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Effects of Ni–Ti–Cu alloy composition and heat treatment temperature after cold working on phase transformation characteristics

K. TSUJI
Materials Research and Development Laboratory, Matsushita Electric Works Ltd, 1048, Kadoma, Osaka 571, Japan
K. NOMURA
Evaluation and Reliability Technology Center, Matsushita Electric Works Ltd, 1048, Kadoma, Osaka 571, Japan

With regard to Ni–50Ti–Cu (at%) shape memory alloys, phase transformation characteristics under no stress were studied at the copper content of 6–9 at% using differential scanning calorimetry and X-ray diffraction analysis. In solution-treated materials, B2-orthorhombic transformation occurs at the copper content of 7.6 at% or more. With the increase in copper content, the temperature for B2-orthorhombic transformation gradually increases, whereas the temperature for the orthorhombic–monoclinic phase transformation resulting from decreasing temperature rapidly falls. The phase transformation temperature in 27% cold-worked materials remains virtually constant, despite the copper content, and increases with increasing heat-treatment temperature. The hysteresis in the B2-orthorhombic transformation stabilized via cold working is as low as ~18 K.

1. Introduction

Ni–Ti–Cu alloys prepared by replacing part of the nickel in a near-equiatomic Ni–Ti alloy with copper, possess the shape memory effect [1, 2]. Many studies have been conducted with regard to this alloy. Reports so far published concern the relationship between copper addition and M_S temperature [2–5]; mechanical characteristics [6–8]; and crystal structure [3, 4, 9–11]. It is revealed that copper addition reduces dependency on chemical composition [2], and diminishes the deformation stress in the martensite condition [7, 8]. The crystal structure of the martensite phase at 8 at % Cu or lower is monoclinic [11]. At 10 at % Cu, two-step transformation from B2 (cubic) to orthorhombic to monoclinic results [4, 10]. Over 10 at % Cu, the alloys become brittle and difficult to cold-work [6, 7].

Although it can be predicted that the phase transformation mode changes near 8 at % Cu, there are few studies on phase transformation in the range of 5–10 at % Cu, which includes that important copper content in its scope. Moreover, regarding the relationship between heat-treatment temperature after cold working and phase transformation temperature in this content range (where workability, the industrially important property, is high) adequate understanding is obtained with Ni–Ti alloys [12, 13] but not with Ni–Ti–Cu alloys. Cold working is an important process for improving thermal fatigue characteristics [14, 15].

Hence the present study, using Ni–50Ti–Cu (at %) alloys (wherein part of the nickel is replaced with 6–9 at % copper) deals with the effects of copper content and heat-treatment temperature after cold working on phase-transformation characteristics. The phase-transformation characteristics were determined by differential scanning calorimetry (DSC), and the crystal structures of certain alloys by X-ray diffraction analysis (XRD).

2. Experimental procedure

Using electrolytic nickel, sponge titanium and copper (all with 99.9% purity) as raw materials, the normal arc-melting technique was applied in the argon atmosphere to obtain Ni–Ti–Cu alloy ingots having the specified chemical composition. The ingots were formed into bars by hot forging and swaging, and cold drawn so that the cold-working rate was retained at 27% in the wire interior, with a diameter of 0.60 mm after final drawing. The chemical composition analysed with inductively coupled plasma (ICP) is shown in Table I. The alloy was prepared in three types, with the titanium proportion set practically constant at 50 at %. Copper contents were designed to be 6.1, 7.6 and 9.2 at %. The alloy wires thus obtained were given

TABLE I Chemical composition (at %) of Ni–Ti–Cu alloy wires

Ti	Cu	Ni
49.7	6.1	Remainder
49.9	7.6	Remainder
49.5	9.2	Remainder

two treatments: (i) solution treatment (1023 K, 3600 s, in vacuum) and (ii) heat treatment (723–823 K, 3600 s, in nitrogen atmosphere). Phase transformation characteristics were determined by revealing the temperature-phase transformation heat relationship using DSC. The measuring temperature range was 233–373 K, with the temperature increase rate set to $10\ \mathrm{K\ min^{-1}}$. XRD analysis was performed using CuK_α as the X-ray source and alloy wires, electrolytically ground after removing the oxidized film with emery paper, under a nitrogen gas spray cooled to 258 K with liquid nitrogen.

