Martensitic transformation of grain-size mixed $\text{Ti}_{51}\text{Ni}_{49}$ melt-spun ribbons

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Abstract

The as-spun and annealed ribbons of grain-size mixed $\text{Ti}_{51}\text{Ni}_{49}$ SMA exhibit the multiple martensitic transformations in which the annealed ribbons possess more obvious transformation peaks and less transformation hysteresis. According to the partial-cycled DSC test, transformation peaks are associated with $\text{B2} \rightarrow \text{R}$ transformation, $\text{R} \rightarrow \text{B19}_1'$ transformation for large grains and $\text{R} \rightarrow \text{B19}_2'$ transformation for small grains during cooling, and $\text{B19}_1' \rightarrow \text{B2}$ transformation for large grains and $\text{B19}_2' \rightarrow \text{B2}$ transformation for small grains during heating.

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1. Introduction

TiNi-based shape memory alloys (SMAs) have great potential for mechanical, biomedical and sports applications because of their excellent properties on shape memory effect (SME), pseudoelasticity (PE) and damping capacity [1]. Ribbons of TiNi-based SMAs of about 20 μm thick can be fabricated by the melt-spinning technique [2–11] in which ribbons of ternary TiNi–Cu SMAs are first and widely investigated [2–7]. This is because TiNi–Cu SMAs have smaller transformation hysteresis, smaller PE hysteresis, lower flow stress level in the martensite state and lower sensitivity of the martensitic transformation starting temperature than the other SMAs. Because of the aforementioned advantages, ribbons of TiNi–Cu SMAs would be a good candidate for applications that required short response time at thermal cycle, such as actuator and sensor. The crystal–amorphous interface [2], TiCu precipitates [3], nucleation and grain growth mechanisms [4], and SME [5] of TiNi–Cu SMA ribbons have been previously investigated.

Compared with the TiNi–Cu melt-spun ribbons, the melt-spun ribbons of binary TiNi SMAs have rarely been studied [7–11]. Miyazaki et al. [9] investigated the texture, SME and the microstructure of as-spun $\text{Ti}_{51}\text{Ni}_{49}$, $\text{Ti}_{50}\text{Ni}_{50}$ and $\text{Ti}_{49}\text{Ni}_{51}$

ribbons. They pointed out that all these as-spun ribbons are fully crystallized with fine grains and the as-spun $\text{Ti}_{49}\text{Ni}_{51}$ ribbons have a strong (1 0 0) texture. The maximum shape recovery strain exceeds 5.5% and 6.0% corresponding to as-spun $\text{Ti}_{51}\text{Ni}_{49}$ and $\text{Ti}_{50}\text{Ni}_{50}$ ribbons, respectively. In the present study, grain-size mixed $\text{Ti}_{51}\text{Ni}_{49}$ melt-spun ribbons were fabricated with most of the large and small grains located at the free surface and copper roller surface of the ribbons, respectively. The multiple martensitic transformations are found to associate with these grain-size mixed $\text{Ti}_{51}\text{Ni}_{49}$ melt-spun ribbons. The characteristics of this multiple martensitic transformation behavior are systematically investigated and discussed.

2. Experimental procedure

$\text{Ti}_{51}\text{Ni}_{49}$ ingot was prepared by conventional vacuum arc–remelting (VAR) method. High purity Ti and Ni raw materials were repeatedly melted six times in an argon atmosphere for homogenization. The ingot was cut into an appropriate size, supplied into a single-roller melt-spinning machine, induction-melted in an argon atmosphere in a quartz crucible at 1250 °C, and subsequently ejected by high pressurized argon out of a 0.4 mm orifice onto a 200 mm-diameter copper roller with the rotating velocity of 4000 rpm. The final ribbons of melt-spinning process were about 20 μm in thickness and 1.1 mm in width. Thereafter, the as-spun ribbons were cut into test specimens, sealed in evacuated quartz tubes and annealed at 650 and 800 °C for different time intervals.

