On the Nature of Martensitic Transformation in the Ternary Ni-Zn-Cu Alloys

By Norihiko Nakanishi*, Masato Hayashi** and Yuichiro Murakami***

The martensitic transformation from the B2 to L1₀ structure, and the composition and temperature dependence of the lattice parameters in the ternary Ni-Zn-Cu alloys were investigated. The axial ratio (c/a) of the L1₀ lattice decreased slightly with increase in temperature and showed a discontinuous drop at the L1₀ to B2 transformation temperature. The nature of this transformation was considered to be slightly of the 2nd order transformation, although it was almost of the 1st order. The habit plane of this martensite was also studied. The phase stability and the characteristics of martensitic transformation in the nickel base alloys were discussed briefly as a function of the electron atom ratio (e/a).

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I. Introduction

The martensitic transformation in the nickel base alloys has been investigated by many metallurgists in alloys such as Ni-Al, Ni-Zn, Ni-Zn-Cu, Ni₃Sn and Ni-Cu-Sn. The Ni-Al⁽¹⁾⁻⁽⁴⁾, Ni-Zn⁽⁵⁾⁻⁽⁸⁾ and Ni-Zn-Cu⁽⁹⁾⁻⁽¹³⁾ alloys undergo a martensitic transformation from the CsCl(B2)-type ordered cubic phase (β_2) to the AuCuI(L1₀)-type ordered tetragonal structure (α'_2), and the Ni₃Sn⁽¹⁴⁾ and Ni-Cu-Sn⁽¹⁵⁾⁽¹⁶⁾ alloys from the DO₃-type ordered cubic phase (β_1) to the 2H-type orthorhombic structure (γ'_1). In the Ni-Al and Ni-Zn-Cu alloys, the martensitic transformation has been reported to be thermoelastic⁽³⁾⁽¹³⁾, and the shape memory effect has been observed⁽²⁾⁽¹²⁾. Considering the increasing interest on the shape memory effect in Ti-Ni and noble metal base β phase alloys⁽¹⁷⁾, it is important to study the martensitic transformation also in the nickel base alloys.

In the binary Ni-Zn alloy, the starting temperature of the B2 to L1₀ transformation upon

cooling is very high (950–1080 K depending on composition)⁽⁵⁾⁽¹⁸⁾. This transformation temperature has been found to be depressed by the substitution of Cu for Ni atoms in Ni_{100-x-y}Zn_yCu_x ($y=48$ and 50) alloys⁽¹⁰⁾⁽¹¹⁾; the starting temperature of the martensitic transformation upon cooling, M_s , is about 290 K, when x equals about 20.5 and 18 in alloys with $y=48$ and 50, respectively. In the ternary Ni-Zn-Cu alloys having Zn concentration more than 50 at %, the martensitic transformation and the composition dependence of lattice parameters have not been studied until now. Moreover, in the binary Ni-Zn alloy, the axial ratio (c/a) of the L1₀ lattice has been shown to decrease slightly, when the temperature has increased up to the transformation temperature⁽⁸⁾, suggesting that the L1₀ to B2 transformation in the Ni-Zn alloy has slightly the nature of the 2nd order transformation. Then in the present work, the composition and temperature dependence of the lattice parameters and phase relation in the Ni_{100-x-y}Zn_yCu_x ($y=52, 54$ and 56) alloys were investigated by X-ray diffraction and optical microscopy. The habit plane of the Ni-Zn-Cu martensite was also analyzed by electron microscopy.

II. Experimental

The Ni-Zn-Cu alloys were prepared by powder metallurgy techniques. The metal powders

* Department of Chemistry, Faculty of Science, Konan University, Kobe 658, Japan.

** Graduate Student, Konan University, Kobe. Present address: New Nippon Electric Co., Ltd., Ohtsu 550, Japan.

*** Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan.

with 99.99% purity were compressed at room temperature and then sintered at 1123 K for 360 ks. Specimen for X-ray analysis was quenched into water at 273 K after annealing at 1123 K for 300 s. Specimens for optical and electron microscopy were prepared by melting of sintered specimens in an evacuated quartz tube at a high temperature near 1300 K and then quenched into water at 273 K after annealing at 1123 K for 72 ks. This specimen was cut and polished into a disc 3 mm in diameter and about 0.2 mm in thickness and quenched from 1023 K to 273 K. This disc specimen was polished by the jet polishing method using a 20% H_2SO_4 solution in methanol. The habit plane was studied by the trace analysis using an electron microscope. This microscope and an X-ray diffractometer used were JEM-100CX and Rigaku RU-3L, respectively.