3. Results and discussion

Figs 1 and 2 show the DSC profiles of Ni–49.7Ti–6.1 Cu (at %) and Ni–49.9Ti–7.6 Cu (at %) alloys, respectively. In both cases (a) represents solution-treated and (b) heat-treated material at 723 K after cold working. It is known that exothermic and endothermic peaks are formed as a result of phase transformation.

In the Ni–49.7Ti–6.1 Cu (at %) alloy, both solution-treated and cold-worked materials form one-step peaks, with no significant difference noted between these materials (Fig. 1). In the 7.6 Cu alloy, however, both materials form one-step peaks and show certain differences: in the solution-treated material, regarding both exothermic and endothermic peaks, the shoulders on the low-temperature side are broad; and in the cold-worked material, such shoulders disappear and become sharp (Fig. 2).

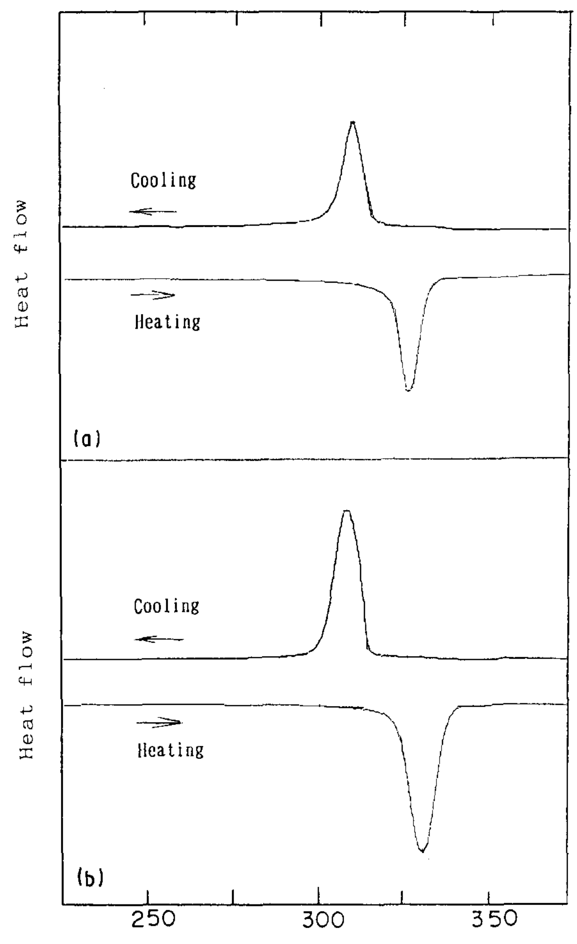

Figure 1 DSC profile of Ni–49.7Ti–6.1 Cu (at %) alloy. (a) Solution treatment; (b) 27% cold working → 723 K heat treatment.

