Deformation Behavior of Melt-spun Ti-Ni-Cu Shape Memory Alloy Ribbons with Various Cu-contents

Anak Khantachawana[+] and Shuichi Miyazaki[++]
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan
[+]Graduate students, University of Tsukuba
[++]Corresponding author, email: miyazaki@ims.tsukuba.ac.jp

In this study, $Ti_{50}Ni_{50-X}Cu_X$(at%) (X=0~40) ribbons were fabricated by melt-spinning process. The mechanical properties, such as shape memory effect and fracture stress, in the melt-spun ribbons with various Cu-contents were investigated. The thickness of the as-spun ribbon was 15μm. The as-spun ribbons were found to be amorphous for all of the Cu-contents. The mechanical properties were sensitively dependent on heat-treatment temperature. Excellent properties such as a relatively high transformation temperature, small temperature hysteresis as well as stable mechanical property were obtained in the $Ti_{50}Ni_{25}Cu_{25}$ ribbon.
Key words: Ti-Ni-Cu, shape memory alloy, rapid solidification, mechanical property, martensite transformation

1. INTRODUCTION

Ti-Ni shape memory alloys (SMAs) are one of the intelligent materials and play important roles for micro-electro-mechanical-systems (MEMS) due to their large shape recovery strain and force [1-3]. It is well known that the third elements added to the Ti-Ni SMA affect the shape memory characteristics and transformation behavior [4-8]. According to the previous works, it can be said that among the third elements substituting for Ni in Ti-Ni alloys, much attention has recently been paid to Cu due to its unique influence to obtain following properties; (1) small transformation hysteresis[9], (2) decrease in sensitivity of transformation temperatures to the alloy compositions, (3) large difference between the flow stress of the parent phase and martensite phase and (4) the improvement of the stability in the transformation cyclic behavior[10-11], etc. Such influences of Cu on shape memory properties are practically important for the development of SMA. However, for the ordinary fabrication process, it is known that the deformability becomes worse with increasing Cu-content in the Ti-Ni-Cu alloy. This problem can be solved by utilizing the melt-spinning technique since Ti-Ni-Cu ribbons with thickness of about 15μm in thickness can be fabricated regardless of their compositions. Moreover, the process of rapid solidification provides very fine grains and microscopically homogeneous substructure with minimum processing steps, thereby reducing cost and improving the shape memory characteristics. According to our previous report[8], it is known that by adding 25at% Cu into Ti-Ni melt-spun ribbon, very small transformation hysteresis and stable mechanical properties can be obtained. Therefore, the effects of Cu-contents on mechanical properties and transformation characteristics are interesting and should be investigated.

The purpose of the present study is to systematically investigate the effects of Cu-content and heat-treatment on the mechanical properties and transformation behavior of $Ti_{50}Ni_{50-X}Cu_X$(at%) melt-spun ribbons by means of Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD), tensile tests, thermal cycling tests under various constant stresses.

2. EXPERIMENTAL PROCEDURE

$Ti_{50}Ni_{50-X}Cu_X$(at%) with X ranging from 0 to 40at% ingots were made by Ar-arc melting method using high purity Ti, Ni and Cu. In order to obtain the homogeneous composition, the ingots were melted and turned over repeatedly for 6 times. These ingots were cut into several pieces by a spark-cutting machine. Some pieces of the ingots were put in a quartz crucible and set in a melt-spinning apparatus. Rapid solidification was carried out by induction melting the ingots in Ar followed by ejecting the molten alloy onto a copper wheel rotating at 50m/s surface velocity. The melt-spun ribbons fabricated by this method were 1mm in width and 15μm in thickness. The ribbon specimens and some pieces cut from the bulk ingot were heat-treated at temperatures ranging from 773 to 1073 for 3.6ks. In order to obtain the shape memory effect, the ribbons must be crystallized. The crystallization temperatures were determined by DSC measurements, the specimens being heated from room temperature to 833K with the heating rate of 10K/min. He gas was purged during the measurement with the flowing rate of 50ml/min. In order to evaluate the deformation behavior, the specimens of 0.6mm in width and 7mm in length were prepared from the melt-spun ribbons for fracture tests, tensile tests and thermal cycling tests under various constant stresses. The fracture tests were performed at room temperature. The tensile tests at various maximum tensile strains were performed at the temperatures ranging from 143K to 403K and thermal cycling tests were carried out with the 10K/min heating and cooling rate.