III. Results

An optical micrograph of a $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy cooled in a furnace is shown in Fig. 1, where the surface relief is observed: the cooling rate is about 0.21 K/s, and the M_s temperature of this alloy is about 883 K. The surface relief in the quenched specimen of Ni–Zn–Cu alloy has been already reported in the previous papers⁽¹²⁾⁽¹³⁾. In the case of the $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ alloy, the surface relief is observed even in a furnace cooled specimen. Then, even during slow cooling, the B2 to L1_0 transformation in the Ni–Zn–Cu alloys is considered to be martensitic in a range of composition where the

Fig. 1 Surface relief of a $\text{Ni}_{40}\text{Zn}_{50}\text{Cu}_{10}$ martensite cooled in a furnace from 1123 K to room temperature.

Fig. 2 Lattice parameters of $\text{Ni}_{100-x-y}\text{Zn}_y\text{Cu}_x$ ($y=52, 54$ and 56) alloys as a function of Cu content (x) at room temperature. a and c show the lattice parameters of the L1_0 lattice, and a_0 that of the B2 lattice. The numbers in the figure represent the concentration of Zn (y). The axial ratio (c/a) in these alloys is shown in Fig. 3.

M_s temperature is below about 880 K[†].

The composition dependence of lattice parameters in the $\text{Ni}_{100-x-y}\text{Zn}_y\text{Cu}_x$ alloys ($y=52, 54$ and 56) observed at room temperature is shown in Fig. 2. The a axis of the L1_0 lattice decreases with increase in x (composition of Cu) in a range of small x and then increases with increase in x after a minimum. The c axis, on the contrary, increases with increase in x in a range of small x . The slope of the c -vs- x curve decreases, as the composition, x , approaches the phase boundary between L1_0 and B2 structures. By the phase change from L1_0 to B2, the a axis is expanded to the value of $\sqrt{2}a_0$ and the c axis shrinks to a_0 , where a_0 is the lattice parameter of the B2 lattice. The change in the

[†] In the binary $\text{Ni}_{50}\text{Zn}_{50}$ alloy⁽⁷⁾, the B2 to L1_0 transformation has been shown to be martensitic in the case of quenching and massive in the case of furnace cooling (the starting temperature of this transformation upon cooling is 1033 K). The B2 to L1_0 transformation is considered to be martensitic in a temperature range where the migration of interface occurs very slowly.

slope of the a (or c)-vs- x curve in a range of x near the phase boundary is suggested to be due to the fact that the $L1_0$ to B2 transformation has slightly the nature of the 2nd order transformation, which will be discussed later.

The axial ratio (c/a) of the $L1_0$ lattice in the $Ni_{100-x-y}Zn_yCu_x$ ($y=52, 54$ and 56) alloys observed at room temperature is shown as a function of the electron atom ratio (e/a) in Fig. 3, together with the results in the alloys

Fig. 3 The axial ratio (c/a) of the $L1_0$ lattice in $Ni_{100-x-y}Zn_yCu_x$ ($y=48, 50, 52, 54$ and 56) alloys as a function of electron atom ratio (e/a) at room temperature. The line with $c/a=0.707$ shows the existence of the B2 lattice in alloy with $y=48$. For the range of the existence of B2 structure in other compositions, see Fig. 2 and refs. (10) and (11). The numbers in the figure represent the concentration of Zn (y). e/a of these alloys is given by $(x+2y)/100$.

with $y=48$ and $50^{(10)(11)}$. In the calculation of e/a , only the number of $s+p$ electrons is taken into account, and e/a of Ni, Cu and Zn atoms is assumed to be 0, 1 and 2, respectively. The axial ratio of the B2 lattice is shown to be 0.707 in this figure, because the B2 lattice is equal to the $L1_0$ lattice with $c/a=1/\sqrt{2}$. The axial ratio increases with increasing e/a in the $L1_0$ phase, and when the e/a of an alloy approaches that of the phase boundary, the slope of the c/a -vs- e/a curve decreases gradually in the $L1_0$ phase. The axial ratio of the $L1_0$ phase drops discontinuously down to 0.707 by the phase change from $L1_0$ to B2. The e/a at the phase boundary is not constant but increases very slightly with increase in Zn content, as shown in Fig. 3.

