. XRD patterns of the arc-melted alloys as starting materials for mechanical milling: (a) Ti₅₀Cu₃₁Ni₁₂Sn₃ and (b) Ti₅₀Cu₃₅Ni₁₂Al₄Sn₆.

3. Results

Fig. 1(a and b) show the XRD patterns of two arc-melted alloys used as the starting materials for the mechanical milling. Also, the microstructures of the arc-melted alloys observed using SEM in backscattered electron mode were illustrated in Fig. 2. In addition, the chemical composition of each zone with different contrast in the SEM images was checked using the energy dispersive X-ray (EDX) analyzer attached to SEM. The phase constituents of each alloy were determined
Fig. 3. XRD patterns of the ball-milled and melt-spun alloys: (a) Ti₅₀Cu₃₅Ni₁₂Sn₃ and (b) Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆.

Based on the XRD results combined with the EDX analysis, as seen in Fig. 1(a), the diffraction peaks of α-Ti phase and intermetallic phases of Ti₃Sn, γ-Cu₄Ti and NiTi were identified in the Ti₅₀Cu₃₅Ni₁₂Sn₃ alloy. These crystalline phases were observed also in the SEM images, as shown in Fig. 2(a). Similarly, the crystalline phases in the Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆ alloy were determined to be Ti₃Sn, NiTi and Ti₂Cu, as seen in Fig. 1(b) and Fig. 2(b). Note that, besides several intermetallic phases, the α-Ti solid solution is absent in the latter with respect to the former.

Fig. 3 shows the XRD patterns of the Ti₅₀Cu₃₅Ni₁₂Sn₃ and Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆ pre-alloyed fragments after milling for 32 h. For comparison, the patterns of the MS ribbons for the two alloys are plotted together. Similar to the MS alloys, the BM powders of the two alloys exhibit a broad diffuse diffraction maximum at 2θ = 35–55° in the XRD patterns, indicating the formation of amorphous phase. No detectable diffraction peaks from any crystalline phase are visible within the sensitivity limit of XRD. The wave number Q<sub>p</sub>, defined as Q<sub>p</sub> = 4π sin θ/λ, of the broad diffuse maximum for the amorphous phase formed by BM is determined to be 26.89 nm<sup>−1</sup> for Ti₅₀Cu₃₅Ni₁₂Sn₃ and 26.64 nm<sup>−1</sup> for Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆, respectively. They are well in agreement with the values of the glassy alloys prepared using MS method, Q<sub>p</sub> = 26.81 nm<sup>−1</sup> for Ti₅₀Cu₃₅Ni₁₂Sn₃ and 26.67 nm<sup>−1</sup> for Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆, respectively. It implies that for a given alloy, the amorphous phase obtained using the different preparation methods is very similar in all cases. Furthermore, it is apparent that the milling-induced amorphization in the Sn-containing alloy system is more complete compared with the Ti–Cu–Ni–Si–B alloy system, in which the α-Ti crystals in the final BM products are even detectable in the XRD patterns [16,21].

Fig. 4 illustrates the TEM bright-field micrographs and corresponding selected area electron diffraction patterns (inset) of the ball-milled (a) Ti₅₀Cu₃₅Ni₁₂Sn₃ and (b) Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆ alloys. As seen in Fig. 4(a), it was observed that a number of spherical particles with the size smaller than about 10 nm are dispersed in the featureless amorphous matrix, as seen in Fig. 4(a). The SAED pattern shows a broad halo, indicating that the amorphous phase is predominant in the sample. Also, the chemical composition of these crystals was checked using the EDX analyzer attached to the TEM. Only Ti was detected as major element together with a small amount of other elements in the alloy. Unfortunately, the phase identification of these particles is difficult owing to the small size. However, it seems reasonable to suppose the particles as the unreacted α-Ti solid solution. By contrast, no unreacted crystallites are observed in the BM Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆ alloy, as seen in Fig. 4(b). The homogeneous contrast indicates that a single amorphous phase formed in the milled product for this alloy. Furthermore, as shown in Fig. 5(a), the high-resolution TEM image also confirms that a small fraction of residual nanocrystal still remained in the BM final product of Ti₅₀Cu₃₅Ni₁₂Sn₃ alloy, as marked by circles in the image, even though it is not observable in the XRD pattern. This is not the case for the Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆ alloy, in Fig. 5(b), in which the BM-induced crystal-to-glass transition is nearly complete. Consequently, the milling-induced amorphization that took place in the Ti₅₀Cu₃₅Ni₁₂Sn₃ alloy is easier than in the Ti₅₀Cu₁₈Ni₂₂Al₄Sn₆ alloy.

Fig. 6 displays the DSC scans in the continuous heating mode with a heating rate of 40 K/min for the two BM alloys,
Fig. 5. High-resolution TEM images of the ball-milled (a) Ti\textsubscript{50}Cu\textsubscript{35}Ni\textsubscript{12}Sn\textsubscript{3} and (b) Ti\textsubscript{50}Cu\textsubscript{18}Ni\textsubscript{22}Al\textsubscript{4}Sn\textsubscript{6} alloys.

