Cu-Content Dependence of Shape Memory Characteristics in Ti-Ni-Cu Alloys*

By Tae Hyun Nam**, Toshio Saburi*** and Ken'ichi Shimizu****

Cu-content dependence of the shape memory characteristics in Ti-Ni-Cu alloys has been investigated by means of electrical resistivity measurements, differential scanning calorimetry and constant load thermal cycling tests. Transformation start temperature for the B19' martensite, M_s , decreased largely, whereas that for the B19 martensite, M'_s , increased slightly with increasing Cu-content. Thus, the temperature range over which the B19 martensite was stable became wide. The maximum recoverable elongation associated with the B2→B19 transformation decreased from 3.2 to 2.7%, and the hysteresis associated with the transformation decreased from 11 to 4 K with increasing Cu-content from 10 to 20 at%. The temperature dependence of stress required to induce the B2→B19 transformation was nearly constant (about 8 MPa/K) without regard to the Cu content for the alloys with above 10 at%Cu. The residual elongation decreased with increasing Cu content.

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Keywords: shape memory alloy, titanium-nickel-copper alloy, constant load thermal cycling test, transformation temperature, transformation elongation, transformation hysteresis

I. Introduction

It has been known that ternary alloying element addition to near equiatomic Ti-Ni shape memory alloys affects their transformation behavior⁽¹⁾⁻⁽⁴⁾ and shape memory characteristics⁽⁵⁾⁻⁽⁸⁾. Among the alloying elements, Cu is a unique one and has the following effect. By substituting Cu for Ni by 10 at%, the alloy transforms in two stages⁽⁴⁾, i.e., from cubic (B2) to orthorhombic (B19), and then from orthorhombic to monoclinic (B19'), whereas the equiatomic Ti-Ni alloy transforms in one stage⁽⁹⁾, i.e., from cubic (B2) to monoclinic (B19'). By further substitution exceeding 10 at%, the alloy transforms in one stage⁽⁴⁾, i.e., from cubic (B2) to orthorhombic (B19).

In addition, substitution of Cu has been known to reduce the composition sensitivity of martensitic transformation start temperature⁽¹⁰⁾, hysteresis of the pseudo-elasticity⁽⁷⁾⁽⁸⁾ and the flow stress level in the martensite state⁽⁷⁾, and to prevent the X-phase (Ti_3Ni_4) precipitation⁽⁷⁾.

Transformation hysteresis associated with the B2⇌B19 transformations in a Ti-Ni-Cu alloy was reported to be about 15 K under zero stress⁽⁴⁾, which is in-between those of the B2⇌B19' and B2⇌R transformations in Ti-Ni alloys. Therefore, in a practical point of view, it is expected that the B2⇌B19 transformations in ternary Ti-Ni-Cu alloys fill the gap in transformation

hystereses between the two types of transformations in binary Ti-Ni alloys. Recently, by means of constant load thermal cycling tests, the present authors showed that the B2⇌B19 transformations in a Ti-40Ni-10Cu (at%) alloy lies in-between the B2⇌B19' and B2⇌R transformations in a thermo-mechanically treated 49.8Ti-50.2Ni (at%) alloy, with respect to the transformation elongation, the transformation hysteresis and the stress dependence of transformation temperatures⁽¹¹⁾. However, the Cu-content dependence of the shape memory characteristics associated with the B2⇌B19 transformations are not known well.

The purpose of the present study is to investigate the Cu-content dependence of shape memory characteristics, such as transformation temperatures, transformation elongations, transformation hystereses, in Ti-Ni-Cu alloys.

