Revisiting the glass-forming ability of Ti–Ni–Si ternary alloys

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ABSTRACT

The compositional dependence of glass-forming ability (GFA) was investigated for the Ti–Ni–Si ternary alloys. Glassy ribbons varied with different thicknesses were fabricated via single-roller melt spinning. The optimized glass-forming composition was located at Ti57Ni35Si8, with a critical thickness of about 200 μm for complete glass formation. By characterizing the microstructure of arc-melted ingots of the Ti–Ni–Si ternary alloys, we demonstrate that the glass formation of the Ti57Ni35Si8 alloy correlates with the (L → Ti2Ni+TiNi+Ti5Si3) ternary eutectic reaction. In addition, the eutectic composition of the (L → Ti2Ni+TiNi+Ti5Si3) ternary and (L → TiNi+Ti5Si3) pseudo-binary eutectic reaction was determined to be in the vicinity of Ti63Ni31Si6 and Ti53Ni37Si10, with the invariant reaction temperature at 1243 and 1424 K, respectively.

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1. Introduction

Over the past decade, numerous new alloys with the capability to form centimeter-scale bulk metallic glasses (BMGs) were discovered, not only in multi-component alloy systems but also in simple ternary alloys [1–8]. The latter are the compositional basis for further development of high-order alloys with a higher glass-forming ability (GFA). However, few Ti-based ternary alloys without toxic element such as Be were found to exhibit a sufficiently high GFA to obtain BMGs [9–17]. Among the BMG family, Ti-based BMGs are of particular technological interest as potential new engineering materials, due to their high specific strength, appreciable plasticity, superior corrosion resistance and relatively low cost.

As shown in the earlier work [18], metallic glasses can be obtained in the Ti–Ni–Si ternary system using rapidly solidification technique, within a composition region of 40–80 at.% Ti, and 0–20 at.% Si. In that study, with a composition interval of 5 at.%, it was suggested that the Ti60Ni30Si10 alloy (defined as Polk's alloy hereafter) has optimal GFA in the system. In addition, it was claimed that the glass transition temperature (Tg) of this Ti-based glass is detectable, Tg = 775 K.

On the other hand, it has been well documented that the alloy system with “deep eutectic” feature favors glass formation. Unfortunately, the liquidus projection of the Ti–Ni–Si ternary phase diagram has not been established [19]. Therefore, the correlation between glass transition and eutectic reaction that the liquid undergoes upon cooling was not addressed for this system. Furthermore, it was demonstrated recently [4,7,20] that, even in a simple alloy system, the GFA of the alloys is strongly composition-dependent. Then, to capture the optimal glass-forming composition in the system, a smaller composition interval such as 1 at.% is necessary. This approach is referred to as “composition pinpointing”. In this regard, it is of interest to uncover the full potential of the GFA for the Ti–Ni–Si ternary alloys by revisiting the compositional dependence of the GFA via composition pinpointing.

In the present work, starting from the Polk's alloy (Ti60Ni30Si10), the compositional dependence of glass formation for the melt-spun alloys was investigated within a region bound by three intermetallic phases, TiNi, Ti2Ni and Ti5Si3, in the Ti–Ni–Si ternary system. Critical thickness of complete glass formation for melt-spun ribbons was determined for a group of alloys in the proximity of Ti60Ni30Si10. Furthermore, correlation between optimized glass-forming composition and eutectic reaction that the liquid undergoes upon cooling was addressed by monitoring the microstructure of arc-melted alloys. The topological and chemical effects of the alloys on the GFA in this ternary system are also discussed.

2. Experimental

Elemental pieces with purity better than 99.9 wt.% were used as starting materials. Master alloy ingots of 20 g in weight with nominal composition (in atomic percentage) were prepared by arc melting under a Ti-gettered argon atmosphere...
in a water-cooled copper crucible. The alloy ingots were melted several times to ensure composition homogeneity. Ribbon samples were fabricated in an Ar atmosphere through induction melting the master alloy in a quartz tube and ejecting it onto a single-roller using a melt-spinner. Surface speed of the copper roller varies from 5 to 39 m/s. The as-quenched ribbons were approximately 3–5 mm wide and 30–200 μm thick. In addition, wedge-shaped samples were prepared using copper mold casting to determine the critical size of glass formation for the selected alloy.