Fig. 6. DSC scans (at a heating rate of 40 K/min) of the ball-milled and melt-spun alloys: (a) Ti\textsubscript{50}Cu\textsubscript{35}Ni\textsubscript{12}Sn\textsubscript{3} and (b) Ti\textsubscript{50}Cu\textsubscript{18}Ni\textsubscript{22}Al\textsubscript{4}Sn\textsubscript{6}.

The glass transition temperature $T_g$, the onset temperature of crystallization $T_x$, the width of the supercooled liquid region $\Delta T_x$, and the heat of crystallization obtained by integrating the area under the peaks $\Delta H_x$, are summarized in Table 1, together with the data from Ref. [19] for comparison. Similar to the MS glass, an endothermic signal associated with the glass transition and two exothermic reactions due to crystallization were observed in the BM Ti\textsubscript{50}Cu\textsubscript{35}Ni\textsubscript{12}Sn\textsubscript{3} alloy, as seen in Fig. 6(a). Nevertheless, the $T_g$ and $T_x$ of the BM alloy shift towards a lower temperature by about 20 K with respect to the MS glass. The crystallization transition for the BM alloy occurs at a temperature range broader than for the MS glass. It reflects that the composition of the amorphous phase in the BM alloy is not as homogeneous as in the MS glass. The $\Delta H_x$ of the BM alloy is about 84\% of that of the MS glass. Assuming that the area under the DSC peaks is proportional to the volume fraction of the amorphous phase, the volume fraction of the residual crystallites in the BM alloy is estimated to be about 16\%. It is approximately consistent with the findings of the TEM observation. It is noticed that the $\Delta T_x$ values of the alloys prepared by the BM and MS

### Table 1

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Synthesis route</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$\Delta T_x$ (K)</th>
<th>$\Delta H_x$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti\textsubscript{50}Cu\textsubscript{35}Ni\textsubscript{12}Sn\textsubscript{3}</td>
<td>BM</td>
<td>652</td>
<td>717</td>
<td>65</td>
<td>4.11</td>
</tr>
<tr>
<td>Ti\textsubscript{50}Cu\textsubscript{35}Ni\textsubscript{12}Sn\textsubscript{3}</td>
<td>MS</td>
<td>675</td>
<td>739</td>
<td>64</td>
<td>4.90</td>
</tr>
<tr>
<td>Ti\textsubscript{50}Cu\textsubscript{18}Ni\textsubscript{22}Al\textsubscript{4}Sn\textsubscript{6}</td>
<td>BM</td>
<td>672 [19]</td>
<td>730 [19]</td>
<td>78 [19]</td>
<td>N/A</td>
</tr>
<tr>
<td>Ti\textsubscript{50}Cu\textsubscript{18}Ni\textsubscript{22}Al\textsubscript{4}Sn\textsubscript{6}</td>
<td>MS</td>
<td>705</td>
<td>771</td>
<td>66</td>
<td>2.68</td>
</tr>
</tbody>
</table>
methods are comparable, both around 64 K. In addition, the $\Delta T_g$ of the MS glass is not as large as 78 K given by Kim et al. [19].

As seen in Fig. 6(b), the crystallization of the Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ glassy alloy proceeds through a single stage, showing one exothermic peak only. The $\Delta T_g$ and $\Delta H_g$ of the BM glassy alloy is 66 K and 2.68 kJ/mol, respectively, comparable to those of the MS glass. But, the $T_g$ and $T_x$ of the BM glassy alloy is 16 K and 18 K lower than that of the MS glass, respectively. This is again likely caused by the minor difference of the composition in the glassy phases formed in the different ways.

The XRD patterns in Fig. 7 display the structural changes associated with the exothermic events in the DSC traces for the two BM alloys. The samples were continuously heated to several temperatures in the DSC, as marked by dots in the curves, then cooled at 320 K/min to room temperature for XRD measurements. For the Ti$_{50}$Cu$_{35}$Ni$_{12}$Sn$_3$ alloy, the XRD patterns show that the amorphous phase transformed into the H$_{9253}$-CuTi phase after the first step of crystallization, followed by the precipitation of Ti$_3$Sn phase corresponding to the second exothermic event. In the case of Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ alloy, the pattern shows that the amorphous phase transformed into the cubic NiTi-type phase and an unidentified phase through one step.

Isothermal DSC traces for the two BM glassy alloys are shown in Fig. 8. The holding temperatures were below the $T_x$ obtained by continuous heating for each alloy. Two detectable exothermic reactions were observed in the trace of the Ti$_{50}$Cu$_{35}$Ni$_{12}$Sn$_3$ alloy. For the Ti$_{50}$Cu$_{35}$Ni$_{12}$Sn$_3$ alloy, only a distinct exothermic signal was displayed. The form of these heat flow signals is of the typical shape for a nucleation and growth process [22]. It further supports the conclusion from the XRD or SAED patterns that the amorphous phase rather than nanocrystalline, which displays monotonically decaying heat flow signals, truly formed in the two BM Ti-based multicomponent alloys.