II. Experimental Procedure

Six kinds of Ti-Ni-Cu alloys were used and their nominal compositions were $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ (at%) ($x=5, 7.5, 10, 12.5, 15, 20$). The alloys were prepared by vacuum induction melting in a graphite crucible. The ingots of $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ (at%) ($x=5, 7.5, 10$) alloys were hot rolled at 1123 K to obtain 1.4 mm thick sheets. Specimens for electrical resistivity measurements, differential scanning calorimetry (DSC) and constant load thermal cycling tests were cut from the sheets. Since $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ (at%) ($x=12.5, 15, 20$) alloys were so brittle that hot rolling could not be made, specimens for the tests were cut directly from the ingots. All the specimens were solution treated at 1123 K for 3.6 ks, and then electropolished with an electrolyte which consists of 95% CH_3COOH and 5% HClO_4 in volume.

Electrical resistivity measurements were made to observe general features of the transformation character-

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** Graduate Student, Suita-Ibaraki Campus, Osaka University.

*** Department of Materials Science and Engineering, Faculty of Engineering, Osaka University, 2-1, Yamada-oka, Suita, Osaka 565, Japan.

**** The Institute of Scientific and Industrial Research, Osaka University, 8-1, Mihoga-oka, Ibaraki, Osaka 567, Japan.

Fig. 1 Electrical resistivity vs. temperature curves for Ti-Ni-Cu alloys.

istics by means of typical four terminal technique. DSC measurements were made to measure the transformation temperatures and the heat of transformation by using a Rigaku DSC-8230 type calorimeter at the cooling/heating rate of 0.17 K/s.

Constant load thermal cycling tests were made to investigate transformation behavior under load. The testing method was the same as that described in the previous paper⁽¹¹⁾. Fluorine compound inert liquid was used as a temperature medium for 5 to 10 at%Cu alloys, whereas silicon oil was used for 12.5 to 20 at%Cu alloys.

III. Results and Discussion

1. Transformation behavior of Ti-Ni-Cu alloys without load

Figure 1 shows electrical resistivity vs. temperature curves of the Ti-Ni-Cu alloys. As can be seen in this figure, the shape of the curves changes strongly depending on Cu content. In the 5 at%Cu alloy, the resistivity vs. temperature curve on cooling has only one minimum, which corresponds to M_s (transformation start temperature of the B19' martensite[†]), whereas in the alloys containing 7.5 to 15 at%Cu, the curve has two minima, one

of which at higher temperature corresponds to M'_s (transformation start temperature of the B19 martensite[†]) and the other to M_s . The separation between the M'_s and M_s is very small (7 K) in the 7.5 at%Cu alloy and increases with increasing Cu content. By increasing Cu content above 15 at%, the resistivity vs. temperature curve on cooling has only one minimum (M'_s) again, as seen in the curve of the 20 at%Cu alloy. The resistivity vs. temperature curve on heating changes in the same manner. That is, in the 5 at%Cu alloy, the curve has only one maximum (A_s), whereas in the alloys containing 7.5 at% to 15 at%Cu, the curve has two maxima, one of which at lower temperature corresponds to A_s and the other corresponds to A'_s . By increasing Cu content above 15 at%, the resistivity vs. temperature curve on heating has only one maximum (A'_s) again, as seen in the curve of the 20 at%Cu alloy.

From X-ray diffraction experiments which have been made on Ti-Ni-Cu alloys at various temperatures⁽¹²⁾, the following has been found. The resistivity increase on cooling after the minimum in 5 at%Cu alloy is due to the B2 $\rightarrow$ B19' transformation. The resistivity increase after

[†] Complete definition of the transformation temperatures are given in the footnote of Table 1.

the first minimum in the 7.5 at%Cu alloy is due to the $B2 \rightarrow B19$ transformation, whereas that after the second minimum is due to inseparable two transformations, $B2 \rightarrow B19'$ and $B19 \rightarrow B19'$. Those after the first and second minima in 10 to 15 at%Cu alloys are due to the $B2 \rightarrow B19$ and $B19 \rightarrow B19'$ transformations, respectively. The resistivity increase after the minimum in the 20 at%Cu alloy is due to the $B2 \rightarrow B19$ transformation. A similar result has been reported by Shugo *et al.*⁽⁴⁾

It is to be noted here that the resistivity increase due to the $B2 \rightarrow B19$ transformation becomes large, whereas that due to the $B19 \rightarrow B19'$ transformation is largest in the 10 at%Cu alloy, and decreases with increasing Cu content.

