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Transformation Behavior and Pseudoelasticity of Aged $Ti_{50}Ni_{25}Cu_{25}$ Shape Memory Ribbon

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ABSTRACT

Transformation behavior and psuedoelasticity (PE) of 435 ºC and 500 ºC-aged $Ti_{50}Ni_{25}Cu_{25}$ melt-spun ribbons are studied. The PE performance of the aged ribbon is characterized by nanoindentation technique. The melt-spun ribbon undergoes crystallization process first during the aging treatment. The PE responses of the $Ti_{50}Ni_{25}Cu_{25}$ ribbon are found best at the aging times of 210~240 min and 10~15 min for the 435 ºC and 500 ºC-aged ribbons, respectively. The smallest remnant depth ratios (RDR) are about 18 % and 22 % for the 435 ºC and 500 ºC-aged ribbons, respectively. However, with prolonged aging treatment, enormous B11 TiCu precipitates deteriorate the transformation behavior of the ribbon, which result in the degradation of PE performance. Experimental results demonstrate that the transformation behavior and performance of $Ti_{50}Ni_{25}Cu_{25}$ melt-spun ribbon are closely related to the aging treatment.

1. INTRODUCTION

TiNiCu ternary shape memory alloys (SMAs) attract attentions around the world due to their lower temperature hysteresis, different transformation sequence and more stable transformation temperature than TiNi binary SMAs (Otsuka 2005). In addition, $Ti_{50}Ni_{50-x}Cu_x$ ternary SMAs exhibit different transformation sequences according to different Cu contents. In conventional bulk $Ti_{50}Ni_{50-x}Cu_x$ ternary alloys, the formation of B2↔B19 transformation is observed if Cu content is higher than 7.5 at. % ($x \geqq 7.5$) (Ramachandran 2013).

To solve the brittle problem of $Ti_{50}Ni_{50-x}Cu_x$ SMAs caused by intermetallic compounds, especially when $x \geqq 20$, melt-spinning technique was employed to

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fabricate TiNiCu ribbons with Cu contents of up to 25 at. % (Furuya 1991, Morgiel 2002, Nam 2005, Liu 2006, Chang 2006, Shelyakov 2013). Due to the rapid quenching process, amorphous $Ti_{50}Ni_{25}Cu_{25}$ ternary ribbons can be obtained and thus suppress the formation of brittle intermetallics in the as-spun ribbon.

In this study, amorphous $Ti_{50}Ni_{25}Cu_{25}$ ternary ribbons were crystallized and aged at different temperatures. The transformation behavior and pseudoelasticity (PE) property at micro-/nano-scale were investigated.

2. EXPERIMENTAL PROCEDURE

The $Ti_{50}Ni_{25}Cu_{25}$ ribbons were prepared by the Institute for Materials Science, Tohoku University, Japan, using a single-roller rapid solidification process (RSP). The melted alloy was first prepared using a conventional vacuum arc remelter and then ejected by pressurized argon gas onto a water-cooled copper roller with a surface velocity of 42 m/s. For crystallization and aging treatment, the ribbons were sealed in quartz tubes, aged in a salt bath for different intervals, and then quenched in water.

The transformation temperature and latent heat of the ribbons were determined using differential scanning calorimetry (DSC, Q10, TA Instruments, USA) with a heating/cooling rate of 10 ºC/min. X-ray diffraction spectra were obtained at room temperature with a high-power monochromatized X-ray diffractometer (XRD, TTRAX Ⅲ, Rigaku Co., Tokyo, Japan) using Cu Kα at a voltage of 50 kV and a current of 300 mA under a scanning rate of 4 º/min. The hardness of the ribbons was measured using a nanoindenter (Hysitron TI 950 TriboIndenter, Minnesota, USA) using a Berkovich probe with a tip radius of 150 nm. The loading, holding, and unloading times were all fixed at 5 sec. A maximum applied force of 7500 μN with a 1500 μN/s loading rate was used to measure the hardness. For each specimen, eight indentations were performed on the cross-section of the ribbon. The hardness is calculated as the average of six data points, with the maximum and minimum ones being deleted. The PE properties of the ribbons were tested by the same nanoindenter using a spherical indenter probe with a tip radius of 5.4 μm. The load function for the PE tests was set at a constant strain rate of 0.1 s^{-1}. The PE results are calculated with at least 5 indentations.