Amorphous nature of the melt-spun ribbons were analyzed by X-ray diffraction (XRD) using a Rigaku D/max 2400 diffractometer with monochromatic Cu Kα radiation (λ = 0.1542 nm), taken from air-side surface of the ribbons. The arc-melted ingots were sectioned transversely and polished for scanning electron microscopy (SEM) observation and XRD analysis. SEM observation of the samples was carried out in Cambridge 5360 scanning electron microscope. The local compositions were determined using an energy dispersive X-ray (EDX) spectrometer attached to the SEM.

The glass transition and crystallization behavior of the glassy ribbons were investigated in a PerkinElmer (DSC-diamond) differential scanning calorimeter (DSC) with alumina container under flowing purified Ar at a heating rate of 40 K/min. A second run under identical conditions was used to determine the baseline after each run. To confirm the reproducibility of experimental results, at least three samples have been measured for each composition. All the measurements of the onset temperature of crystallization (Tc) were reproducible within the error of ±1 K. The heat of crystallization ΔHc for the glassy phase was determined by integrating the area under the DSC curve. Melting behavior of the alloys was measured in a Netzsch 404 DSC with alumina container, using a heating rate of 20 K/min.

3. Results

3.1. Compositional dependence of glass-forming ability

Fig. 1 displays the composition diagram of Ti–Ni–Si ternary alloys at Ti-rich corner. The Polk’s alloy (Ti60Ni30Si10) is marked
by a diamond. In terms of phase diagram of Ti–Ni–Si ternary [19], we have drawn schematic tie-lines between Ti$_5$Si$_3$ (Mn$_5$Si$_3$ prototype, $P_6_3/mcm$) and Ti$_2$Ni (big cube structure) or TiNi (B2 structure) [21] phases in the diagram. It suggests that a eutectic reaction of (L → Ti$_5$Si$_3$ + TiNi + Ti$_2$Ni) is likely to be present and involved in the competition with glass formation during undercooling of the melt. Additionally, the currently investigated alloys are situated in a region marked by a smaller triangle, as seen in Fig. 1.

Fig. 2(a)–(c) show the composition maps of glass formation for the melt-spun Ti–Ni–Si ternary alloys fabricated using the wheel speeds (WS) of 39, 20 and 10 m/s, respectively. For the ribbons prepared at WS = 39 m/s, thickness of the samples varies in the range of 37–64 μm. In this case, fully amorphous ribbons can be obtained at 11 compositions around Polk’s alloy [marked as an arrow in Fig. 2(a)], and partially amorphous samples are obtained in the remaining compositions, among the investigated 13 compositions within a region of 56–60 at.% Ti, 30–38 at.% Ni and 4–10 at.% Si, as seen in Fig. 2(a). It is noticed that the Polk’s composition cannot be fabricated into fully glassy samples under our processing conditions. For the complete glass formation, the Si content in the alloy should not exceeds 8 at.%.

As the representative, Fig. 3(a) and (b) show XRD patterns of melt-spun ribbons fabricated under WS = 39 m/s for the Ti$_{60}$Ni$_{40}$–$x$Si$_x$ and Ti$_{58}$Ni$_{42}$–$x$Si$_x$ ($x = 4, 6, 8, 10$) two series alloys [as marked as a lines I and II in Fig. 2(a)], respectively. As seen in Fig. 3(a) and (b), a single amorphous phase formed for the alloys of $4 \leq x \leq 8$, indicated by a broad diffusive diffraction maximum at $2\theta = 35–50^\circ$. For the Ti$_{60}$Ni$_{50}$Si$_{10}$ alloy, diffraction peaks from crystalline phases TiNi, Ti$_2$Ni and Ti$_5$Si$_3$ superimpose on the halo of amorphous phase. In the case of Ti$_{58}$Ni$_{42}$Si$_{10}$, only crystalline phase Ti$_5$Si$_3$ is detectable [see Fig. 3(b)], indicating that the primary crystallization of Ti$_5$Si$_3$ phase competes with glass formation for the two alloys with a high Si content.