The temperature dependence of the lattice parameters in the $Ni_{34}Zn_{52}Cu_{14}$, $Ni_{36}Zn_{54}Cu_{10}$ and $Ni_{36}Zn_{56}Cu_8$ alloys are shown in Fig. 4. In the $L1_0$ phase, the a axis increases and c axis decreases gradually with increase in temperature. By the $L1_0$ to B2 transformation, the a axis jumps discontinuously up to the value of $\sqrt{2}a_0$ and the c axis drops down to a_0 . The temperature dependence of the axial ratio (c/a) of the $L1_0$ lattice in these alloys is also shown in Fig. 5. The axial ratio decreases with increase in temperature and drops discontinuously down to 0.707 by the $L1_0$ to B2 transformation. This tendency of the axial ratio depending on

Fig. 4 Temperature dependence of the lattice parameters in $Ni_{34}Zn_{52}Cu_{14}$, $Ni_{36}Zn_{54}Cu_{10}$ and $Ni_{36}Zn_{56}Cu_8$ alloys. a , c and a_0 means the same parameters as those in Fig. 2. Numbers in the figure represent the concentration of Zn in these specimens. The dotted lines show the region where the coexistence of the $L1_0$ and B2 structures was observed. The axial ratio (c/a) in these alloys is shown in Fig. 5.

temperature is similar to that depending on e/a shown in Fig. 3 and suggests that the $L1_0$ to B2 transformation has slightly the 2nd order nature although it is almost of the 1st order transformation.

The change in atomic volume (ΔV) accompanying the $L1_0$ to B2 transformation upon heating, which was measured by X-ray diffraction in several Ni–Zn–Cu alloys, is listed in Table 1: ΔV is in a range from 0.16 to 0.48 % in these alloys. The change in atomic volume (ΔV) accompanying with the martensitic transformation has been reported to be about 2.2–2.7 % in the Fe–Ni alloy⁽¹⁹⁾ and in the order of 0.3 % in the β phase alloy⁽²⁰⁾. The value of ΔV

Fig. 5 Temperature dependence of the axial ratio (c/a) of the $L1_0$ lattice in $Ni_{34}Zn_{52}Cu_{14}$, $Ni_{36}Zn_{54}Cu_{10}$ and $Ni_{36}Zn_{56}Cu_8$ alloys. The line with $c/a = 0.707$ shows the existence of the B2 structure in $Ni_{34}Zn_{52}Cu_{14}$ alloy. The dotted line shows the region where the coexistence of the $L1_0$ and B2 structures was observed. For the range of the existence of B2 structure in other compositions, see Fig. 4. The numbers in the figure show the concentration of Zn in these specimens.

Table 1 The increase of atomic volume (ΔV) associated with the $L1_0$ to B2 transformation upon heating in Ni–Zn–Cu alloys. The starting temperature of $L1_0$ to B2 transformation upon heating, A_s , of these alloys is also shown in this table.

Ni–Zn–Cu alloy	$\Delta V/\%$	A_s/K
Ni–52Zn–14Cu	0.16	670
Ni–54Zn–10Cu	0.475	710
Ni–54Zn–14Cu	0.32	230
Ni–56Zn–8Cu	0.48	675
Ni–56Zn–10Cu	0.24	250

in the Ni–Zn–Cu alloy is in the same order as that in the β phase alloy which undergoes a thermoelastic martensitic transformation.

The contour line where the M_s temperature of the ternary Ni–Zn–Cu alloy is 293 K is shown in Fig. 6. The composition of Cu on this line decreases with increase in Zn content. The e/a on this line is not constant, but increases very slightly with increase in Zn content, which was also represented in Fig. 3. The composition dependence of the M_s temperature in the ternary Ni–Zn–Cu alloys has been reported in the previous papers⁽¹⁰⁾⁽¹¹⁾.