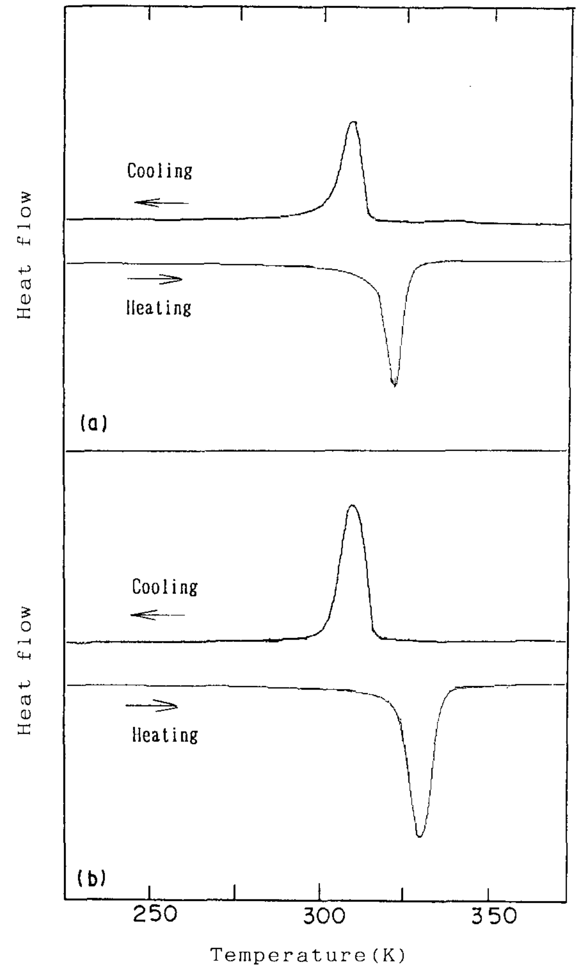

Figure 2 DSC profile of Ni–49.9Ti–7.6 Cu (at %) alloy. (a) Solution treatment; (b) 27% cold working → 723 K heat treatment.

In Ni–49.5Ti–9.2 Cu (at %) alloy, the solution-treated material forms two-step peaks, and in the cold-worked material the peak on the low-temperature side disappears, forming a one-step peak [16]. Similar results are reported with Ni–49.8Ti–8.0 Cu (at %) and Ni–50Ti–10 Cu (at %) alloys [17].

In comparing the DSC profiles between solution-treated and cold-worked materials in the three alloy compositions, it is revealed that the phase-transformation start temperature, A_s, during heating shifts toward the high-temperature side as an effect of cold working, consequently increasing hysteresis.

Consideration of Ni–49.9Ti–7.6 Cu (at %) alloy is as follows. With regard to the phase transformation of the solution-treated Ni–50Ti–Cu (at %) alloy, it is revealed that the alloy undergoes a two-step transformation at 10 at % Cu from B2 to orthorhombic to monoclinic, and a B2-orthorhombic transformation at 20 and 30 at % [4, 10]. Introduction of working distortion into the material's interior at 9.0 at % Cu inhibits orthorhombic–monoclinic transformation, forming a one-step transformation from B2 to orthorhombic [16].

Table II provides measurements of the phase transformation heat of the solution-treated Ni–49.9Ti–7.6 Cu (at %) alloy, and of that heat-treated at 723 K after cold working. The results indicate that cold

