Annealing effects on the crystallization and shape memory effect of Ti\textsubscript{50}Ni\textsubscript{25}Cu\textsubscript{25} melt-spun ribbons

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Abstract

As-spun Ti\textsubscript{50}Ni\textsubscript{25}Cu\textsubscript{25} ribbon is fully amorphous with a lower wavenumber $Q_p$ than the amorphous Ti--Ni alloys owing to its high Cu content. Both crystallization activation energy $E_a$ and onset temperature $T_x$ for Ti\textsubscript{50}Ni\textsubscript{25}Cu\textsubscript{25} ribbon are lower than those for Ti\textsubscript{50}Ni\textsubscript{50} ribbon, indicating that the former has lower thermal stability. When Ti\textsubscript{50}Ni\textsubscript{25}Cu\textsubscript{25} ribbon is annealed at 300 °C for 3 min, the initial as-crystallized grains contain a low Cu content and perform a prominent shape memory effect. Through prolonging the annealing time, more grains are crystallized in the ribbon but it becomes more fragile and its recoverable strain decreases. This is due to the increasing Cu content in the crystallized grains. Crystallized Ti\textsubscript{50}Ni\textsubscript{25}Cu\textsubscript{25} ribbon can exhibit a good shape memory effect only under appropriate annealing conditions.

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1. Introduction

TiNi-based alloys are known as the most important shape memory alloys (SMAs) with good shape memory effect (SME), superelasticity (PE) and damping capacity (DC) [1]. Substituting Cu for Ni in binary Ti--Ni SMA has been known to lower the transformation hysteresis, the superelasticity hysteresis, and the flow stress level in the martensite state. The narrow hysteresis of Ti--Ni--Cu ternary SMAs has the potential for applications which require short response times during thermal cycling [2]. Adding Cu into Ti--Ni binary SMAs also has been reported to reduce the sensitivity of the martensitic transformation start temperature, Ms, to compositional changes and to prevent Ti\textsubscript{3}Ni\textsubscript{4} precipitation [2--4]. Moreover, the transformation sequence in Ti--Ni--Cu SMAs depends on the Cu content. For Cu contents below 10 at.%, the monoclinic B19$'$ martensite is formed on cooling from the cubic B2 austenite. When the Cu content is approximately in between 10 and 15 at.%, the two-stage transformation behavior of B2 $\leftrightarrow$ B19 $\leftrightarrow$ B19$'$ is obtained where B19 is an orthorhombic martensite [5]. In the case of a higher Cu content, the second step is inhibited and only B2 $\leftrightarrow$ B19 appears [2,6]. Unfortunately, it was found that Cu additions exceeding 10 at.% embrittle the alloy and seriously reduce the workability and shape recovery strain [2,7]. This restrains the application of high Cu content Ti--Ni--Cu SMAs.

In recent years, melt-spinning techniques have been utilized to fabricate high Cu content Ti--Ni--Cu ternary SMAs in order to avoid the aforementioned restriction of workability. Ti\textsubscript{50}Ni\textsubscript{25}Cu\textsubscript{25} (at.%) ribbon has been widely studied because of its small transformation hysteresis, large transformation strain, and one-stage B2 $\leftrightarrow$ B19 transformation compared to conventionally fabricated Ti--Ni--Cu wire [8]. Fabrication of Ti--Ni--Cu ternary SMA ribbons by means of the melt-spinning technique has been shown to be suitable for producing alloys with controllable amorphous or crystalline structures. Nevertheless, the as-spun Ti--Ni--Cu ribbon is amorphous and shows no SME if the ribbon is fabricated using a high cooling rate in