In Fig. 2 are shown the DSC curves which correspond to the electrical resistivity vs. temperature curves in Fig. 1. In contrast to the latter curves, the shape of the former curves scarcely changes depending on Cu content. That is, irrespective of Cu-content, only one clear peak appears on each of the cooling and heating curves. The clear peaks in the cooling and heating curves for the 5 at%Cu alloy are known to be due to the $B2 \rightleftharpoons B19'$ transformations and those for 7.5 at%Cu to 20 at%Cu alloys to be due to the $B2 \rightleftharpoons B19$ transformations, from X-ray diffraction experiments⁽¹²⁾.

It should be noted here that DSC peaks for the

$B19 \rightleftharpoons B19'$ transformations are very diffuse and almost indiscernible, whereas the peaks for the $B2 \rightleftharpoons B19$ transformation are very sharp and clear. This is contrary to the change in electrical resistivity, Fig. 1, where the resistivity increase due to the $B19 \rightarrow B19'$ transformation is large, whereas that due to the $B2 \rightarrow B19$ transformation is small. The diffuse DSC peaks for the $B19 \rightleftharpoons B19'$ transformations are not suitable for determining the transformation temperatures.

Since the $B2 \rightleftharpoons B19$ transformations are clear in the DSC curves and the $B19 \rightleftharpoons B19'$ transformations are clear in the electrical resistivity vs. temperature curves, the former transformation temperatures are determined from the DSC curves and the latter from the electrical resistivity vs. temperature curves, respectively. The transformation temperatures were determined by the extrapolation method⁽¹³⁾⁽¹⁴⁾ and they are shown in Table 1.

In order to see the relations among the three phases, B2, B19, B19', in Ti-Ni-Cu alloys, M_s' and M_s are plotted against Cu content in Fig. 3. As seen in Fig. 3, with increasing Cu content, the M_s' increases slightly, and the M_s decreases largely. Therefore, the temperature range over which the B19 martensite is stable becomes wider with increasing Cu content.

Heat of transformation was obtained by measuring the

Fig. 2 DSC curves for Ti-Ni-Cu alloys.

Table 1 Transformation temperatures of $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ (at%) alloys*.

x	M'_s	M'_f	A'_s	A'_f	M_s	M_f	A_s	A_f
5					309	295	311	330
7.5	297		305	310	290	220	236	298
10	313	300	315	324	292	179	192	300
12.5	322	304	315	333	280	170	180	286
15	327	310	319	337	249		203	262
20	329	314	320	338				

* The primed M'_s and M'_f are start and finish temperatures of the forward transformation and A'_s and A'_f are those of the reverse transformation, respectively, for the $\text{B2} \rightleftharpoons \text{B19}$, and the non-primed ones are those for the $\text{B19} \rightleftharpoons \text{B19}'$ transformation. The transformation temperatures in 5 at%Cu alloy are for the $\text{B2} \rightleftharpoons \text{B19}$ transformation.

Fig. 3 Cu-content dependence of transformation temperatures (M'_s , M_s) in Ti-Ni-Cu alloys.

integral areas of peaks of the DSC curves. The obtained values are given in Table 2. The heat of transformation for the $\text{B2} \rightarrow \text{B19}'$ is larger than that for the $\text{B2} \rightarrow \text{B19}$, and the latter decreases slightly with increasing Cu content. The heat of transformation for the $\text{B19} \rightarrow \text{B19}'$ could not be obtained because the DSC peaks for the $\text{B19} \rightarrow \text{B19}'$ are very diffuse and almost indiscernible. In addition, since the $\text{B2} \rightarrow \text{B19}$ and $\text{B2} \rightarrow \text{B19}'$ transformations in the 7.5 at%Cu alloy are not separated in the DSC curve, the heat of transformation for the individual transformation could not be obtained.