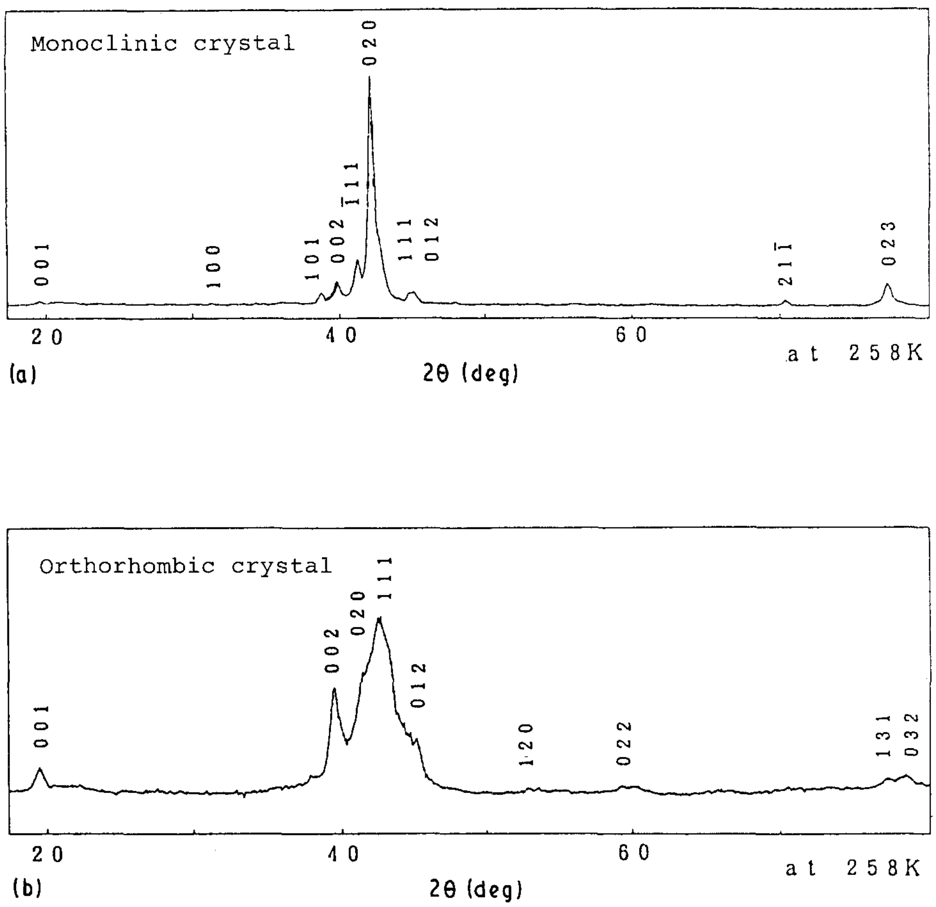

Figure 3 XRD pattern of Ni–49.9Ti–7.6 Cu (at %) alloy. (a) Solution treatment; (b) 27% cold working → 723 K heat treatment.

TABLE II Heat absorbed and generated accompanying phase transformation of Ni–49.9Ti–7.6 Cu (at %) alloy

Treatment	Heat generation (kJ mol^{-1})	Heat absorption (kJ mol^{-1})
(i) Solution treatment	1.07	1.12
(ii) 27% cold working → 723 K heat treatment	0.83	0.80

working decreases phase transformation heat by 0.24 kJ mol^{-1} in the exothermic process, and by 0.32 kJ mol^{-1} in the endothermic. In the Ni–49.7Ti–6.1 Cu (at %) alloy exhibiting B2-monoclinic one-step transformation [11, 16], the phase-transformation heat remains virtually constant whether or not cold working is given. This suggests that cold working inhibited orthorhombic–monoclinic transformation in the 7.6 at % Cu alloy.

Using this alloy, the crystal structure of the martensite phase after phase transformation was determined using XRD for two types of material: (i) solution-treated and (ii) heat-treated at 723 K after cold working. It is known that at 258 K, the measuring temperature, phase transformation is completed in both materials (solution-treated and cold-worked) based on the DSC profile in Fig. 2. The XRD pattern is indicated in Fig. 3. The indices in the diagram are based on the monoclinic crystal in the solution-treated material (a) and the orthorhombic in cold-worked material (b), which implies that all diffraction peaks can be expressed by an index in respective crystal systems. Lattice constants were calculated by the least-squares method (the interplanar spacing is the linear function of the lattice constant). Lattice constants are as follows: $a_0 = 0.28733$ nm, $b_0 = 0.42763$ nm and $c_0 = 0.45575$ nm and $\beta = 96.4126°$ in monoclinic martensite; and $a_0 = 0.28739$ nm, $b_0 = 0.43167$ nm and $c_0 = 0.45548$ nm in orthorhombic martensite. The crystal structure of the material solution-treated at 258 K is monoclinic, and of the material heat-treated at 723 K after 27% cold working it is orthorhombic.

These results show that in Ni–49.9Ti–7.6 Cu (at %) alloy, as well as 9.0 at % Cu alloy [16], cold working inhibits orthorhombic–monoclinic transformation, and that temperatures of 223 K (threshold in DSC measurement) or higher cause a B2-orthorhombic one-step transformation.