4. Discussion

As is well known, the mechanical alloying (or mechanical milling) technique has been widely used as a unique means for producing a wide variety of far-from-equilibrium materials [23–26]. Although the mechanical attrition is a complex dynamic process, the shear deformation caused by the ball–powder–ball collision was taken account as the central event. Several modeling, covering the mechanistic, atomistic, thermodynamic and kinetic aspects, has been proposed for the mechanism explanation [27]. Regarding the milling-induced amorphization in the multicomponent alloy systems, the operative mechanism has been discussed in Ref. [28]. We believe that the chemical disordering of the system, induced by shear deformation [29,30], is likely to be responsible for the crystal-to-glass transition in the multicomponent alloy system.

In the present work, the pre-alloyed fragments rather than the mixture of element powders were used as the starting materials. It significantly reduced the contents of gaseous impurities such as oxygen and nitrogen in the initial state since the element Ti is the absorber of these gaseous elements. In such a case where several crystalline phases were included, the milling-induced full amorphization occurs concurrently with complete chemical mixing. It is noticed that the initial crystalline phases in the two starting alloys for BM is slightly different. For the Ti$_{50}$Cu$_{35}$Ni$_{12}$Sn$_3$ alloy, the initial state of the alloy is a mixture of $\alpha$-Ti phase and several intermetallic phases including Ti$_3$Sn, $\gamma$-CuTi and NiTi. In contrast, only three intermetallic phases of NiTi, Ti$_2$Cu and Ti$_3$Sn exist in the Ti$_{50}$Cu$_{18}$Ni$_{22}$Al$_4$Sn$_6$ alloy. It has been revealed in binary alloy systems that the BM-induced amorphization can
be achieved in the alloys with intermetallic compound composition of NiTi [31,32], CuTi [33], Ti$_5$Cu$_{33}$ and Ti$_5$Sn [34]. In other words, the crystal-to-glass transition easily occurs in the system containing intermetallics instead of solid solution. Therefore, the milling-induced glass formation can be realized in the Ti$_5$(Cu$_{33}$)Al$_2$Sn$_6$ alloy without α-Ti solid solution, where all the crystalline phases in the starting material are easy to be vitrified under BM. The homogeneous amorphous phase with a nominal composition of the alloy formed in the final BM product. In contrast, due to the presence of α-Ti solid solution in the initial state, the milling-induced amorphization is incomplete in the Ti$_5$(Cu$_{33}$)Al$_2$Sn$_6$ alloy. It indicates that the nominal composition of this alloy is somewhat beyond the glass-forming range under the current milling condition.

In addition, it should be mentioned that the amount of residual Ti-rich particles in the BM Ti$_{50}$Cu$_{35}$Ni$_{12}$Sn$_3$ sample is significantly less than in the BM Ti$_{50}$Cu$_{35}$Ni$_{12}$Sn$_3$ milling condition. The milling-induced amorphization is incomplete in the BM Ti$_{50}$Cu$_{35}$Ni$_{12}$Sn$_3$ alloy. This indicates that the nominal composition of this alloy is somewhat beyond the glass-forming range under the current milling condition.

Finally, the BM and MS samples for both alloys display similar structural feature from XRD results and thermal properties associated with the glass transition and crystallization. It implies that the amorphous states obtained by two different methods are essentially identical, no matter what their method of preparation. Similar findings were observed also in the BM Zr–Al–Ni–Cu–Co [35] and Ti–Zr–Hf–Ni–Cu–Ag–Al [28] multicomponent alloy systems with an intermetallic phase mixture as starting materials.

### 5. Summary

Using pre-alloyed fragments as starting materials, mechanical milling results in the amorphization in the two Sn-containing Ti-based multicomponent alloys, Ti$_5$(Cu$_{33}$)Ni$_{12}$Sn$_3$ and Ti$_5$(Cu$_{33}$)Al$_2$Sn$_6$. In the ball-milled Ti$_5$(Cu$_{33}$)Ni$_{12}$Sn$_3$ alloy, the glass formation is predominant but a small fraction of unreacted nanocrystals still remains. In contrast, nearly complete amorphization is achievable in the ball-milled Ti$_5$(Cu$_{33}$)Al$_2$Sn$_6$ alloy. The amorphization extent in the final milled products is associated with whether the α-Ti phase exists in the initial microstructure of the alloys. In both cases, the crystallization behavior and thermal properties of the ball-milled glassy alloys are comparable to those of the melt-spun glasses. The two ball-milled Ti-based glassy alloys exhibit a distinct glass transition and a wide supercooled liquid region of about 60 K. Compared with the Ti-based alloys containing Si and B metalloid elements, the glass formation by mechanical milling is easily achieved in the Sn-containing Ti-based multicomponent alloy systems.

### Acknowledgement

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China under contract nos. 50371084 and 50323009.

### References