2. Transformation behavior of Ti-Ni-Cu alloys under load

Thermal cycling tests were made on the Ti-Ni-Cu alloys under various applied stresses (from 3.4 MPa to

Table 2 Heat of transformation (ΔH) of $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ (at%) alloys obtained by DSC measurements*.

x	5	10	12.5	15	20
ΔH (kJ/mol.)	-1.46	-0.93	-0.90	-0.93	-0.86

* The value of 5 at%Cu alloy is associated with the $\text{B2} \rightarrow \text{B19}'$ transformation and the others are associated with the $\text{B2} \rightarrow \text{B19}$ transformation.

164.3 MPa). In order to observe the characteristics of the Cu-content dependence of the transformation behavior, the elongation (ϵ)-temperature (T) curves under about 40 MPa are compared as shown in Fig. 4.

The curve for the 5 at%Cu alloy shows that the specimen, on cooling, starts to elongate suddenly at a temperature. This sudden elongation is ascribed to the $\text{B2} \rightarrow \text{B19}'$ transformation, and therefore the temperature is defined as its M_s under load ($M_s(l)$)^{††}. A tangential extrapolation method⁽¹³⁾⁽¹⁴⁾ was used to determine the $M_s(l)$, as indicated in the figure. The temperature, where the $\epsilon-T$ loop is closed, is defined as $M_f(l)$. The elongation associated with the $\text{B2} \rightarrow \text{B19}'$ transformation is that occurring between $M_s(l)$ and $M_f(l)$. $A_s(l)$ and $A_f(l)$ on heating are defined as shown in the figure.

In the cooling curve for the 7.5 at%Cu alloy, the sudden elongation seen at a temperature is ascribed to the $\text{B2} \rightarrow \text{B19}$ transformation, and therefore the temperature is defined as its $M'_s(l)$. A large elongation occurs in a very narrow (less than 3 K) temperature range. On further cooling, the elongation increases gradually, and $M'_f(l)$ and $M_s(l)$ are not distinguished. This seems to be because the separation between the M'_s and M_s is very small, as shown in Figs. 1 and 2, and the two transformations overlap with each other. Therefore, the elongations associated with the $\text{B2} \rightarrow \text{B19}$ and $\text{B2} \rightarrow \text{B19}'$ transformations could not be obtained separately.

The curve for the 10 at%Cu alloy is characterized by the two stages which correspond to the $\text{B2} \rightarrow \text{B19}$ and $\text{B19} \rightarrow \text{B19}'$ transformations. The elongation associated with the first stage is ascribed to the $\text{B2} \rightarrow \text{B19}$ transformation and that associated with the second stage is to the $\text{B19} \rightarrow \text{B19}'$ transformation.

The sudden elongation seen in the cooling curves for the 12.5 to 20 at%Cu alloys is ascribed only to the $\text{B2} \rightarrow \text{B19}$ transformation, and the temperatures where the sudden elongations start are $M'_s(l)$. The temperature where the $\epsilon-T$ loop is closed is defined as $M'_f(l)$. The elongation associated with the $\text{B2} \rightarrow \text{B19}$ transformation is that occurring between $M'_s(l)$ and $M'_f(l)$.

As for the Cu-content dependence of transformation elongation, the following is found from Fig. 4. The elongation associated with the $\text{B2} \rightarrow \text{B19}$ transformation decreases from 2.7 to 2.1% with increasing Cu content from 10 to 20 at%. The transformation elongation associated with the $\text{B2} \rightarrow \text{B19}'$ under the same load (40 MPa)

^{††} In order to distinguish the transformation temperature under load from that without load (M_s), the former is designated as $M_s(l)$.

Fig. 4 Elongation (ϵ)-temperature (T) curves under the nearly same load (about 40 MPa) for Ti-Ni-Cu alloys.

Fig. 5 Temperature dependence of transformation stress in Ti-Ni-Cu alloys.

is smaller than those associated with the B2→B19, as seen in the 5 at%Cu alloy. However, if we compare maximum recoverable elongation, that associated with the B2→B19' is larger than that associated with the B2→B19 (see Fig. 7).