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the melt-spinning procedure. Therefore, a proper thermal annealing procedure is required to crystallize the as-spun amorphous ribbon. Previous studies on Ti50Ni25Cu25 ribbon focused on the microstructure of the partially or fully crystallized alloys, the precipitates generated after thermal treatment, and their effects on the martensitic transformation [8–13]. However, only little works referred to the effect of annealing on the SME and on the mechanical properties of the crystallized Ti50Ni25Cu25 ribbon [14,15]. Liu [14] stated that a Ti50Ni25Cu25 melt-spun ribbon annealed at 500 °C for 15 min exhibits a well-defined SME and a good superelastic shape recovery strain with low hysteresis. No other annealing condition was presented because the ribbon annealed at a temperature higher than 500 °C shows poorer mechanical properties. Cheng and Xie [15] reported the influence of the annealing temperature on the shape memory properties of a Ti50Ni25Cu25 ingot was cut into an appropriate size and then induction-melted in an argon atmosphere in a quartz crucible and arc remelting (VAR). The ingot was re-melted six times in an argon atmosphere for homogenization. The as-melted Ti50Ni25Cu25 ribbon was set as 10 mm and the heating and cooling rates were 3 °C/min. Microstructure observations and composition analysis for the ribbons annealed at 500 °C for different time intervals were performed with a Philips XL 30 SEM instrument equipped with an EDS unit.

3. Experimental results

3.1. Crystallization of Ti50Ni25Cu25 melt-spun amorphous ribbon

Fig. 1 displays the XRD diffraction pattern of as-spun Ti50Ni25Cu25 ribbon. As illustrated in Fig. 1, only a broad amorphous peak appears near 2θ = 41.8°. It reveals that the as-spun Ti50Ni25Cu25 ribbon is completely amorphous. The position of this broad amorphous peak can be represented by the wavenumber Qa = 4πsin θ/λ, which is inversely proportional to the mean nearest-neighbor distance of the local ordering clusters of amorphous alloys [16]. The Qa value calculated from Fig. 1 is plotted in Fig. 2 and is compared with the results from the rapid quenching melt-spun Ti–Ni and Ti–Ni–Cu SMA ribbons [17], mechanical alloyed powders [16] and sputtered thin films [18,19].

Fig. 3 displays the DSC curves for Ti50Ni25Cu25 melt-spun ribbons with different heating rates to determine the crystallization activation energy. The peak temperature, Tp, and the onset temperature, Ts, of crystallization are also denoted in Fig. 3. There is only one-stage of crystallization obtained in Ti50Ni25Cu25 melt-spun amorphous ribbon. The two-stage crystallization behavior of rapid quenched Ti50Ni30 and Ti60Ni40 ribbons [20] is not observed. As clearly shown in Fig. 3, the crystallization temperatures, Tp and Ts, rise with increasing heating rate. According to the results obtained in Fig. 3, the crystallization activation energy, Eα, can be determined from Kissinger’s relation [21]:

\[ E_\alpha = -\frac{Q_a}{\ln\left(\frac{T_p}{T_s}\right)} \]

Fig. 1. XRD pattern for the as-spun Ti50Ni25Cu25 amorphous ribbon.
mention activation energy for Ti50Ni25Cu25 ribbon is calculated as 341 kJ/mol. As shown in Fig. 3, $E_a = 341$ kJ/mol. As shown in Fig. 3, $E_a = 341$ kJ/mol. When the ribbon is annealed at 500 °C for 90 s, a small (200)$_{B2}$ peak appears at around $2\theta = 61^\circ$. After annealing at 500 °C for 100 s, the intensity of the (200)$_{B2}$ peak increases. When the ribbon is annealed for 110 s, besides the (200)$_{B2}$ peak, the other two peaks (110)$_{B2}$ and (211)$_{B2}$ develop at $2\theta = 42^\circ$ and 76°, respectively. When the annealing time is extended to 3 min, the (110)$_{B2}$ peak becomes dominant and has a greater intensity than the others. After annealing for 60 min, the diffraction pattern is similar to that of the ribbon annealed at 500 °C for 3 min. However, now an extra peak (002)$_{B19}$ of B19 martensite appears at $2\theta = 41^\circ$ because a partial B2 $\rightarrow$ B19 transformation occurs at room temperature. Fig. 6(b) plots the evolution of the lattice parameter of B2 parent phase as calculated from the XRD results of (200)$_{B2}$ and (110)$_{B2}$ shown in Fig. 6(a). As indicated in Fig. 6(b), the lattice parameter of the B2

$$\ln\left(\frac{\alpha}{T_p}\right) = C - \frac{E_a}{RT_p} \quad (1)$$

where $C$ is a constant, $\alpha$ is the heating rate, $E_a$ is the crystallization activation energy, and $R$ is the gas constant. Fig. 4 plots $\ln\left(\frac{\alpha}{T_p}\right)$ versus $1/T_p$ based on the DSC results shown in Fig. 3 for Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon. The crystallization activation energy for Ti$_{50}$Ni$_{25}$Cu$_{25}$ ribbon is calculated as 341 kJ/mol. As shown in Fig. 3, $T_x$ for Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon with the cooling rate of 30 °C/min is detected at 477 °C. This crystallization temperature, $T_x$, is plotted versus the Ti content of the Ti$_x$Ni$_{1-x}$ alloys in Fig. 5 with the results obtained from other studies [16–19].