The composition of as-spun $\text{Ti}_{51}\text{Ni}_{49}$ ribbons was detected by JEOL JXA-8600SX electron probe microanalyzer (EPMA). The average chemical composition of as-spun ribbons is $\text{Ti}_{51.69}\text{Ni}_{48.31}$ (in at.%). The full crystallization of

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the as-spun ribbons was confirmed by TA 5100 high temperature differential scanning calorimetry (DSC) and Philips PW1830 X-ray diffractometer.

Transformation temperatures and enthalpies of as-spun and annealed ribbons were determined by TA Q10 DSC with $10^{\circ}\text{C}/\text{min}$ heating and cooling rate and the temperature scanning range was from -150 to $+150^{\circ}\text{C}$. Microstructure observation was done by Nikon FX-35DX optical microscope (OM). The etching solution was composed of $\text{HF}:\text{HNO}_3:\text{H}_2\text{O}=4:5:10$ (in volume). The etching time was about 10–15 s. From the OM images under $1000\times$ magnification, the average grain size of annealed ribbons was estimated by the linear intercept method [12]. The numbers of intercepted grains were at least 10 and 50 for large and small grains, respectively.

3. Results and discussion

3.1. Microstructure observation

Fig. 1(a) shows the typical cross-sectional OM micrograph and Fig. 1(b) and (c) are the top-viewed OM micrographs of as-spun grain-size mixed $\text{Ti}_{51}\text{Ni}_{49}$ ribbons. As seen in Fig. 1(a), as-spun $\text{Ti}_{51}\text{Ni}_{49}$ ribbons are fully crystallized and most of the large and small grains are located at the free surface and copper roller surface of the ribbons, respectively. Fig. 1(b) shows the zone containing strip-shaped large grains (the average grain size of shorter width is about $4.5\text{ }\mu\text{m}$) and equiaxed-shaped small grains (the average grain size is about $0.8\text{ }\mu\text{m}$) in the edge of as-spun ribbons. Fig. 1(c) shows the zone containing equiaxed-shaped large grains (the average grain size is about $6.8\text{ }\mu\text{m}$) and equiaxed-shaped small grains (the average grain size is about $0.8\text{ }\mu\text{m}$) in the middle of as-spun ribbons. The total area of large grains is slightly larger than that of small grains. The grain shape and size distributions formed in Fig. 1 are attributed to the heterogeneous nucleation and thermal flow direction during the

Fig. 2. The DSC curve of the as-spun ribbon of grain-size mixed $\text{Ti}_{51}\text{Ni}_{49}$ SMA.

solidification process. After $800^{\circ}\text{C} \times 6\text{ h}$ annealing, the average grain sizes of equiaxed-shaped large grains, strip-shaped large grains and equiaxed-shaped small grains are about 7.6, 5.2 and $1.2\text{ }\mu\text{m}$, respectively. This indicates that the grain growth of large grains is insignificant (about 11.8% and 15.6% increase in length for equiaxed-shaped and strip-shaped large grains, respectively) but that of equiaxed-shaped small grains is comparatively obvious (about 50% in length).

3.2. DSC measurement

Fig. 2 shows the DSC curve of as-spun grain-size mixed $\text{Ti}_{51}\text{Ni}_{49}$ ribbons. As can be seen, the transformation peaks are

Fig. 1. The cross-sectional and top-viewed OM micrographs of as-spun $\text{Ti}_{51}\text{Ni}_{49}$ ribbons. (a) Cross-sectional view of as-spun ribbons, (b) top view near the edge of as-spun ribbons and (c) top view in the middle of as-spun ribbons.