The habit plane of the $Ni_{31.5}Zn_{48}Cu_{20.5}$ martensite was investigated by the trace analysis in several specimens with different orientations by electron microscopy. The traces of the habit

Fig. 6 Phase relation in the ternary Ni–Zn–Cu alloys. The full line shows the contour line where the M_s temperature is 293 K. The dashed line represents the phase boundary of the B2 phase at a temperature 123 K.

Fig. 7 Habit plane normal referred to the matrix of B2 phase in $Ni_{31.5}Zn_{48}Cu_{20.5}$ alloy. Arcs in the figure represent the traces of normals observed in different specimens. The open circle shows the theoretical habit plane calculated by Kajiwara⁽²¹⁾. A closed triangle shows $(2, 13, 14)_{B2}$.

plane normals determined by the one surface analysis in different thin foils are shown in Fig. 7. They are close to $(2, 13, 14)_{B2}$ and the theoretical habit plane⁽²¹⁾.

IV. Discussion

The martensitic transformation in the ternary Ni-Zn-Cu alloys was studied. The volume change associated with the $L1_0$ to B2 transformation, ΔV , is fairly small (about 0.16–0.48%) in the Ni-Zn-Cu alloys, which may be favorable for the thermoelastic martensitic transformation. The axial ratio (c/a) of the $L1_0$ lattice in the Ni-Zn-Cu alloys decreases slightly with increase in temperature; this is in good agreement with that reported in the binary Ni-Zn alloy⁽⁸⁾. In the tetragonal martensite phase in alloys such as In-Tl⁽²²⁾, Mn-Cu⁽²³⁾ and V_3Si ⁽²⁴⁾, the axial ratio has been found to be dependent on temperature; the martensitic transformation in these alloys is close to the 2nd order transformation, compared with that in the β phase alloys⁽²⁵⁾. The result revealed in Fig. 5 suggests that the $L1_0$ to B2 transformation of the Ni-Zn-Cu alloy has slightly the nature of 2nd order transformation although it is almost of the 1st order. Any temperature dependence of the axial ratio in the martensite phase of the noble metal base β phase alloys has not yet been reported. The temperature coefficient of the elastic constant, dC'/dT ($C' = (C_{11} - C_{12})/2$), in the $Ni_{50-x}Zn_{50}Cu_x$ alloy has been reported to be positive

and in the same order with that in the noble metal base β phase alloys⁽²⁶⁾⁽²⁷⁾. ΔV in Ni-Zn-Cu is also in the same order with that in the β phase alloy. Thereby, the nature of the martensitic transformation in the Ni-Zn-Cu alloy is considered to be close to that of the β phase alloy, but slightly has the 2nd order nature.

Kajiwar⁽²¹⁾ has analyzed theoretically the crystallography of the B2 to $L1_0$ transformation and shown that the habit plane of the $L1_0$ martensite changes as a function of the axial ratio (c/a). The traces of habit plane normals determined by the trace analysis are fairly in good agreement with the theoretical habit plane calculated by Kajiwar⁽²¹⁾. The habit plane is considered to be close to $(2, 13, 14)_{B2}$ plane in the Ni-Zn-Cu alloy, as shown in Fig. 7. In the β phase alloys, the habit plane of the 2H martensite has been reported to be close to the planes such as $\{122\}_\beta$ and $\{133\}_\beta$ and that of the 18R (or 9R) martensite to the planes such as $\{155\}_\beta$, $\{166\}_\beta$ and $\{2, 11, 12\}_\beta$ ⁽²⁸⁾. In the Ni-Al alloy, the habit plane of the $L1_0$ martensite has been found to be close to $\{2, 14, 15\}_{B2}$ plane⁽⁴⁾. The observed habit plane normals in the Ni-Zn-Cu alloy are located close to that of the thermoelastic martensite in these alloys.

In the nickel base alloys, the martensitic transformation has been observed in alloys such as Ni-Al, Ni_3Sn and Ni-Ti, as summarized in Table 2. In alloys such as Ni-Al, Ni-Zn and Ni-Zn-Cu, the structure of martensite phase is

Table 2 Martensitic transformation in the Ni-base alloys. The range of composition and the electron atom ratio (e/a) where the martensitic transformation has been observed is also listed in this table. The e/a of Ni-Ti and Ni-Ti-Fe alloys is not shown here because it contains 3d electrons.