Fig. 4(a) and (b) displays the corresponding DSC traces of these melt-spun alloys. In these scans, at least two exothermic events caused by crystallization of the amorphous phase are present. No significant endothermic signal associated with the glass transition was detected prior to crystallization. It indicates that these alloys do not exhibit a detectable supercooled liquid region, unlike most of the BMG-forming alloys. Thermal properties measured from DSC traces for these metallic glasses are listed in Table 1, including the onset temperature of crystallization for the two main steps ($T_{x1}$ and $T_{x2}$) and total heat release of the crystallization ($\Delta H_x$). The crystallization temperatures shift to a higher temperature with increasing Si content in the alloys, which is consistent with the findings in previous work [18]. Based on the XRD patterns and heat release of
crystallization, volume fraction of the amorphous phase in the as-spun Ti56Ni37Si7 and Ti57Ni36Si7 alloys is estimated to be near 90 vol.%, thus the critical thickness for complete glass formation is less than ~50 μm.

Reducing the wheel speed down to 20 and 10 m/s, the ribbon thickness increased up to 60–80 and 120–150 μm, respectively. In the case of WS = 20 m/s, fully amorphous ribbons can be obtained at six compositions, as seen in Fig. 2(b). The XRD patterns and DSC traces for these melt-spun alloys are not shown here. For the ribbons fabricated with the WS of 10 m/s, fully amorphous ribbons are achieved only at three compositions (Ti56Ni37Si7, Ti57Ni36Si7 and Ti57Ni35Si8), and the remaining compositions are partially amorphous, as shown in Fig. 2(c).

Fig. 5(a) show XRD patterns of melt-spun ribbons fabricated under WS = 10 m/s for the Ti57Ni35Si8, Ti57Ni36Si7 and Ti56Ni37Si7 three alloys. Thickness of the ribbons increases up to 200–250 μm. In terms of the results from the XRD and DSC, Ti57Ni35Si8 alloy has the largest fraction of amorphous phase among these three alloys. Fig. 6(a) and (b) display the XRD pattern and DSC scan for the melt-spun Ti57Ni35Si8 alloy at WS = 5 m/s, respectively, as the representative, indicating partial glass formation with a small amount of residual crystalline phase. Fig. 6(c) shows a SEM image of the longitudinal cross-sectional surface of the ribbon. Crystals formed near the air-side surface in the sample can be observed. Thus, the critical thickness of glass formation is estimated to be around 200 μm. To examine the feasibility to form BMGs, Ti57Ni35Si8 alloy was cast into a wedge-shaped sample using copper mold injection casting [22–26]. Fig. 6(d) shows an optical micrograph of longitudinal cross-sectional surface of the as-cast wedge samples for the Ti57Ni35Si8 alloy. As seen in Fig. 6(d), the critical thickness for glass formation reaches ~700 μm.

### 3.2. Eutectic reaction related to glass formation

Fig. 7(a) and (b) show the DSC curve near and above melting temperatures during heating and XRD pattern taken from the cross-section for the Ti57Ni35Si8 arc-melted ingot, respectively. As seen in Fig. 7(a), three endothermic events are involved during the melting process for this alloy, indicating that the best glass-forming composition is off-eutectic. The onset temperature (defined as Tm) and end temperatures (defined as Tw) of the melting for this alloy is determined to be about 1233 and 1459 K, respectively, as marked by arrows in Fig. 7(a). It is noticed that the Tm of Ti57Ni35Si8 alloy is about 24 K lower than invariant temperature (about 1257 K) of binary peritectic reaction of (L + TiNi → Ti2Ni) [21]. It implies that the liquid of Si-containing ternary alloy is more thermodynamically stable than the Ti–Ni binary alloys, favoring glass formation. As shown in Fig. 7(b), only three crystalline phases, Ti5Si3 (α = 0.7444 nm, c = 0.5143 nm), TiNi (α = 0.2972 nm) and Ti2Ni (α = 1.27 nm), are identified in the XRD pattern of the arc-melted Ti57Ni35Si8 alloy. It further confirms that the compositions we have studied indeed reside in the region enclosed by three compounds, TiNi, Ti5Si3 and Ti2Ni, as indicated in Fig. 1.