### 3.2. Annealing effect in Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon

#### 3.2.1. XRD measurements

Fig. 6(a) shows XRD results of Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon annealed at 500 °C for different time intervals. As indicated in Fig. 6(a), the as-spun ribbon and the ribbon annealed at 500 °C for 60 s are completely amorphous. When the ribbon is annealed at 500 °C for 90 s, a small (200)$_{B2}$ peak appears at around $2\theta = 61^\circ$. After annealing at 500 °C for 100 s, the intensity of the (200)$_{B2}$ peak increases. When the ribbon is annealed for 110 s, besides the (200)$_{B2}$ peak, the other two peaks (110)$_{B2}$ and (211)$_{B2}$ develop at $2\theta = 42^\circ$ and 76°, respectively. When the annealing time is extended to 3 min, the (110)$_{B2}$ peak becomes dominant and has a greater intensity than the others. After annealing for 60 min, the diffraction pattern is similar to that of the ribbon annealed at 500 °C for 3 min. However, now an extra peak (002)$_{B19}$ of B19 martensite appears at $2\theta = 41^\circ$ because a partial B2 $\rightarrow$ B19 transformation occurs at room temperature. Fig. 6(b) plots the evolution of the lattice parameter of B2 parent phase as calculated from the XRD results of (200)$_{B2}$ and (110)$_{B2}$ shown in Fig. 6(a). As indicated in Fig. 6(b), the lattice parameter of the B2

![Fig. 3. DSC curves with different heating rates for Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon.](image)

![Fig. 4. Kissinger’s plots for the data obtained from DSC curves in Fig. 3.](image)

![Fig. 5. Crystallization temperature, $T_x$, of Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon versus Ti content in comparison with the results of rapid quenched samples [17], mechanically alloyed powders [16] and sputtered films [18,19].](image)
phase of Ti$_{50}$Ni$_{25}$Cu$_{25}$ ribbon gradually decreases from 0.305 nm to about 0.304 nm with an increased annealing time.

3.2.2. DSC results

Fig. 7 shows the DSC results of Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon annealed at 500 °C from 3 min to 3 h. The measured DSC cooling and heating curves for each specimen are approximately the same, and thus only the cooling curves are discussed. As shown in Fig. 7, the specimen for each annealing time exhibits a single-stage B$_2$ → B$_{19}$ transformation in cooling. The Ms temperatures of B$_2$ → B$_{19}$ martensitic transformation and their transformation enthalpies $\Delta H$ shown in Fig. 7 are plotted in Fig. 8(a) and (b), respectively. Upon increasing the annealing time, as illustrated in Figs. 7 and 8, the transformation temperatures of the crystallized Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon drastically shift to a higher temperatures and the corresponding $\Delta H$ value gradually increases with the prolonged annealing time. The $\Delta H$ value

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Fig. 6. (a) XRD patterns for Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon annealed at 500 °C for different time intervals, and (b) change of the lattice parameter calculated form (200)$_{B2}$ and (110)$_{B2}$ shown in (a) as a function of the annealing time.

Fig. 7. DSC curves for Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon annealed at 500 °C for different time intervals.