3. RESULTS AND DISCUSSIONS

The as-spun $Ti_{50}Ni_{25}Cu_{25}$ ribbons were crystallized and aged at 435 ºC and 500 ºC, where 435 ºC is below and that 500 ºC is above the crystallization temperature of 460 ºC (Chang 2006). Figures 1 (a) and (b) show the XRD spectra of differently aged $Ti_{50}Ni_{25}Cu_{25}$ ribbons at 435 ºC and 500 ºC, respectively. From Fig. 1 (a), it is observed that a broad diffraction mound appears at about 40~44º, which indicates a high volume fraction of the ribbon still remains amorphous when the aging time is 150 min. The diffraction peaks from B2 parent phase appear and become sharper when the aging time is increased from 210 min to 300 min. However, with prolong aging treatment, such as 800 min, the B2 diffraction peaks become broad and furthermore, weak diffractions from TiCu precipitates can be detected. Similarly, as seen from Fig. 1 (b), the 500 ºC × 1min aged ribbon still contains great amount of amorphous volume. The B2 diffraction peaks are sharpest at the aging time of 15 min and then become broadened with prolonged aging treatment. At the same time, TiCu precipitates are also detected when aging time is longer than 15 min. It is noticed that for both aging temperatures, the B2 diffraction peaks firstly develop from amorphous condition and become sharper as the crystallization process moves forward, and then broaden again. The reason for B2 diffraction peak to broaden significantly after prolonged aging treatment is that plate-like TiCu precipitates form along the $\{100\}_{B2}$ planes of the B2 matrix. Figure 2 shows a TEM bright field image of the 500 ºC × 100 min aged ribbon. From Fig. 2, the microstructure of 500 ºC × 100 min aged ribbon contains high density of plate-like TiCu precipitates along $\{100\}_{B2}$ planes. The B2 lattice and $\{100\}_{B2}$ spacing is significantly distorted by these plate-like TiCu precipitates and thus result in the broadened $(200)_{B2}$ diffraction peak after long-term aging treatment.

Figure 3 shows the nanoindentation hardness evolution of 435 ºC and 500 ºC aged ribbons. The hardness of 435 ºC aged ribbon slightly increases when the aging time is less than 200 min. After the aging time excess 200 min, the hardness of the 435 ºC aged ribbon decreases rapidly, which indicates the phase composition of the ribbon starts to be predominated by crystallized phase at this aging condition. With increasing aging treatment, the hardness reaches a minimum value and then the hardness increases again. On the other hand, the 500 ºC-aged ones undergo crystallization process in a much shorter time that the hardness of 500 ºC aged ribbon does not increase in the very early stage of aging. The increment of hardness in the early aging stage of 435 ºC aged ribbon may correspond to the reduction of free volume and the nucleation of nanocrystals during the aging treatment (Gu 2013).

Except for this early-stage hardening, the hardness of 500 ºC aged ribbon basically exhibits a similar trend to that of the 435 ºC aged one. The crystallization process causes the hardness decreases to a minimum and then raises again. The hardness increment observed after it reaches the minimum is originated from the increment in volume of coherent TiCu precipitates, as can be seen in Fig. 2. These enormous TiCu precipitates harden but at the same time embrittle the ribbon. It is noticed that both aging conditions result in a same minimum hardness of about 5.4 GPa. This feature indicates that the ribbon is fully crystallized at these aging conditions (435 ºC for 300 min and 500 ºC for 15 min). Additionally, the hardness of the 435 ºC-aged ribbons decreases after prolonged aging, which may due to the growth and the coherence loss of the TiCu precipitates.