Although the phase-transformation peak of solution-treated material is of the one-peak type (as shown in Fig. 2), two-step transformation from B2 to orthorhombic to monoclinic occurs between 286 and 316 K (during cooling). However, phase transformations from B2 to orthorhombic and from orthorhombic to monoclinic overlap, forming a single peak.

Based on these findings and results already publicized [4, 10], the phase diagram of Ni–50Ti–Cu (at %) alloy can be completed. Fig. 4 provides such a diagram, relating copper content and phase transformation temperature, M_S. B2-orthorhombic transformation of copper occurs at 7.6 at % or higher. With

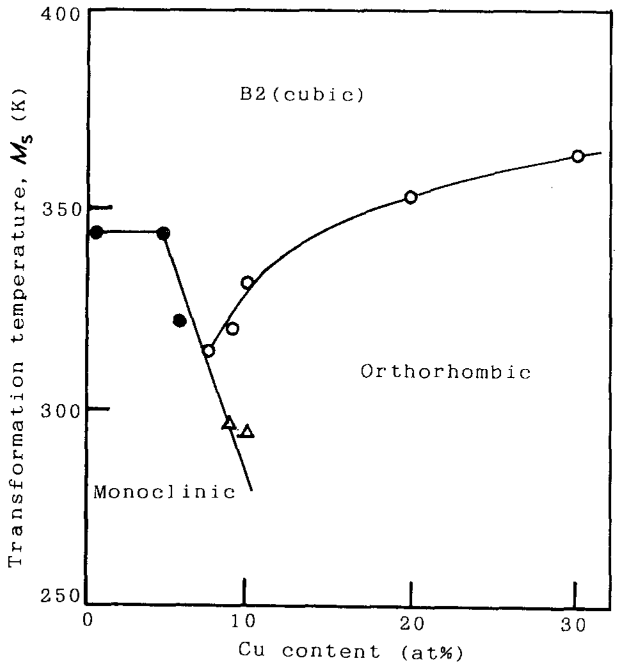

Figure 4 Phase diagram between Cu content and transformation temperature of solution-treated Ni–50Ti–Cu (at %) alloys [4, 10]. ○, B2-orthorhombic; △, orthorhombic–monoclinic; ●, B2-monoclinic.

the increase in copper content, the B2-orthorhombic phase transformation temperature gradually increases, and the temperature for the orthorhombic-monoclinic phase transformation resulting from decreasing temperature rapidly falls. At 6.1 at % Cu or lower, however, B2-monoclinic transformation occurs. Above 5 at % Cu, phase transformation temperature rapidly decreases.

We now consider the phase transformation temperatures when heat treatment is given at various temperatures after cold working. Fig. 5 shows the DSC profile of Ni–49.5Ti–9.2 Cu (at %) alloy. When the heat-treatment temperature is elevated to 823 K, the shoulders on the low-temperature side of both exothermic and endothermic peaks become broad. This can be attributed to alleviated processing strain in the material's interior, which triggers orthorhombic–monoclinic phase transformation. With regard to 6.1 and 7.6 at % Cu alloys DSC profiles were also obtained. In both alloys, broad shoulders as seen in 9.2 at % Cu alloy (Fig. 5c) were not noted, even though the heat-treatment temperature was increased to 823 K. Hysteresis tended to diminish in all alloys as the heat-treatment temperature increased.

Based on the obtained DSC profiles, the relationship between copper content and phase transformation temperature of alloys heat-treated at various temperatures after cold working was determined: the result is shown in Fig. 6. The phase-transformation temperature in the diagram represents the phase-transformation start temperature, M_S, from B2 to orthorhombic in 9.0 and 7.6 at % Cu alloys, and that from B2 to monoclinic in 6.0 at %. The phase-transformation temperature remains virtually constant, despite the copper content, except for an increase of 2–3 K at 9.1 at %. This agrees with the

