RAPID PUBLICATION

Thermo-mechanical Phase Transformation of Rapidly Quenched Ti-Ni-Cu Ribbons

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The thermo-mechanical transformation (i.e., the shape memory effect (SME)) of a rapidly quenched Ti-Ni-Cu alloy was investigated. Some comparisons in the properties with the phase transformation (i.e., transformation temperature, thermal hysteresis, its stress dependence, ability of energy conversion, etc.) were done between rapidly quenched (RQ) $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}(\text{at}\%)$ ribbons and conventional polycrystalline $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$, $\text{Ti}_{50}\text{Ni}_{50}(\text{at}\%)$ wires. The self-deformation associated with the phase transformation (i.e., SME) in the RQ ribbons was 3–4 times larger than that of the conventional polycrystalline alloy wires, and the hysteresis curve of strain vs temperature was narrow in shape and changed sharply at the transformation points under increasing applied stress. Since the RQ ribbons became smaller in self-deformation and broader in hysteresis loop by annealing at 973 K, the inferiority of SME in the recrystallized structure with grain nucleation, subsequent grain growth and lower dislocation density was confirmed. From the characterization of the conversion from thermal energy into mechanical energy, the RQ material has more efficient energy conversion ability than the recrystallized polycrystalline materials. More superior characteristics in SME will be anticipated in the microstructural region produced by more rapid solidification control.

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I. Introduction

The titanium-nickel alloy of an approximately equi-atomic concentration has been attracting attention by its unique nature of the shape memory effect (SME)⁽¹⁾⁽²⁾. SME is associated with a reversible thermoelastic martensitic transformation, therefore, a shape memory alloy (SMA) has the energy convertible function from thermal into mechanical energy.

If a new thermosensitive shape memory alloy which has a higher energy convertible function is developed by alloy designing such as the control of chemical compositions⁽³⁾, material processing (i.e., heat treatment⁽⁴⁾, working process) and renovation of the manufacturing method^{(5)–(7)}, considerably strong impacts and wide applications will be expected in the various engineering fields such as thermal devices (i.e. thermo-sensor), biomaterials, robotic actuators, heat engines, etc.⁽⁸⁾.

Based on these situations, we have investigated the thermo-mechanical phase transformation (i.e., shape memory effect) of the rapidly quenched (RQ) Ti-Ni-Cu ribbons made by a melt-spinning technique as one of the

studies on newly manufactured SMA materials. Some comparisons of the material properties with SME (i.e., thermal hysteresis, its stress dependence and energy conversion ability) are made between RQ and conventional polycrystalline alloys. In this paper the ability of energy conversion in SMA is simply termed “energy convertibility”. As a result, much greater SME and higher energy convertibility are expected in RQ Ti-Ni-Cu ribbons.

II. Experimental Procedures

$\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}(\text{at}\%)$ alloy was prepared by arc-melting high purity metals (titanium 99.8%, nickel and copper 99.99%) in an argon atmosphere. The alloy was rapidly quenched in the argon gas atmosphere using a melt-spinning machine where the mother alloy was induction melted in a BN coated quartz crucible and ejected with a pressurized argon gas out of a 0.3 mm orifice onto a copper roller (dia=200 mm) rotating at a surface velocity of 80 m/s (4000 rpm). The testing specimen size of melt-spun ribbons was 0.03 mm (thickness) $\times$ 1.0 mm (width) $\times$ 200 mm (length). In order to compare the shape memory effect of the rapidly quenched material with the conventional polycrystalline materials, $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}(\text{at}\%)$ and $\text{Ti}_{50}\text{Ni}_{50}(\text{at}\%)$ commercial alloy wires were also prepared. The sizes, typical examples of metallurgical microstructures and heat treatments of the specimens are listed in Table 1. The polycrystalline $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ and $\text{Ti}_{50}\text{Ni}_{50}$ wires were fully annealed to remove the strain in-

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Table 1 Nominal compositions, heat treatments, enthalpy changes, sizes and typical microstructures of tested specimens.