As for the Cu-content dependence of transformation hysteresis, the following is found also from Fig. 4. The hysteresis associated with the B2⇌B19' transformations in the 5 at%Cu alloy is 17 K, which is larger than those associated with the B2⇌B19 transformations in the alloys with 7.5 to 20 at%Cu. The hysteresis associated with the B2⇌B19 transformations decreases from 12 to 4 K with increasing Cu-content from 7.5 to 20 at%.

(1) Stress dependence of transformation temperatures

The transformation temperatures, $M_s'(l)$ and $M_s(l)$, obtained from $\varepsilon-T$ curves under various loads are plotted against the stresses in Fig. 5. Those of the 5 at%Cu alloy increase linearly with increasing applied stress in the stress range below 40 MPa, above which a deviation from the linearity occurs. Similarly, the deviation from linearity occurs at 90 MPa in the alloys with 10 to 20 at%Cu. We believe that these deviations from linearity are closely related to the plastic deformation introduced during the transformation under load. However, the true origin of the deviation is not clear yet. In this way, those stress vs. temperature curves are divided into two sections. However, the stress vs. temperature curve for the 7.5 at%Cu alloy is divided into three sections, i.e., below 60 MPa, from 60 to 80 MPa and above 80 MPa. The slope of the curve below 60 MPa represents the temperature dependence of stress required to induce the B2→B19 transformation, and that between 60 and 80 MPa does the temperature dependence of stress required to induce the B2→B19' transformation. The temperature extrapolated to zero stress (dotted line) for the B2→B19' transformation agrees well with M_s obtained from an electrical resistivity vs. temperature curve. The change of the slope at 80 MPa is considered to be due to plastic deformation introduced during the transformation under load.

The temperature dependence of the stress required to induce the B2→B19' transformation is almost constant without regard to the Cu content, i.e., 4.6 MPa/K in 5 at%Cu alloy and 4.5 MPa/K in 7.5 at%Cu alloy. Also, the stress required to induce the B2→B19 transformation in the alloys with 10 to 20 at%Cu is almost constant (about 8 MPa/K) without regard to the Cu content but that in the 7.5 at%Cu alloy (12.5 MPa/K) is different from it. The stress level where plastic deformation occurs increases from 40 to 90 MPa with increasing Cu content from 5 to 10 at%, but it is almost constant (about 90 MPa) for the alloys with Cu contents above 10 at%.

(2) Stress dependence of transformation elongation and residual elongation

The transformation elongation and residual elongation obtained from thermal cycling tests under various

stresses are plotted against applied stress, as shown in Fig. 6(a) and (b), respectively. The residual elongation is defined as an unrecoverable elongation after thermal cycling, i.e., cooling the specimen to a temperature of $M_f'(l)$ or $M_f(l)$ and then heating it to a temperature above $A_f'(l)$ or $A_f(l)$ under load.

In the 5 at%Cu alloy, the transformation elongation associated with the B2→B19' is seen to increase slowly for stresses less than 20 MPa and quickly above 20 MPa with increasing applied stress. When the stress is less than 50 MPa, the transformation elongation is almost completely recoverable on heating, and hence the residual elongation is nearly zero, Fig. 6(b). Therefore, the transformation elongation at 50 MPa, i.e., 3.3% is the maximum recoverable one.

The transformation elongation plotted in Fig. 6(a) for the alloys containing Cu from 10 to 20 at% is associated with the B2→B19. As seen in Fig. 6(a), its stress dependence is quite different from that associated with the B2→B19' transformation in the 5 at%Cu alloy. That is, the former increases quickly for stresses less than 30 MPa and slowly above 30 MPa with increasing applied stress. Since, in the alloys containing Cu from 10 to 20 at%, the residual elongations are nearly zero for stresses less than about 90 MPa, Fig. 6(b), the transformation elongations at 90 MPa are the maximum recoverable ones. The obtained maximum recoverable elongations are plotted against Cu-content in Fig. 7, from which they are found to decrease linearly with increasing Cu content.