3. RESULTS AND DISCUSSION

3.1 Crytallization temperatures and transformation temperatures

It is found that all the as-spun ribbons were amorphous regardless of Cu-content. The crystallization peaks of $Ti_{50}Ni_{40}Cu_{10}$ (at%) and $Ti_{50}Ni_{25}Cu_{25}$(at%) as-spun ribbons were shown in Fig.1. The exothermic peaks corresponding to the crystallization show the peak temperatures T_c^* at 792K and 763K for $Ti_{50}Ni_{40}Cu_{10}$ (at%) and $Ti_{50}Ni_{25}Cu_{25}$(at%) as-spun ribbons, respectively. For more details, the variations in the crystallization peak temperature T_c^* with increasing Cu-content is shown in Fig.2. It is obviously seen that T_c^* strongly depends on Cu-content, in other words, T_c^* abruptly decreases with increasing Cu-content. Moreover, it should be mentioned that these T_c^* temperatures seem to be comparatively higher than those of the sputter-deposited thin films with similar alloy compositions [12]

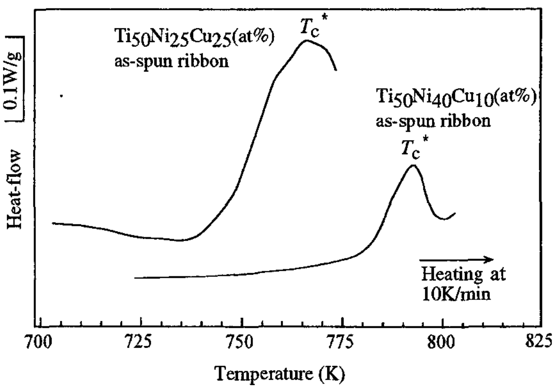

Fig. 1 Crystallization peak temperature of $Ti_{50}Ni_{40}Cu_{10}$ and $Ti_{50}Ni_{25}Cu_{25}$ as-spun ribbons

Fig.3 shows the representative DSC curves of $Ti_{50}Ni_{40}Cu_{10}$ (at%) and $Ti_{50}Ni_{25}Cu_{25}$(at%) ribbons heat-treated at 1073K for 3.6ks. A set of single-stage forward and reverse transformations between B2 (cubic) and B19 (orthorhombic) phases can be confirmed in both specimens. Since our previous work showed that the R-phase transformation can be confirmed in a Ti-50.0at%Ni binary alloy ribbon heat-treated at 1073K for 3.6ks [13], it can be known from these results that one effect of Cu-addition is to hinder the R-phase transformation. On the other hand, the transformation hysteresis (defined as the difference between reverse transformation peak temperature A^* and martensite transformation peak temperature M^*) for the martensite transformation decreases from 20K to 10K with increasing Cu-content from 10at% to 25at%. It is known that small transformation temperature hysteresis is desirable when the specimen is applied for an actuator because the response rate can be increased due to the narrow actuation temperature range. Fig.4 shows the Cu-content dependence of M_s temperature of the ribbons heat-treated at 1073K for 3.6ks. For comparison, the M_s temperatures of the mother ingots were also plotted together. It is seen that the M_s temperature shows the minimum value of 235K in the ribbon with no Cu-content. The M_s temperature gradually increases with increasing of Cu-content from 5at% to 20at% and seems to be constant around 320K with further increasing Cu-contents. On the other hand, M_s temperatures of the mother ingots show a small Cu-content dependence when compared with those of the ribbons.

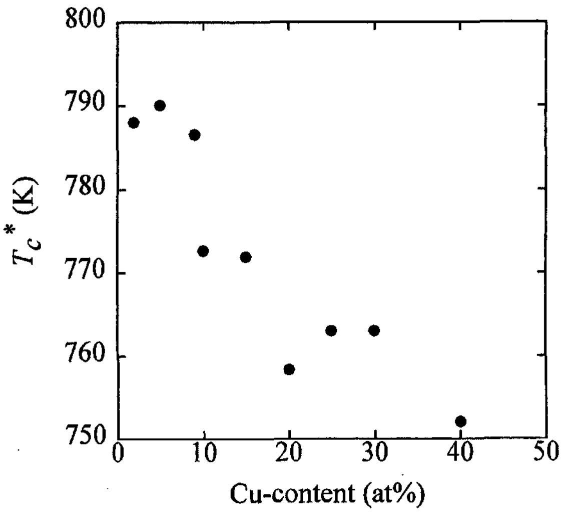

Fig. 2 Cu-content dependence of crystallization temperature T_c*.