Specimen	Composition (at%)	Heat treatment	ΔH (J/g)	Size (mm)
Rapid quench	Ti ₅₀ -Ni ₄₀ -Cu ₁₀	As quenched	11.0	1.0(<i>w</i>) × 0.03(<i>t</i>) × 200(<i>l</i>) Ribbon
		723 K, 1.5 h → IQ	12.5	
		973 K, 3 h, IQ	12.4	
		973 K, 200 h, IQ	13.4	
Poly-crystal	Ti ₅₀ -Ni ₅₀	1073 K, 2 h, IQ	8.2	0.4(ϕ) × 200(<i>l</i>) Wire
	Ti ₅₀ -Ni ₄₀ -Cu ₁₀	→ 673 K, 1 h, IQ	7.3	0.5(ϕ) × 200(<i>l</i>) Wire

IQ; ice water quench, *w*; width, *t*; thickness, *l*; length, ϕ ; diameter, ΔH ; enthalpy change.

troduced during manufacturing processes. The rapidly quenched Ti₅₀Ni₄₀Cu₁₀ ribbons were annealed in a vacuum quartz tube to obtain the shape-memory heat treated (623 K) or recrystallized and grain grown (973 K) samples. The grain size of each sample was 2–3 μm in “as quenched” and “723 K, 1.5 h, IQ”, extremely fine 0.02–0.1 μm in “973 K, 3–200 h, annealed” and 10–15 μm in the Ti₅₀Ni₅₀, Ti₅₀Ni₄₀Cu₁₀ wires. The changes in strain (i.e., self-deformation) with temperature during a thermal cycling (i.e., strain-temperature hysteresis curve) were measured under several stress (σ) conditions. Heating-up and cooling-down of the specimens were done in a temperature controllable water-bath. The amount of the deformation (i.e., elongation and contraction) of specimen was detected by the potentiometer connected to the pulley and recorded continuously on the X(temperature)-Y(strain) recorder⁽⁹⁾. Heat transfer (i.e., absorbed heat mass) in the inverse transformation process from A_s to A_f was measured by a differential scanning calorimeter (DSC) at a heating rate of 10 K/min between 293 K (20°C) and 373 K (100°C).

III. Results and Discussion

In most cases, SMA is used as one of the machinery components in the devices under stressed conditions (i.e., biasing, prestraining forces, etc.), so that the shape memory effect (i.e., hysteresis curve and its shape) under stress condition is more essential for evaluating the functionality of SMA. A typical example of the strain

vs temperature hysteresis curves of the two rapidly quenched Ti₅₀Ni₄₀Cu₁₀ ribbons (as quenched, SME heat treated) and Ti₅₀Ni₅₀, Ti₅₀Ni₄₀Cu₁₀ wires under the same stress condition ($\sigma \approx 65$ MPa) is shown in Fig. 1. The range of strains (Y axis) of each hysteresis curve contains

Fig. 1 Typical examples of the strain vs temperature hysteresis curves of the rapidly quenched Ti₅₀Ni₄₀Cu₁₀(at%) ribbons and the conventional polycrystalline Ti₅₀Ni₄₀Cu₁₀, Ti₅₀Ni₅₀(at%) wires under the same stress condition ($\sigma \approx 65$ MPa).

about 1% strain due to the thermal expansion of the measuring apparatus itself. As shown in the figure, the cross point of the two tangent lines from the crooked curves was determined as the martensitic transformation starting (M_s), finishing (M_f) points and inverse transformation starting (A_s), finish (A_f) points. The shape of hysteresis of the rapidly quenched ribbons was narrow and its curve changed sharply at the transformation points, while that of the wires was small and broadened in the horizontal direction. Under the same stress $\sigma \div 65$ MPa condition, the self-deformations (i.e., strain) associated with thermal phase transformations (i.e., SME) in the rapidly quenched $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ ribbons are 3–4 times larger than those of polycrystalline $\text{Ti}_{50}\text{Ni}_{50}$, $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ wires, and the temperature difference between A_f and M_f is considerably smaller in the case of the RQ alloys than in the wires samples. Therefore, by using RQ material we can utilize the very large shape memory effect (SME) and extract the mechanical energy from the medium having a very small temperature difference.

Next, a comparison of the hysteresis curves under increasing applied stresses is shown in Fig. 2. Although the narrow shape of the hysteresis in the RQ alloy was still preserved, the shape of the $\text{Ti}_{50}\text{Ni}_{50}$ and $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ wires became wider and plump at the phase transformation points (A_s , A_f , M_s , M_f) under a larger stress, so that the temperature difference between A_f and M_f increased during one thermal cycling. These qualitative improvements of SME in the rapidly quenched Ti–Ni alloy might be thought to arise from the several factors as follows. (1) very fine grain and microscopically homogeneous substructure, (2) regularity or anisotropy of crystal grain, subgrain or variants, (3) dislocation morphology (structure, density, etc.), (4) internal stresses due to dense defects introduced during the rapid quenching process, and (5) changes of crystal structure by rapid solidification, etc. As a first step of the investigation for making clear the most predominant one with superior SME in the RQ ribbon among the possible factors indicated above, the changes in thermal hysteresis loops with recrystallization of the RQ ribbon and its substructure were investigated by adopting the heat treatment, i.e. annealing at 973 K in a vacuum environment. As shown in Fig. 3,