Empirically, the cooling rate for the arc-melted ingot for binary Ti alloys can be estimated to be at the order of magnitude of ~10 K/s [27]. As a result, the solidified microstructure formed under such non-equilibrium condition can be used as an indicator to monitor the crystallization events competing with the glass formation during cooling of the melt. Fig. 8(a) and (b) show the backscattered SEM (BSEM) images of the arc-melted Ti57Ni35Si8 alloy. The lateral surface of the ingots was polished for SEM observation, under which it was shown that the microstructure is uniform throughout the sample from top to bottom. Fig. 8(a) shows a high-magnification BSEM image for the boxed region in Fig. 8(a). Chemical compositions measured with the EDX analysis for the

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**Table 2**

Thermal properties (determined using DSC at a heating rate of 40 K/min) of melt-spun alloys prepared using a wheel speed of 10 m/s.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Ribbon thickness (μm)</th>
<th>T1 (K)</th>
<th>T2 (K)</th>
<th>ΔHx (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti57Ni35Si8</td>
<td>133 ± 9</td>
<td>805</td>
<td>870</td>
<td>4.6 ± 0.5</td>
</tr>
<tr>
<td>Ti56Ni36Si7</td>
<td>140 ± 5</td>
<td>793</td>
<td>878</td>
<td>3.1 ± 0.4</td>
</tr>
<tr>
<td>Ti57Ni37Si8</td>
<td>121 ± 10</td>
<td>805</td>
<td>879</td>
<td>3.0 ± 0.4</td>
</tr>
</tbody>
</table>

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**Table 3**

Composition measured with EDX analysis for Ti57Ni35Si8 alloy.

<table>
<thead>
<tr>
<th>Area</th>
<th>Ti (at.%)</th>
<th>Ni (at.%)</th>
<th>Si (at.%)</th>
<th>Normalized phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>51 ± 1</td>
<td>48 ± 1</td>
<td>1.0 ± 0.5</td>
<td>TiNi</td>
</tr>
<tr>
<td>B</td>
<td>63 ± 1</td>
<td>4 ± 1</td>
<td>33 ± 1</td>
<td>Ti5Si3</td>
</tr>
<tr>
<td>C</td>
<td>67 ± 1</td>
<td>31 ± 1</td>
<td>2.0 ± 0.5</td>
<td>Ti2Ni</td>
</tr>
</tbody>
</table>
areas marked as A–C in Fig. 8(b) are determined, as tabulated in Table 3. Then, the dendrite-like phase with a lighter contrast (A), darker phase (B) and dendrite-like phase with a gray contrast (C) can be identified as the TiNi, Ti₅Si₃ and Ti₂Ni phases, respectively. This identification is consistent with the XRD analysis for the alloy [see Fig. 7(b)]. As shown in Fig. 8(b), the TiNi (A) and Ti₅Si₃ (B) two phases solidified as the coupled-growth colony (A+B), showing typical eutectic features. The volume fraction of such eutectic colonies is estimated to be 60–70%. In the inter-colony regions, Ti₂Ni phase (C) formed together with a small fraction of other phases which is unidentified within BSEM resolution. Moreover, it was shown that a small amount of Si, around 1.5 at.%, can dissolve in both binary compounds, TiNi and Ti₂Ni. These findings demonstrate that solidification of the alloy melt at least undergoes the pseudo-binary eutectic reaction of (L → Ti₅Si₃ + TiNi).

To investigate whether the (L → Ti₅Si₃ + TiNi + Ti₂Ti) eutectic reaction is present within the investigated composition region, microstructures of a series of arc-melted Ti–Ni–Si ternary alloys were examined. In terms of the phase selection for these alloys, the alloys are classified into three groups. Their composition regions are drawn in Fig. 9 and symbolized as zones I, II and III, respectively. The microstructures of the alloys within zone II are quite similar to the case of Ti₅₇Ni₃₅Si₈ alloy, as seen in Fig. 8.