As seen in Fig. 6(b), residual elongation decreases with increasing Cu content. This means that amounts of irreversible microstructural changes (for example, introduction of dislocations) during the forward and reverse transformations become small with increasing Cu content. It is thought that this is related to the Cu-content dependence of the transformation hysteresis in Fig. 4. That is, the irreversible microstructural changes which may hinder the motion of the interface between the parent and martensite phases become small, and consequently the transformation hysteresis small, with increasing Cu content.

(3) Heat of transformation associated with the B2→B19 transformation

The effect of stress (σ) on transformation temperature (T) is described by the Clausius-Clapeyron type equation⁽¹⁵⁾:

$$d\sigma/dT = \Delta H \cdot \rho / T_0 \cdot \varepsilon$$

where ΔH is the heat of transformation, T_0 the equilibrium temperature, ε the transformation elongation and ρ the density. This equation describes the relation among $d\sigma/dT$, ΔH , T_0 and ε in a monocrystalline material. Using this equation, the heat of transformation can be calculated from $d\sigma/dT$, T_0 , ε which are experimentally obtained for the monocrystalline material.

We think that it is applicable also to a polycrystalline material if we assume an ideal case that each grain

Fig. 6 Stress dependence of transformation elongations, (a), and residual elongations, (b), in Ti-Ni-Cu alloys. Only the B2→B19 transformation elongation is plotted in the 10 at%Cu alloy.

Fig. 7 Cu-content dependence of maximum recoverable elongations in Ti-Ni-Cu alloys.

transforms completely to the variants most favourable with respect to the applied stress. In this case, in order to obtain the heat of transformation, we should use $d\sigma/dT$, T_0 , ϵ for the polycrystalline material for the ideal case. However, the ideal $d\sigma/dT$, T_0 , ϵ for the polycrystalline material are difficult to estimate from an experiment. Thus, we tentatively used $d\sigma/dT$, ϵ , T_0 obtained from the $\sigma-T$ relation (Fig. 5), from the $\epsilon-T$ curves (the obtained values which correspond to the maximum recoverable elongation are shown in Fig. 7 and Table 3) and as $1/2 (M_s + A_f)^{(18)}$, respectively. The ratio of the molar mass to the molar volume is used as the density, which is about

Table 3 Calculated heat of transformation associated with the B2→B19 transformation in $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ (at%) alloys.

x	$d\sigma/dT$ (MPa/K)	T_0 (K)	ϵ	ΔH (kJ/mol.)	$\Delta H'$ (kJ/mol.)
10	8.4	319	0.032	-0.72	-1.19
12.5	8.3	328	0.030	-0.69	-1.17
15	8.2	332	0.029	-0.67	-1.14
20	7.8	334	0.027	-0.60	-1.00

6.4 g/cm^3 . The calculated heats of transformations, ΔH , are shown in Table 3. As seen in the table, the heat of transformation associated with the B2→B19 decreases slightly with increasing Cu-content. This Cu-content dependence agrees with that of the heat of transformation obtained by the DSC measurement, Table 2, the value itself being a little different from each other.

The calculated values (Table 3) are about 25% smaller than the experimental values obtained by DSC measurement (Table 2). A similar disagreement between the calculated value and the experimental one has been reported by Miyazaki *et al.* for a polycrystalline Ti-Ni-Fe alloy⁽⁵⁾. They interpreted this disagreement in the way as follows. They made constant temperature tensile tests to obtain the relation between σ and T , and adopted the Lüders elongation as ϵ . As pointed out by them, since transformation was not completed in the region where

the Lüders elongation occurs, ε was underestimated. Thus, the calculated value was smaller than the experimental one.