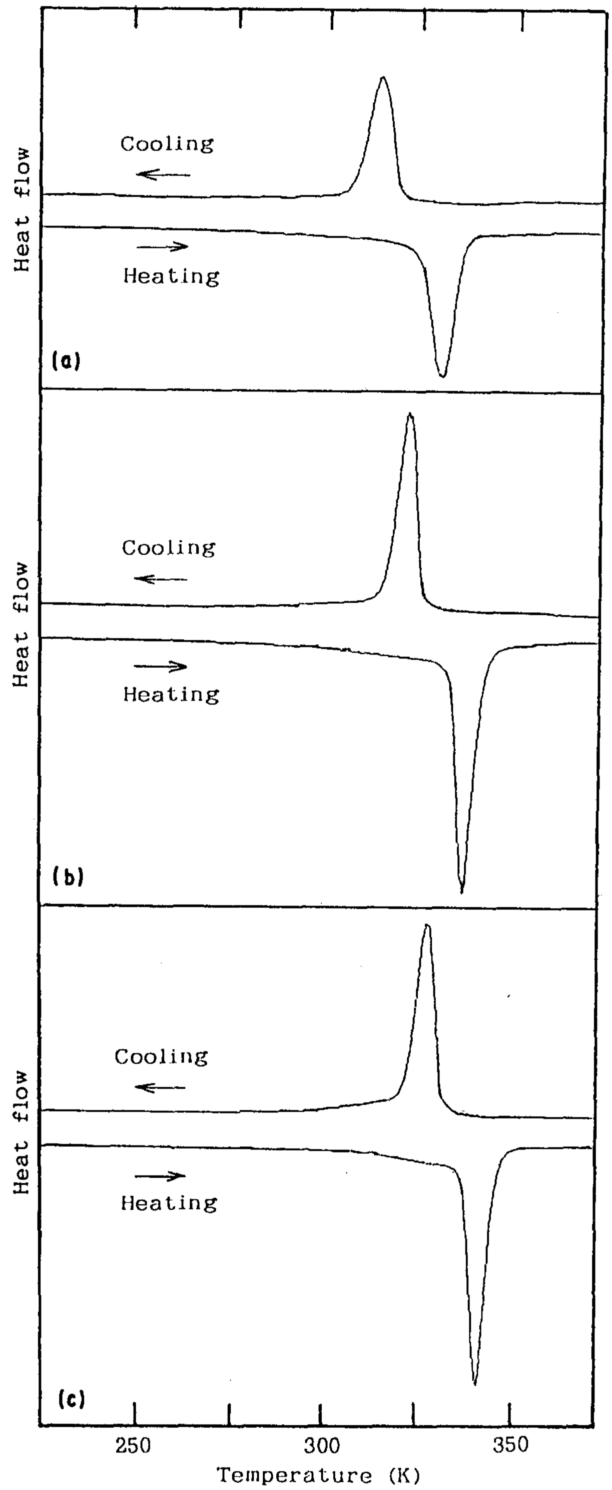

Figure 5 DSC profile of Ni–49.5Ti–9.2 Cu (at %) alloy (27% cold worked). Heat treatments (a) 723; (b) 773; (c) 823 K.

results reported in References 2 and 4. With the increase in heat-treatment temperature, however, phase-transformation temperature increases at all compositions, in agreement with the results for Ni–50Ti–10 Cu (at %) [17, 18].

Fig. 7 indicates the relationship between hysteresis and copper content of alloys heat treated at 723 K after 27% cold working. Hysteresis was here calculated based on phase-transformation temperature obtained by DSC, and is in the static condition under no stress. It registers 22 K in 6.1 at % Cu alloy and rapidly decreases at 7.6 at % or more of copper, reaching ~ 18 K. Thus hysteresis in B2-orthorhombic