Fig. 10(a) and (b) illustrate the BSEM images of the arc-melted Ti₅₆Ni₃₄Si₁₀ and Ti₅₈Ni₃₃Si₁₄ alloys, as the representative of zones I and III, respectively. These alloys are marked using an up-side-down triangle and a square in Fig. 9, respectively. Crystalline phases presented as different contrast are identified in terms of the chemical compositions from EDX analysis. For the Ti₅₆Ni₃₄Si₁₀ alloy, it was found that the Ti₅Si₁₃ phase solidified as the primary phase, as seen in Fig. 10(a). Similar to the Ti₅₇Ni₃₅Si₈ in Fig. 8, the eutectic colonies consisting of the TiNi and Ti₅Si₃ together with a small fraction of Ti₂Ni phase are observed as well. In the case of Ti₅₆Ni₃₃Si₁₄ alloy, as shown in Fig. 10(b), besides the TiNi phase as the primary phase and the eutectic colonies composed of the coupled TiNi and Ti₅Si₃, three-phase eutectic colonies composed of co-existing TiNi, Ti₅Si₃ and Ti₂Ni are observed, as marked by a circle in Fig. 10(b).

Based on the chemical compositions from the EDX analysis, the eutectic composition of the (L → Ti₅Si₃ + TiNi) pseudo-binary eutectic and (L → Ti₅Si₃ + TiNi + Ti₂Ni) ternary eutectic can be estimated to be Ti₅₃Ni₃₇Si₁₀ and Ti₆₃Ni₃₁Si₆, respectively. They are marked as the e and E point, respectively, in Fig. 9. It is of interest to note that the optimized glass-forming composition, Ti₅₇Ni₃₅Si₈, is located on the tie-line between e and E, and away from the E.

Fig. 10(c) and (d) display the BSEM images of the arc-melted Ti₅₆Ni₃₃Si₁₀ (e) and Ti₆₃Ni₃₁Si₆ (E) alloys, respectively. As shown in Fig. 9(c), the arc-melted Ti₅₃Ni₃₇Si₁₀ alloy exhibits a typical eutectic feature consisting of coupled Ti₅Si₃ and TiNi phases. It demonstrates that the Ti₅₃Ni₃₇Si₁₀ is near the composition of the (L → Ti₅Si₃ + TiNi) eutectic. Similarly, extremely fine eutectic structure consisting of the three phases Ti₅Si₃, TiNi and Ti₂Ni is observed in the arc-melted Ti₆₃Ni₃₁Si₆ (E) alloy, as seen in Fig. 10(d). It indicates that this composition is quite close to the ternary invariant eutectic point of the (L → Ti₅Si₃ + TiNi + Ti₂Ni).

Fig. 11 displays the corresponding DSC scans near and above the melting temperatures during heating for the arc-melted Ti₅₃Ni₃₇Si₁₀ (e) and Ti₆₃Ni₃₁Si₆ (E) alloys. The Ti₅₂Ni₃₈Si₁₀ (e) exhibits nearly a single melting event, indicating that the alloy is...
Fig. 7. (a) DSC scan near and above melting temperatures during heating (at a heating rate of 20 K/min) and (b) XRD pattern taken from the cross-sectional surface for the Ti$_{57}$Ni$_{35}$Si$_8$ arc-melted ingots.

Fig. 8. Backscattered SEM images taken from the cross-sectional surfaces of Ti$_{57}$Ni$_{35}$Si$_8$ arc-melted ingots. (b) High-magnification image of the boxed area in (a).

Fig. 9. Composition diagram of the arc-melted Ti–Ni–Si ternary alloys with different solidification features (see text). $e$ and $E$ represent the nominal eutectic composition for the ($L\rightarrow Ti_5Si_3 + TiNi$) and ($L\rightarrow Ti_5Si_3 + TiNi + Ti_2Ni$) reaction, respectively.