The PE behavior of the aged ribbon tested by a nanoindenter is evaluated by the depth recovery ratio (DRR), which is calculated as:

$$\text{Depth recovery ratio (DRR)} = \frac{recoverable\ depth}{maximum\ depth} \times 100\% \qquad (1)$$

For each indentation, the average contact pressure (ACP) is calculated as:

$$\text{Average contact press (ACP)} = \frac{P}{A_c} = \frac{P}{\pi(2Rh_c - h_c^2)} \qquad (2)$$

where P is the indentation force, A_c is contact area, R is the tip radius and h_c is the contact depth.

Figure 4 (a) and (b) show the DRR of the 435 ºC and 500 ºC aged ribbons, respectively, under various ACP. Figure 4 (a) shows the DRR of ribbons aged at 435 ºC for 210, 300 and 400 minutes, which exhibit lower hardness among ribbons with various aging time. As can be seen from Fig. 4 (a), the applied ACP is ranging from 1.5

– 3.5 GPa and the DRR decrease monotonously with increasing applied ACP. From Fig. 4 (a), no apparent change in DRR with respect to aging time is observed. The reason for the unapparent PE response is possibly from the nanoscale precipitate embedded in the B2 matrix. The lengthy time required for ribbons to crystalize in 435 ºC inevitably results in massive precipitation to occur. As a consequence, the PE behavior is strongly influence by the precipitates. On the other hand, the 500 ºC aged ribbons, as shown in Fig. 4 (b), show a different trend. For the 15 min and 60 min aged ribbons, an obvious step is observed at ACP between 2.5 – 3.0 GPa, where the DRR remains at about 80 %. However, with prolonged aging treatment, such as 180 min, the step is indistinct and the DRR drops monotonously. This feature reveals that a pronounced PE response is occurred at the ACP range of 2.5 – 3.0 GPa for the well-crystallized ribbon aged at 500 ºC. But with prolonged aging treatment, the high density of TiCu precipitates hinders the martensitic transformation, as can be seen in Fig. 2, thus results in poorer PE response. It is also noted that, for the 15 min and 60 min aged ribbon, when ACP is higher than 3.0 GPa, the DRR drops rapidly. This feature implies that when the ACP is higher than 3.0 GPa, the stress induced martnesite is plastically deformed and thus cannot transform reversely back to parent phase, which leads to small DRR.

4. CONCLUSIONS

Amorphous $Ti_{50}Ni_{25}Cu_{25}$ ribbon is crystallized and aged at 435 ºC and 500 ºC for different intervals to investigate its transformation behavior and PE response. Since 435 ºC is lower and 500 ºC is higher than the crystallization temperature of $Ti_{50}Ni_{25}Cu_{25}$ ribbon, the 435 ºC aged ribbon needs much more time to complete crystallization process. XRD diffractions show that the B2 diffraction peaks of both 435 ºC and 500 ºC aged ribbons become obvious and sharper when aged from the amorphous condition. But with prolonged aging treatment, the B2 diffraction peak becomes broadened due to the formation of plate-like TiCu precipitates along $\{100\}_{B2}$ planes. From nanoindentation hardness tests, the hardness of the ribbons reach a minimum, which is regarded as the condition of fully crystallization. The conditions for the minimum hardness of 435 ºC and 500 ºC aged ribbons are 300 min and 15 min, respectively. The PE tests reveal that the 435 ºC aged ribbon doesn’t show abrupt change of DRR with increasing ACP. However, the 500 ºC aged ribbon shows pronounced PE response under ACP of about 2.5 - 3.0 GPa for the well-crystallized ribbon. But the high density of TiCu formed after prolonged aging treatment will hinder and deteriorate the PE performance of the ribbon. Experimental results demonstrate that with aging temperature slightly above the crystallization temperature, the time needed to obtain a fully crystallized ribbon can be significantly reduced, in which a pronounced PE property can be obtained simultaneously.

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