Fig. 3. The DSC curves of $\text{Ti}_{51}\text{Ni}_{49}$ ribbons annealed at (a) $650^\circ\text{C} \times 12\text{ h}$ and (b) $800^\circ\text{C} \times 2\text{ h}$.

broad with small transformation enthalpies (about 10 J/g) and transformation hysteresis is quite large (about 200°C). This is because as-spun $\text{Ti}_{51}\text{Ni}_{49}$ ribbons contain plenty of defects and residual stress. At the same time, the grain size inherent in ribbons is finer than that of ingots prepared by the VAR. The grain boundaries and defects can act as barriers to the martensitic transformation as a result of extra energy required during transformation [6]. Thus fine-grain ribbons which have lots of grain boundaries would be expected to have lower transformation temperatures and smaller transformation enthalpies, as shown in Fig. 2.

Fig. 3(a) and (b) shows the DSC curves of $\text{Ti}_{51}\text{Ni}_{49}$ ribbons annealed at $650^\circ\text{C} \times 12\text{ h}$ and $800^\circ\text{C} \times 2\text{ h}$, respectively. Comparing Fig. 3 with Fig. 2 shows that the transformation peaks become sharp with large transformation enthalpies (about 24 J/g) while transformation hysteresis becomes small obviously. This is because the annealing treatment has two effects on the ribbons: (1) eliminating internal defects and residual stress and (2) fostering growth of fine grains. In this study, annealing temperatures were 650 and 800°C , which are high enough to eliminate the internal defects and residual stress in a short time, as evidenced by the transformation enthalpy shown in Fig. 4, which can reach about 23 J/g within 10 min.

Figs. 2–4 also show that $\text{Ti}_{51}\text{Ni}_{49}$ ribbons exhibit multiple martensitic transformations, i.e., there are three and two apparent transformation peaks in the cooling and heating curves, respectively, regardless of the annealing temperatures and time are. In order to understand what kinds of martensitic transformations are associated with these multiple peaks, partial-cycled DSC test was performed. Fig. 5 shows the partial-cycled DSC curves of $\text{Ti}_{51}\text{Ni}_{49}$ ribbons annealed at $800^\circ\text{C} \times 2\text{ h}$. As seen in Fig. 5, the specimen is cooled to peak 1 (52.6°C) and then instantly heats up; a new peak, peak 6, immediately appears which is not found in the full-cycle curve. This means that peak 1 is a R-phase transformation due to its small transformation hysteresis (about 7°C) and small transformation enthalpy (about 7.8 J/g). Also seen in Fig. 5, the specimen is cooled to peak 2 (45.5°C) and then instantly heats up; peak 6 also appears immediately but becomes smaller while another peak, peak 4, appears at higher

Fig. 4. Transformation temperatures and enthalpies vs. annealing time plots for specimens annealed at (a) 650°C and (b) 800°C . The terminology of peaks 1–5 is indicated in Fig. 2.

temperature. This means that peak 2 is a martensitic transformation peak due to its large transformation hysteresis between peaks 2 and 4 (about 35.4°C). At the same time, the occurrence of peak 6 indicates that a small amount of R-phase still

Fig. 5. The partial-cycled DSC curves of $\text{Ti}_{51}\text{Ni}_{49}$ ribbons annealed at $800^\circ\text{C} \times 2\text{ h}$.

exists if the cooling temperature is stopped at peak 2 during the partial-cycled test. For the specimen which is cooled to peak 3 (33.4 °C) and then instantly heats up, peak 6 does not appear but peaks 4 and 5 appear and both become larger. This means that peak 3 is also a martensitic transformation peak due to its large transformation hysteresis between peaks 3 and 5 (about 42.6 °C).