Fig. 9. Composition diagram of the arc-melted Ti–Ni–Si ternary alloys with different solidification features (see text). $e$ and $E$ represent the nominal eutectic composition for the ($L\rightarrow Ti_5Si_3 + TiNi$) and ($L\rightarrow Ti_5Si_3 + TiNi + Ti_2Ni$) reaction, respectively.

4. Discussion

As indicated by the current work, variation of the Ti and Ni contents in the Ti–Ni–Si ternary system has an effect on the GFA, significantly stronger than that of the Si content. Apparently the chemical interaction between the constituent elements plays a role in the changes in the GFA. In Ti–Ni–Si ternary system, the interaction between Si and Ti is obviously stronger with respect to the Ti–Ni pairs, as indicated by the more negative heat of mixing for Ti–Si ($\\Delta H_{\text{mix}} = -66 \text{ kJ/mol}$) than that for Ti–Ni ($\\Delta H_{\text{mix}} = -35 \text{ kJ/mol}$) [28]. Then, the Si content higher than 8 at.% favors the formation of the stable compound Ti$_5$Si$_3$ with a melting temperature of 2403 K [21] during the cooling of the melt.

Compared with the Ti–Ni binary alloys [29,30], the GFA of the Ti–Ni–Si ternary alloys is elevated but only marginally. A high cooling rate, such as that in melt spinning, remains necessary for the glass formation. The alloys do not have the BMG-forming capability, after a careful "composition pinpointing" search. It is quite similar to the case of the Ti–Ni–Al and Ti–Ni–Sn ternary alloys [31,32]. In these two systems, the best glass-forming composition was located at Ti$_{54}$Ni$_{32}$Al$_{14}$ and Ti$_{56}$Ni$_{38}$Sn$_6$, respectively, with the critical thickness of ~90 and ~100 μm, respectively [31,32]. Evidently, the GFA of the Ti–Ni–Si ternary is superior to either the Ti–Ni–Al or the Ti–Ni–Sn ternary.
Fig. 10. Backscattered SEM images taken from the cross-sectional surfaces of arc-melted ingots of several representative alloys. (a) Ti58Ni32Si10 (in zone I), (b) Ti58Ni38Si4 (in zone III), (c) Ti52Ni38Si10 (E) and (d) Ti63Ni31Si6 (E).

Fig. 11. DSC scans near and above melting temperatures during heating (at a heating rate of 20 K/min) for the arc-melted alloys of Ti52Ni38Si10 (E) and Ti63Ni31Si6 (E).

5. Conclusions

(1) Within the composition region bordered by three compounds, TiNi, Ti2Ni and Ti5Si3, in the Ti–Ni–Si ternary system, the optimized glass-forming composition is located at Ti57Ni35Si8. For this alloy, critical thickness of complete glass formation for the melt-spun ribbon is around 200 μm. For the wedge-shaped casting sample, critical thickness to form a single glassy phase can reach ~700 μm. The glass-forming ability of the Ti57Ni35Si8 is significantly stronger than that of the Ti60Ni30Si10 found in a previous study without the “compositional pinpointing” search.

(2) The optimized glass-forming composition, Ti57Ni35Si8, is near but off the ternary eutectic reaction of (L → TiNi + Ti2Ni + Ti5Si3). The eutectic composition of the (L → Ti2Ni + TiNi + Ti5Si3) ternary eutectic and (L → TiNi + Ti5Si3) pseudo-binary eutectic reaction was determined to be around Ti60Ni30Si10 and Ti53Ni31Si8, respectively, with their respective invariant reaction temperature at 1243 and 1424 K, respectively.

(3) Compared with the Ti–Ni–Al and Ti–Ni–Sn ternary alloys [31,32], the Ti–Ni–Si ternary alloy exhibits a higher glass-forming ability, which is however inferior to that of the Ti–Cu–Ni ternary [33] and insufficient to form bulk metallic glasses. Our work uncovers the full potential of the glass-forming ability in this system via the systematic examination of the compositional dependence.

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