Fig. 2 Variations of the thermal hysteresis curves with increasing applied stress in rapidly quenched $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ (at%) ribbon and the conventional polycrystalline $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$, $\text{Ti}_{50}\text{Ni}_{50}$ (at%) wires.

the shape of the hysteresis loop (strain vs temperature curve) gradually became smaller in the strain (Y axis) range and wider in the temperature range between A_f and M_f with an increase of the annealing time. This heat-treatment caused the decrease in dislocation density and the recrystallized grain growth as shown in the photographs in Fig. 4. Taking into account the thermal hysteresis curves shown in Figs. 1, 3 and 4, it can be concluded that SME is larger in the RQ ribbons of “as quenched” and “723 K aged for the SME heat-treatment”, and it becomes weak by the microstructural changes with 973 K recrystallization processes in the Ti–Ni–Cu system. From the metallurgical substructure and electron diffraction patterns shown in Fig. 4, the RQ ribbons appear to have a larger grain size than the recrystallized RQ materials, indicating that the grain size is not a predominant factor for high SME in RQ. The authors would like to attribute

Fig. 3 Variations of the shape of strain vs temperature hysteresis curve associated with 723 K aging for shape memory treatment and 973 K annealing for recrystallization in $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ ribbons.

Fig. 4 Variations of metallurgical microstructures with heat treatments for 723 K aging for shape memory treatment or 973 K annealings for recrystallization in $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ ribbons.

its cause to the interactive effects of (1) the extraordinary regularity or anisotropy of crystal or variants and (2) the high resistance to yielding, plastic deformation due to the high dislocation density in RQ material. However, more investigation, including the cooling rate (i.e., roll speed) dependence on SME or substructure in melt-spinning, is required to make clear the mechanism of superior SME in RQ material.

The changes of transformation temperature, A_s , A_f , M_s , M_f in the RQ ribbons and conventional polycrystalline alloy wires at applied stress $\sigma \div 65$ MPa are shown in Table 2. The maximum temperature difference in one transformation cycle, $\Delta T = A_f - M_f$, is an essential factor for designing a more efficient thermal sensor or a semi-permanent SME heat engine which works by heat sources having considerably a small temperature

difference. The temperature difference between ΔT generally decreased in the rapidly quenched microstructure. Based on this result, a much narrower temperature difference between M_f and A_f in one thermal cycle is anticipated towards the microstructural region produced by more rapid solidification control.

Finally, for the engineering applications of SMA Ti-Ni alloys to energy-efficient heat engines, thermal actuators, etc., the characterization of the energy convertibility or recollectability from thermal sources to mechanical power is made by comparing the case of the RQ material with that of conventional polycrystalline wire samples. In order to characterize the thermal energy convertibility or recollectability into mechanical energy, two parameters⁽¹⁰⁾, $\eta (= \sigma \cdot \varepsilon / \Delta q)$, where σ = loading stress, ε = strain range in SMA during phase transforma-

Table 2 Variation of each transformation temperature, A_s , A_f , M_s , M_f and temperature range $\Delta T (= A_f - M_f)$ in a thermal cycle, and variations of two parameters for evaluating the thermal energy convertibility $\eta (= \sigma \cdot \varepsilon / \Delta q)$ or recollectability from thermal sources $\mu (= \sigma \cdot \varepsilon / 2)$ in the tested specimens at applied stress $\sigma \div 65$ MPa.

Specimen	Composition (at%)	Heat treatment	M_f (K)	M_s (K)	A_s (K)	A_f (K)	ΔT (K)	μ (MPa)	η (%)
Rapid quench	$\text{Ti}_{50}\text{-Ni}_{40}\text{-Cu}_{10}$	As Quenched	309.5	310.1	317.9	319.8	10.3	1.64	2.99
		723 K, 1.5 h, IQ	310.0	313.3	316.5	319.6	9.6	1.53	2.45
		973 K, 3 h, IQ	309.6	315.7	316.5	322.5	12.9	1.25	2.02
		973 K, 200 h, IQ	322.4	327.5	334.8	338.6	16.2	1.29	1.93
Poly-crystal	$\text{Ti}_{50}\text{-Ni}_{50}$	1073 K, 2 h, IQ	301.9	308.8	324.2	331.5	29.6	0.29	0.70
	$\text{Ti}_{50}\text{-Ni}_{40}\text{-Cu}_{10}$	→673 K, 1 h, IQ	318.4	325.1	324.8	332.9	14.5	0.58	1.59

M_s and M_f ; Martensitic transformation starting and finishing temperature.