3.3. Discussion on the multiple martensitic transformations

From aforementioned partial-cycled DSC results, we propose that peaks 1–6 in Fig. 5 are associated with $B2 \rightarrow R$ transformation, $R \rightarrow B19_1'$ transformation, $R \rightarrow B19_2'$ transformation, $B19_1' \rightarrow B2$ transformation, $B19_2' \rightarrow B2$ transformation and $R \rightarrow B2$ transformation, respectively. Melt-spun ribbons of TiNi–Cu SMAs also reveal the multiple-stage martensitic transformation due to the existence of TiCu precipitates [3]. For bulk Ni-rich TiNi SMAs, Ti_3Ni_4 coherent precipitates can cause multiple-stage martensitic transformation [13–15] and this multiple-stage martensitic transformation is associated with a unique transformation path with several steps, for instance an assisted martensite at high temperature by the strain fields around coherent precipitates, followed at lower temperature by non-assisted martensite. Ti_2Ni precipitates form in the annealed bulk $Ti_{51}Ni_{49}$ SMA [16], but up to now no report indicates that precipitation of Ti_2Ni in $Ti_{51}Ni_{49}$ SMA can cause multiple-stage martensitic transformation. However, it has been pointed out that the multiple martensitic transformations can be observed in severely cold-rolled and annealed $Ti_{50}Ni_{50}$ specimens, which comprise grains of different sizes [17]. The same situation can also be applied to this study. Thus, we propose that peaks 1 and 6 correspond to $B2 \leftrightarrow R$ transformation for both large and small grains, peaks 2 and 4 correspond to $R \rightarrow B19_1'$ and $B19_1' \rightarrow B2$ transformations, respectively, for large grains, while peaks 3 and 5 correspond to $R \rightarrow B19_2'$ and $B19_1' \rightarrow B2$ transformations, respectively, for small grains. There are more evidences that support our arguments: (1) from Figs. 3(b) and 5, the hysteresis of peaks 2 and 4 is 35.4 °C, which is smaller than that of peaks 3 and 5, say 42.6 °C. Peaks 3 and 5 correspond to small grains which have more grain boundaries to resist martensitic transformation and should have larger hysteresis than peaks 2 and 4 corresponding to large grains. (2) The transformation enthalpies of peaks 2 and 4 are slightly higher than those of peaks 3 and 5, as shown in Fig. 3. This phenomenon is consistent with the total areas of large and small grains shown in Fig. 1 in which the total area of large grains is slightly larger than that of small grains, as indicated in Section 3.1. Moreover, as shown in Figs. 3–5, the $B2 \rightarrow R$ transformation does not separate into $B2 \rightarrow R_1$ and $B2 \rightarrow R_2$ for large and small grains, respectively, regardless of the annealing conditions. We propose that this characteristic comes from the difference in transformation strain associated with $B2 \leftrightarrow R$, $R \rightarrow B19'$ and $B19' \rightarrow B2$ transformations. $B2 \leftrightarrow R$ transformation has much smaller transformation strain ($\sim 1\%$) than $R \rightarrow B19'$ and $B19' \rightarrow B2$ ones ($\sim 10\%$) [18], therefore, the effect of grain size can be neglected in the $B2 \leftrightarrow R$ transformation.

4. Conclusions

The as-spun ribbons of grain-size mixed $Ti_{51}Ni_{49}$ SMA have most of the large and small grains at the free surface and copper roller surface of the ribbons, respectively. The as-spun and annealed ribbons have intrinsic multiple martensitic transformations with three and two peaks appearing in the cooling and heating DSC curves, respectively. The annealed ribbons can exhibit more obvious multiple martensitic transformations than as-spun ones with less transformation hysteresis and higher transformation enthalpy. According to the partial-cycled DSC test, we conclude that the peaks of transformations are associated with $B2 \rightarrow R$ transformation, $R \rightarrow B19_1'$ transformation for large grains, $R \rightarrow B19_2'$ transformation for small grains during cooling, and $B19_1' \rightarrow B2$ transformation for large grains and $B19_2' \rightarrow B2$ transformation for small grains during heating. The occurrence of the multiple martensitic transformations in ribbons of $Ti_{51}Ni_{49}$ SMA is due to the coexistence of large and small grains distributed in the ribbons. The reason why both $R \rightarrow B19'$ and $B19' \rightarrow B2$ transformations are separated into two peaks which correspond to large and small grains, while the $B2 \leftrightarrow R$ transformation is not separated into two peaks is that the $B2 \leftrightarrow R$ transformation exhibits much smaller transformation strain than $R \rightarrow B19'$ and $B19' \rightarrow B2$ transformations.

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