3.2 Mechanical properties

In order to evaluate the deformation behavior of melt-spun ribbons, thermal cycling tests under various constant stresses were performed. Fig.5 shows typical result which

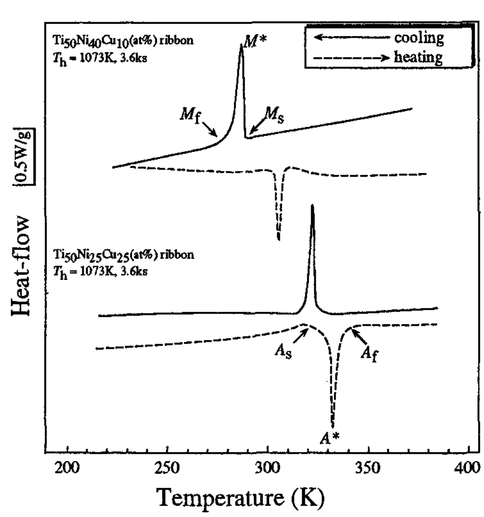

Fig. 3 DSC curves of $Ti_{50}Ni_{40}Cu_{10}$ and $Ti_{50}Ni_{25}Cu_{25}$ ribbons heat-treated at 1073K for 3.6ks

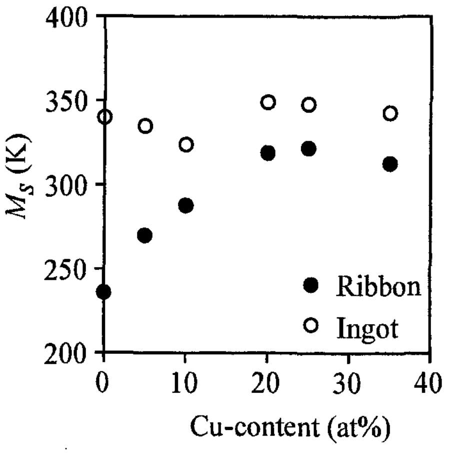

Fig. 4 Cu-content dependence of M_s temperature in the ribbon and mother ingot heat-treated at 1073K for3.6ks

shows strain-temperature curves of a $Ti_{50}Ni_{40}Cu_{10}$(at%) ribbon heat-treated at 873K for 3.6ks. The solid and dashed lines correspond to cooling and heating processes, respectively. An arrow indicates the M_s point detected under each applied stress. A cross mark corresponds to the fracture. A set of single-stage forward and reverse transformations between parent phase (B2) and martensite phase (B19) can be confirmed upon cooling and heating. It is clear that M_s gradually increases with increasing of applied stress. This satisfies the Clausius-Clapeyron relationship, implying that the martensite phase is stabilized by an applied stress. The shape recovery strain ε_A shows the maximum value of almost 2% under the applied stress of 150MPa. It should be noted that no slip deformation can be detected under any applied stresses from this figure.

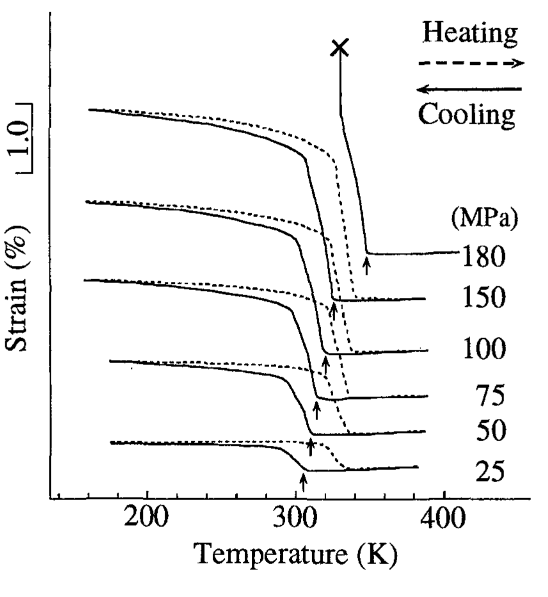

Fig. 5 Strain-temperature curves under various constant stresses obtained in a $Ti_{50}Ni_{40}Cu_{10}$ ribbon heat-treated at 873K for 3.6ks.