Alloy system	Change of structure	Range of composition/ at %	e/a	References
Ni-Al	B2 $\rightarrow$ $L1_0$	34–38Al	1.02–1.20	(1)–(4)
Ni-Zn	B2 $\rightarrow$ $L1_0$	48–56Zn	0.96–1.12	(5)–(8)
Ni-Zn-Cu	B2 $\rightarrow$ $L1_0$	{48–56Zn {0–22Cu	0.96–1.24	{(9)–(13), {This work
Ni_3Sn	$DO_3 \rightarrow$ 2H	25Sn	1.0	(14)
Ni-Cu-Sn	$DO_3 \rightarrow$ 2H	{25Sn {0–18Cu	1.0–1.18	(15)(16)
Ni-Ti	{B2 $\rightarrow$ distorted {B19	49–51Ti	—	(29)
Ni-Ti-Fe	{B2 $\rightarrow$ intermediate {phase $\rightarrow$ dist. B19	{50Ti {0–4Fe	—	(30)(31)

Fig. 8 The starting temperature of the martensitic transformation from B2 to L1₀ structure upon cooling, M_s , in nickel base alloys such as Ni-Al⁽³⁾, Ni-Zn⁽⁵⁾⁽¹⁸⁾ and Ni_{52-x}Zn₄₈Cu_x⁽¹⁰⁾ alloys as a function of the electron atom ratio (e/a).

the L1₀ structure. In alloys such as Ni₃Sn and Ni-Cu-Sn, it is the 2H structure. The martensite phase in these alloys is considered to occur in a range of e/a from about 0.96 to 1.24. The transformations in Ti-Ni and Ti-Ni-Fe alloys are very complicated⁽²⁹⁾⁻⁽³¹⁾ and then shown briefly in this table.

The starting temperature of the martensitic transformation from the B2 to L1₀ structures upon cooling, M_s , in the Ni-Zn⁽⁵⁾, Ni-Zn-Cu⁽¹⁰⁾ and Ni-Al⁽³⁾ alloys is shown in Fig. 8 as a function of the electron atom ratio (e/a). The M_s temperature has a tendency to decrease with increase in e/a . These results indicate that the L1₀ structure occurs in a range of e/a below about 1.2 in these alloys. In the noble metal base alloys, the β phase (*bcc*) occurs in a range of e/a near 1.48 and the α phase (*fcc*) in a range of e/a below about 1.36: this is the so-called Hume-Rothery rule. However, in the nickel base alloys, the disordered *fcc* phase does not exist in this range of e/a , because the ordering energy of atomic pairs in the B2-type ordered phase of nickel base alloys is very large⁽¹¹⁾. In this case, the martensitic transformation may be favorable for the formation of the close-packed structure such as L1₀ in a range of e/a below about 1.2. Figure 9 represents the rela-

Fig. 9 Relation between the Fermi sphere and the {101} Brillouin zone of *bcc* (real line) and *bct* (dotted line) lattices in an alloy with e/a of 1.2. In this figure, the Brillouin zone due to the B2-type superstructure is not shown for simplicity, and that of the L1₀ structure is denoted by that of *bct* with $c/a=1.23$.

tion between the Fermi sphere at $e/a=1.2$ and the Brillouin zones. By the cubic to tetragonal transformation, the {101} Brillouin zone of the B2 structure approaches the Fermi sphere at $e/a=1.2$, as shown in the figure. Then the electronic energy may decrease as a result of the cubic-to-tetragonal transformation. This may be one reason of the B2 to L1₀ transformation in alloys such as Ni-Al and Ni-Zn-Cu. Because the e/a at the phase boundary is not constant as revealed in Fig. 3, the phase stability of the Ni-Zn-Cu alloys may be affected partly by another factor such as the difference in atomic radius among the constituent atoms.

The martensite phase with 2H structure in the Ni₃Sn and Ni-Cu-Sn alloys has been found in a range of e/a from about 1 to 1.18 as listed in Table 2. This may also be affected by the decrease of electronic energy due to the B2 to 2H transformation⁽¹⁵⁾. A more detailed theoretical analysis of the electronic energy is expected to clarify the origin of martensitic transformation in the nickel base alloys.

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