A_s and A_f ; Inverse transformation starting and finishing temperature.

ΔT ; Range of transformation temperature ($= A_f - M_f$).

μ and η ; Thermal energy collectability and convertibility at applied stress $\sigma \div 65$ MPa.

tion[†], Δq =absorbed heat mass per weight during the transformation which is measured by DSC) and $\mu(=\sigma \cdot \varepsilon/2)$ are discussed. η is defined as shown in ref. (11) by the ratio of strain energy work density (i.e., $(\sigma \cdot \varepsilon)/2$) to absorbed heat mass (Δq) in the inverse transformation process from A_s and A_f .

In practical applications of SMA to the heat engine, several factors with the material property have to be taken into account such as the recovery stress (i.e., large SME for a powerful SMA heat engine), the shape of thermal hysteresis (i.e., the small transformation temperature range, A_f – M_f , sharpness and small sweeping area within the hysteresis loop for elevating the resistance against degradation of SME) and the fatigue life⁽¹¹⁾ of SMA elements. Table 2 shows the data with η and μ under a rather small stress value $\sigma \div 65$ MPa below the yield stress of the Ti–Ni–Cu alloy system. As shown in the table, the evaluating parameter, η , indicates a maximum in RQ $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ ribbons and another parameter, μ is 3–5 times larger than those of the polycrystalline $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ or $\text{Ti}_{50}\text{Ni}_{50}$ wires^{††}.

Moreover, it can be anticipated that more large values of energy convertibility (η) or reconvertibility (μ) will exist in a more rapidly quenched microstructure region because these two parameters clearly become small not only by recrystallization with 973 K annealing of $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ ribbons but in the case of larger polycrystalline $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$, $\text{Ti}_{50}\text{Ni}_{50}$ wires. After all, if we can develop a new material having more large SME as well as a more high energy convertible function of thermal energy by adopting a novel technique such as rapid solidification, there will be great impact on the fields of engineering devices, especially, energy development which is being regarded as one of the most important and urgent problems in the world.

IV. Summary and Conclusions

An investigation of the thermo-mechanical transformation, i.e., the shape memory effect (SME) of the rapidly quenched $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ (at%) ribbon was carried out. Some comparisons with the phase transformation (i.e.,

transformation temperature, thermal hysteresis and its stress dependence, energy convertibility, etc.) were done between the rapidly quenched (RQ) $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ ribbons and polycrystalline $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$, $\text{Ti}_{50}\text{Ni}_{50}$ alloy wires. Self-deformation associated with the phase transformation (i.e., SME) in the RQ ribbons was 3–4 times larger than that of the conventional polycrystalline wire samples, and the hysteresis curve of strain vs temperature was narrow and changed very sharply at each transformation point in spite of the increase of applied stress. Since RQ ribbons became smaller in self-deformation and broader in the shape of the hysteresis loop by 973 K annealing the inferiority of SME in the recrystallized microstructure (i.e., lower dislocation density, nucleation, subsequent growth of recrystallized grain, etc.) was clearly confirmed. Its superiority seems to be attributed to an interactive effect of (1) extraordinary regularity in the anisotropy of crystals or variants and (2) high resistance to yielding, plastic deformation due to high dislocation density in RQ material. These results suggest that the rapidly quenched Ti–Ni–Cu ribbon is able to have the superiority of SME as well as high resistance against the degradation in SME during long-term cyclic use or applications in the engineering field. From the characterization of the conversion from thermal energy into mechanical energy, the RQ material has more efficient energy convertibility than the conventional polycrystalline material, and still more superior characteristics in SME will be anticipated in the metallurgical microstructure region produced by more rapid solidification control.

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[†] A parameter, energy convertibility $\eta(=(\sigma \cdot \varepsilon)/\Delta q)$ was calculated by using the absorbed heat mass per weight Δq under zero stress by DSC. In several papers⁽¹²⁾, the stress dependence of enthalpy ΔH (i.e., equal to Δq) has been discussed, however, in a recent paper by Jardine⁽¹³⁾, it was reported that ΔH value of Ti–Ni coil and thermal efficiency in phase transformation did not change so much under loading conditions. Based on these situations, we decide to adopt and calculate η value as one of the parameters for characterizing the thermal convertibility during thermo-mechanical transformation in the Ti–Ni alloy system.

^{††} A parameter, strain energy density, $\mu(=(\sigma \cdot \varepsilon)/2)$ seems to become important especially in the case of open system SME engine utilizing the natural heat energy sources having a considerable small temperature difference such as the ocean temperature differential dynamo⁽¹⁴⁾ and low thermal sources abandoned from factories or power plants.