Fig. 8. Change of (a) the Ms transformation temperature and (b) the transformation enthalpy as a function of the annealing time. The data are taken from DSC curves shown in Fig. 7.
3.2.3. Tensile test results

Fig. 9(a) shows the selected strain—temperature curves under a constant stress (90 MPa) for the Ti50Ni25Cu25 melt-spun ribbon annealed at 500 °C for different time intervals. In order to compare the shape recovery effect of each specimen, only a low stress (90 MPa) was applied to ensure that no residual deformation would be retained after the test. Fig. 9(b) plots the evolution of the measured recoverable strain from Fig. 9(a). As illustrated in Fig. 9(a) and (b), each Ti50Ni25Cu25 melt-spun ribbon exhibits a well-defined shape recovery effect when the specimen is annealed for more than 3 min. Among them, the specimen annealed at 500 °C for 3 min has the maximum recoverable strain of about 2%, as indicated by the double arrows in Fig. 9(a). When the annealing time is prolonged, however, the recoverable strain gradually decreases and the specimen becomes more brittle. When the Ti50Ni25Cu25 ribbon is annealed at 500 °C for 3 h, the specimen becomes very fragile and fractures during the tensile test.

4. Discussion

4.1. Amorphous characteristics of Ti50Ni25Cu25 melt-spun ribbon

As shown in Fig. 2, the \( Q_p \) values of sputtered Ti\(_{49.96}\)Ni\(_{40.09}\)Cu\(_{9.95} \) amorphous films are very close to the line fitted for those of melt-spun Ti\(_{50}\)Ni\(_{25}\)Cu\(_{25} \) amorphous ribbons and mechanically alloyed Ti\(_{50}\)Ni\(_{1-x}\) powders. However, the \( Q_p \) value of Ti50Ni25Cu25 melt-spun ribbons calculated in this study, and also that of sputtered Ti\(_{49.96}\)Ni\(_{40.09}\)Cu\(_{9.95} \) films [19], is lower than those of the amorphous Ti\(_{50}\)Ni\(_{1-x}\) SMAs deviating from the fitted line. The wavenumber \( Q_p \) is inversely proportional to the mean nearest-neighbor distance of the local-ordering clusters of the amorphous alloys. This indicates that the addition of Cu to replace Ni in Ti—Ni binary SMAs changes the short range ordering of the amorphous phase, though the size of Cu atom \( (r_{Cu} = 0.1413 \text{ nm}) \) is close to that of Ni atom \( (r_{Ni} = 0.1377 \text{ nm}) \). In other words, the atomic arrangement of the local cluster both in the Ti50Ni25Cu25 melt-spun ribbon and in the Ti\(_{49.96}\)Ni\(_{40.09}\)Cu\(_{9.95} \) sputtered film is looser than that in Ti\(_{50}\)Ni\(_{1-x}\) SMAs. Therefore, the average bonding strength for the local cluster in Ti—Ni—Cu ribbon/film is weaker than that in Ti\(_{50}\)Ni\(_{1-x}\). Furthermore, as illustrated in Fig. 2, the Ti50Ni25Cu25 ribbon exhibits a lower \( Q_p \) value than the Ti\(_{49.96}\)Ni\(_{40.09}\)Cu\(_{9.95} \) film. This feature indicates that a Ti50Ni25Cu25 ribbon with a higher Cu content than a Ti\(_{49.96}\)Ni\(_{40.09}\)Cu\(_{9.95} \) film can exhibit looser bonding in the amorphous phase.

As shown in Fig. 4, the \( E_a \) value for Ti50Ni25Cu25 melt-spun ribbon is calculated as 341 kJ/mol. The \( E_a \) and \( T_x \) values for Ti50Ni50 melt-spun ribbon are also measured in this study as 430 kJ/mol and 522 °C (for 30 °C/min heating rate), respectively [22]. Fig. 5 indicates that \( T_x \) for a Ti50Ni25Cu25 ribbon is about 40 °C lower than that for a Ti50Ni50 ribbon. Both \( T_x \) and \( E_a \) are important indicators of the thermal stability of amorphous material, i.e., the lower values of \( T_x \) and \( E_a \) represent the lower stability of the amorphous phase [23]. As shown in Fig. 5, \( T_x \) of the mechanically alloyed powder is the lowest among those of sputtered thin films and melt-spun ribbons. The lowest level of amorphous stability of the mechanically alloyed powder may have been due to hydrogen contamination [16] and the large number of defects introduced during the mechanical alloying process.