Polycrystalline materials were used also in the present study. However, constant load thermal cycling tests were used for obtaining the relation between σ and T , and the maximum value of the recoverable elongation which occurs between $M'_s(l)$ and $M'_f(l)$ was adopted as ε . Since $M'_f(l)$ was defined as the temperature where the ε - T curve is closed, we believe that the transformation was complete when $M'_f(l)$ was attained. Therefore, no underestimation of ε due to an incompleteness of transformation may be implied. Nevertheless, the calculated value and the experimental value do not agree, as mentioned before. The disagreement may be explained by considering that the variants near grain boundaries are not oriented to the direction which is in favour of the applied stress, because the stress field near the grain boundaries hinders the variants to orient to the applied stress. Since recoverable deformation in shape memory effects is generally accomplished by means of reorientation of martensite variants⁽¹⁹⁾, the recoverable transformation elongation decreases with decreasing volume ratio of the favourably oriented variants. Larger stresses are needed to orient the variants near grain boundaries to the direction. However, plastic deformation occurs before the stress level is reached.

In contrast to the disagreement in heat of transformation between the calculated and the experimentally obtained on polycrystalline materials, good agreements have been reported on monocrystalline materials; i.e., on a Au-Cd alloy by Miura *et al.*⁽¹⁶⁾ and on a Ti-Ni alloy by Takei *et al.*⁽¹⁷⁾. According to Takei *et al.*⁽¹⁷⁾, the experimentally obtained transformation elongation was close to that predicted by calculating the shape-changes.

If we adopt calculated maximum elongation for monocrystal as ε , the calculated heat of transformation ($\Delta H'$) are found to be about 25% larger than the experimental, as shown in Table 3. Therefore, a good agreement between the experimental and calculated heat of transformation is obtained if we adopt an intermediate value of the experimental elongation for polycrystal and the calculated maximum elongation for monocrystal. The ideal ε for the polycrystalline material is considered to correspond to the intermediate value. However, it is very difficult to obtain the ideal elongation experimentally, since stress fields near grain boundaries hinder the variants to orient to applied stress, as mentioned before.

In order to know the reason for the Cu-content dependence of heat of transformation, the Cu-content dependence of $d\sigma/dT$, ε and T_0 used in the calculation are examined. $d\sigma/dT$ associated with the B2→B19 transformation is almost constant (about 8 MPa/K) without regard to Cu-content, Fig. 5, and T_0 increases with increasing Cu content, Table 3. These Cu-content dependences of $d\sigma/dT$ and T_0 are contrary to the decrease in the heat of transformation. On the other hand, ε decreases with increasing Cu content, Fig. 7. Therefore, the decrease in heat of transformation with

increasing Cu content is concluded to be due to the decrease in transformation elongation, ε .

IV. Conclusions

The relation between shape memory characteristics (transformation temperature, transformation elongation, transformation hysteresis) and Cu content in $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ (at%) ($x=5, 7.5, 10, 12.5, 15, 20$) alloys was investigated by means of electrical resistivity measurements, differential scanning calorimetry and constant load thermal cycling tests. The results obtained are summarized as follows:

(1) The increase in resistivity due to the B2→B19 transformation becomes large, whereas that due to the B19→B19' transformation is largest at 10 at%Cu, and decreases with increasing Cu content.

(2) M'_s increases slightly, whereas M_s decreases largely with increasing Cu content. Thus, the temperature range where the B19 martensite is stable becomes wider with increasing Cu content.

(3) The maximum recoverable elongation associated with the B2→B19' transformation in the 5 at%Cu alloy is 3.3%, and that associated with the B2→B19 transformation decreases from 3.2 to 2.7% with increasing Cu content from 10 to 20 at%.

(4) The transformation hysteresis associated with the B2⇌B19' in 5 at%Cu alloy is 17 K, and that associated with the B2⇌B19 decreases from 12 to 4 K with increasing Cu-content from 7.5 to 20 at%.

(5) The temperature dependence of stress required to induce the B2→B19 transformation is nearly constant (about 8 MPa/K) without regard to Cu-content for the alloys with Cu contents above 10 at%.

(6) Residual elongation decreases with increasing Cu content.

(7) Heat of transformation associated with the B2→B19 decreases slightly with increasing Cu content.

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