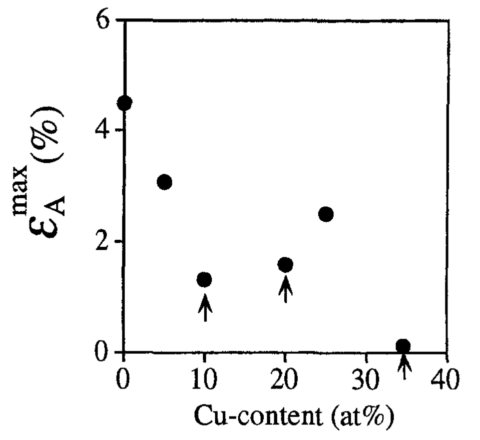

Fig. 6 Cu-content dependence of the maximum recovery strain obtained from a set of strain-temperature curves.

The fracture occurred under relatively low applied stress of 180MPa. On the other hand, it is found that the fracture stress can be increased with increasing the heat-treatment temperature to 1073K. Fig.6 shows the effect of Cu-content on the maximum recovery strain ε_A^{max}, which was obtained from the strain-temperature curves of specimens heat-treated at 1073K for 3.6ks. The arrow indicates ε_A^{max} obtained from the specimen which fractured prior to the introduction of slip deformation. Then larger values are intrinsically expected for such specimens. It is seen that ε_A^{max} decreases with increasing Cu-contents except for a $Ti_{50}Ni_{25}Cu_{25}$(at%) ribbon. Our previous observation [8] showed that $Ti_{50}Ni_{25}Cu_{25}$(at%) ribbon represents a very small transformation hysteresis (around 10K), relatively high transformation temperature and high critical stress for slip. Thus, it should be mentioned that this material ($Ti_{50}Ni_{25}Cu_{25}$) is optimum for utilizing in micro-actuator devices.

In order to evaluate the strength of the ribbons in martensite and parent phases, the tensile tests were carried out at various temperatures. Fig.7 shows the typical tensile stress-strain curves measured at 355K for a $Ti_{50}Ni_{25}Cu_{25}$(at%) ribbon heat-treated at 1073K for 3.6ks. The specimen was first loaded up to a point numbered 1, then unloaded followed by heating to 393K in order to make the specimen reveal complete reverse transformation to the parent phase. Then, after setting the temperature to the original one, the next tensile tests were conducted in the similar way with increasing the number to increase the transformation strain.

Since this test temperature is a little above A_f temperature, the pseudoelasticity curves can be confirmed for each tensile test. It is seen that the stress for inducing martensite is around 250MPa irrespective of the number of cyclic deformation. All the curves during loading overlap each other. This means that few plastic strain is introduced during each cyclic deformation. In other words, the residual strain induced after each cyclic deformation was

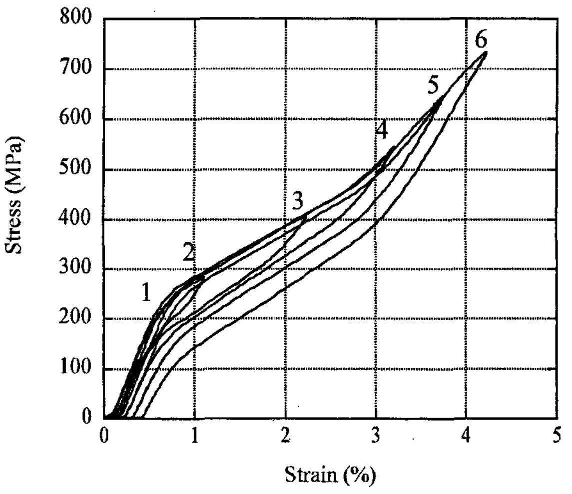

Fig. 7 Stress-strain curves measured at 355K in a $Ti_{50}Ni_{25}Cu_{25}$ ribbon heat-treated at 1073K for 3.6ks.

almost removed by the reverse transformation during heating. On the other hand, strain of about 4% was confirmed upon unloading in the last cyclic deformation, indicating a stable superelasticity.

4. SUMMARY

(1) All as-spun $Ti_{50}Ni_{50-X}Cu_X$(at%) (X=0~40) ribbons were amorphous.
(2) The melt-spun ribbons become brittle with increasing Cu-content.
(3) Small transformation hysteresis was obtained with adding Cu more than 20at%.
(4) High strength and stable mechanical properties were obtained in the $Ti_{50}Ni_{25}Cu_{25}$(at%) ribbon heat-treated at 1073K for 3.6ks.

ACKNOWLEDGEMENT

This work was partially supported by the Grants-in-Aids for Fundamental Scientific Research (Kiban A (1999-2001) and Kiban A (2002-2004) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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(Received April 18, 2003; Accepted April 30, 2003)