As is also apparent from Figs. 4 and 5, all Ti—Ni—Cu specimens have lower \( T_x \) and \( E_a \) values than Ti—Ni binary SMAs in both sputtered films and melt-spun ribbons. This feature indicates that the replacement of Ni by Cu indeed lowers the thermal stability of the amorphous phase and assists in crystallization occurring. Chen and Park [24] demonstrated that the stability of an amorphous alloy is dominated by the strength of the interactions between the constituent atoms. The relative strength of the interactions between different constituent atoms can be determined by comparing their mixing enthalpies. Different constituents have a stronger tendency to form an amorphous alloy when they have a larger negative mixing enthalpy [25]. Previous studies have revealed that
Ti–Ni has a larger negative enthalpy than Ti–Cu, and Ni–Cu even has a positive enthalpy of mixing [26,27]. Therefore, the interaction strength between Ti and Ni atoms is stronger than that of the interaction strength between Ti and Cu, and the interaction between Ni and Cu is the weakest. As a result, the amorphous alloy becomes less stable when Cu atoms are partially substituted for the Ni in Ti–Ni binary SMAs because the average bonding strength between the atoms is decreased. Consequently, the Ti–Ni–Cu ribbon has lower $T_x$ and $E_a$ values than those of Ti$_{50}$Ni$_{50}$ ribbon because the latter has a stronger tendency to form an amorphous structure.

4.2. Crystallization of annealed Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon

4.2.1. Annealing effect on the crystallization

As demonstrated in Fig. 1, the as-spun Ti$_{50}$Ni$_{25}$Cu$_{25}$ ribbon is completely amorphous. Fig. 6 reveals that the crystallized degree of the Ti$_{50}$Ni$_{25}$Cu$_{25}$ ribbon can be controlled by the annealing time. As can be seen from Figs. 7–9, DSC and tensile test results also show that the annealing condition significantly influences the shape memory behavior of the crystallized ribbon. Both the transformation temperature and enthalpy detected in the DSC test increase with a prolonged annealing time due to an increase in the crystallization volume. However, as illustrated in Fig. 9, with an increase in the annealing time, the crystallized ribbon loses recoverable strain and simultaneously becomes brittle. In order to disclose the characteristics of these annealing effects, SEM observation with EDS analysis for the crystallized Ti$_{50}$Ni$_{25}$Cu$_{25}$ ribbon was conducted.

Fig. 10(a)–(d) shows SEM micrographs of Ti$_{50}$Ni$_{25}$Cu$_{25}$ ribbon annealed at 500 °C for 1 min, 3 min, 15 min and 3 h, respectively. As shown in Fig. 10(a), there are some spherical particles with a diameter of about 10 μm embedded in the amorphous matrix. The specimen annealed at 500 °C for 1 min does not show any crystallized peak for the XRD measurement in Fig. 6. This means that these spherical particles are not crystallized grains but are rather small bubbles produced during the melt-spinning technique retained in the amorphous matrix following the rapid solidification process [12]. The boundaries between these spherical particles and the amorphous matrix can act as nucleation sites of the crystallized grains during annealing. When the specimen is annealed at 500 °C for 3 min, as illustrated in Fig. 10(b), some small crystallized grains with diameters of 1–3 μm appear in these spherical particles. As shown in Fig. 10(c) and (d), there are more crystallized grains that developed within a prolonged annealing time interval and, therefore, the area of the amorphous matrix is reduced. Table 1 lists the EDS analyses for the chemical composition of points 1–8 denoted in Fig. 10. As depicted in point 1 of Table 1, the Cu content in the small bubble is 22.9 at.% which is slightly less than 25 at.% when the ribbon is annealed at 500 °C for 1 min. After annealing for 3 min, however, the Cu percent of the as-crystallized grains drops to only about 16.6 at.%, as shown in point 3 of Table 1. This phenomenon reveals that the as-crystallized grains contain a much lower Cu content than the amorphous

![Fig. 10. SEM micrographs of Ti$_{50}$Ni$_{25}$Cu$_{25}$ melt-spun ribbon annealed at 500 °C for (a) 1 min (b) 3 min (c) 15 min and (d) 3 h.](image-url)
matrix. Through prolonging the annealing time to 15 min, the Cu content in the crystallized grains raises to about 23.4 at.%, as indicated in point 5 of Table 1. After annealing at 500 °C for 3 h, as shown in points 7 and 8 of Table 1, the compositions of the crystallized grains and the amorphous matrix are almost the same. This reveals that sufficient annealing can result in a homogeneously crystallized Ti₅₀Ni₂₅Cu₂₅ ribbon.