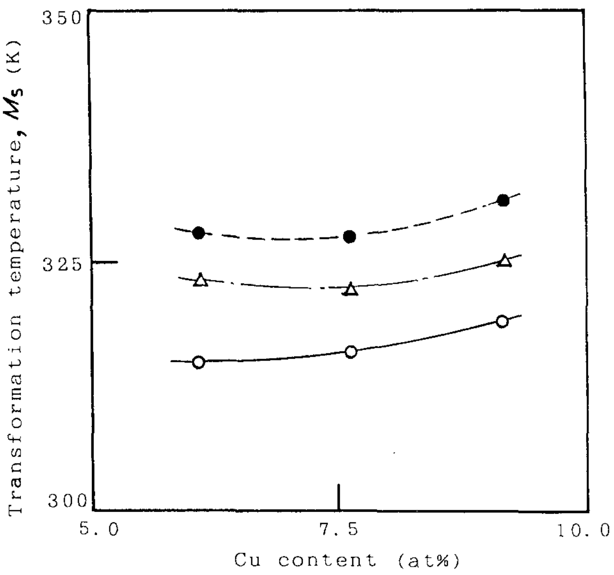

Figure 6 Relationship between Cu content and transformation temperature of Ni–50Ti–Cu (at %) alloy (27% cold worked). Heat treatments ○, 723; △, 773; ●, 823 K.

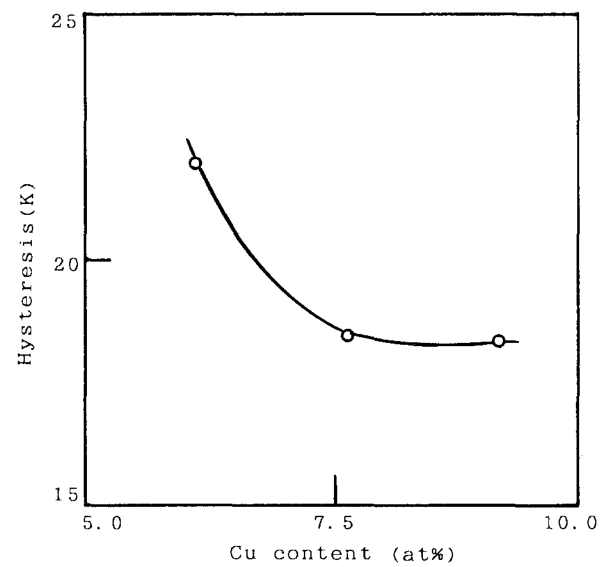

Figure 7 Relationship between Cu content and hysteresis of Ni–50Ti–Cu (at %) alloys (723 K heat treatment after 27% cold working).

transformation stabilized via cold working is smaller than that in B2-monoclinic transformation. This characteristic is advantageous in industrial applications.

The Ni–50Ti–10 Cu shape-memory alloy is best suited to application as an actuator in industry [8]. The features of this alloy: small hysteresis and low strength of the martensite phase [8], result from the B2-orthorhombic transformation [16], and the threshold of the copper content for this transformation is revealed in the present paper. Practicality requires that thermal fatigue is as low as possible: thus alloy processing cannot do without cold working. Furthermore, the relationship between heat-treatment temperature after cold working and phase-transformation temperature is very important in application, as has been revealed by this study. Thus the present results are important in terms of industry as well as engineering science.

4. Conclusions

In Ni–Ti–Cu alloys replacing part of the nickel content in near-equiatomic Ni–Ti alloy with 6–9 at % Cu, the effects on phase-transformation characteristics of alloy composition and heat-treatment temperature after cold working were studied using DSC and XRD analysis. In solution-treated materials, B2-orthorhombic transformation occurs at 7.6 at % or more of copper. With the increase in copper content, the phase-transformation temperature gradually increases, whereas the temperature for orthorhombic to monoclinic resulting from decreasing temperature rapidly falls. Introduction of working distortion into the interior of Ni–50Ti–7.6 Cu (at %) alloy inhibits orthorhombic–monoclinic phase transformation, consequently permitting a one-step transformation from B2 to orthorhombic only.

In 27% cold-worked materials, the phase-transformation temperature remains constant, despite the copper content. However, it increases with increasing heat-treatment temperature, diminishing hysteresis. The hysteresis in B2-orthorhombic transformation stabilized via cold working is $\sim$ 18 K, low compared with B2-monoclinic transformation.

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