From Fig. 6, the only XRD peak obtained in the as-crystral-

2.2. Annealing effect on shape memory properties

When Ti₅₀Ni₂₅Cu₂₅ ribbon is mildly annealed, as shown in Fig. 10(a), no obvious phase transformation and well-defined shape recovery can be obtained. After annealing at 500 °C for 3 min, as shown in Fig. 10(b), small crystallized grains appear. At this time, the recoverable strains reach a maximum, as indicated in Fig. 9. Through prolonging the annealing time, more crystallized grains form, as illustrated in Fig. 10(c) and (d), however, the amount of recoverable strain decreases, as shown in Fig. 9. We propose that the degenerated shape recovery effect is mainly due to the composition alteration in the crystallized grains of annealed Ti₅₀Ni₂₅Cu₂₅ ribbon. The as-crystralized grains contain a lower Cu content and perform a prominent shape recovery effect. Through prolonging the annealing time, on the other hand, the increased Cu content in the crystallized grains results in brittle characteristics and a low recoverable strain. This feature is similar to the results obtained in bulk Ti—Ni—Cu alloys [2,31] in which the variation in Cu content influences the lattice parameters of the phases and changes the recoverable strain during B2 ↔ B19 transformation. Therefore, the crystallized grains in the longer annealed Ti₅₀Ni₂₅Cu₂₅ ribbon contain a higher copper content which embrittles the annealed ribbon and reduces the shape recovery effect. Consequently, a Ti₅₀Ni₂₅Cu₂₅ ribbon exhibits a good shape memory effect only under appropriate annealing conditions, such as annealing at 500 °C for 3 min in this study.

5. Conclusions

The amorphous Ti₅₀Ni₂₅Cu₂₅ melt-spun ribbons which are partially crystallized by 500 °C annealing have been investigated by means of XRD, DSC, DMA and SEM tests. As shown by the XRD results, the as-spun Ti₅₀Ni₂₅Cu₂₅ ribbon is fully amorphous with the lowest wavenumber Qₑ among the amorphous Ti—Ni and Ti—Ni—Cu alloys fabricated by mechanical alloying, rapid quenching and sputter deposition. This indicates that the high Cu content of Ti₅₀Ni₂₅Cu₂₅ ribbon can loosen the atomic bonding in the amorphous phase. The Eₑ value of Ti₅₀Ni₂₅Cu₂₅ ribbon is 341 kJ/mol calculated from the DSC data using Kissinger’s method. The Tₛ for Ti₅₀Ni₂₅Cu₂₅ ribbons is about 40 °C lower than that for Ti₅₀Ni₅₀ ribbons. These characteristics indicate that the as-spun Ti₅₀Ni₂₅Cu₂₅ ribbon has a lower thermal stability than Ti₅₀Ni₅₀ ribbon from the viewpoint of the mixing enthalpy. Crystallization degree in a Ti₅₀Ni₂₅Cu₂₅ ribbon can be controlled by appropriate annealing. When a Ti₅₀Ni₂₅Cu₂₅ ribbon is annealed at 500 °C for less than 1 min, no obvious phase transformation and well-defined shape recovery can be obtained. When a Ti₅₀Ni₂₅Cu₂₅ ribbon is annealed at 500 °C for 3 min, the initial as-crystralized grains contain a lower Cu content than the amorphous matrix, but they exhibit a prominent shape memory effect. Through prolonging the annealing time, more grains are nucleated and the Cu content in the crystallized grains gradually increases. The more the grains are crystallized, the more the annealed ribbons become fragile and, as a consequence, their recoverable strain deteriorates. This feature is related to

Table 1

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<td>Amorphous</td>
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the increased Cu content in the crystallized grains which can embrittle the annealed ribbon and influence the lattice parameters of the phases and affect the recoverable strain during the B2 ↔ B19 transformation. Consequently, Ti50Ni25Cu25 ribbons can exhibit a good shape memory effect only under appropriate annealing condition.

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