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Occupancy Sites of Constituent Atoms and their Effects on the Martensitic Transformations in some Cu-Based and Ti-Ni-Based Ternary Alloys

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Abstract. Atomic configurations in β phase Cu-Al-Ni, Cu-Au-Zn and Cu-Zn-Al ternary alloys before and after martensitic transformations, and occupancy sites of third elements X in the B2 parent lattice of Ti-Ni-X ternary alloys, where X = 3d elements, Pd and Au, have been investigated by means of an electron channeling enhanced microanalysis method, called ALCHEMI. Large increases in M_s and A_s temperatures by several tens of K or more observed in the β phase alloys upon aging at ambient temperatures are attributed to ordering in the parent phase and to disordering in the martensite phase, respectively, both taking place between certain atoms occupying specific sites. The occupancy sites of third elements X in Ti-Ni-X alloys have been systematically examined, changing compositions in the following formulae: $\text{Ti}_{0.5-x}\text{Ni}_{0.5}X_x$, $\text{Ti}_{0.5-x/2}\text{Ni}_{0.5-x/2}X_x$ and $\text{Ti}_{0.5}\text{Ni}_{0.5-x}X_x$, where $x \leq 0.05$. While Fe, Co and Pd atoms occupy the Ni site preferentially, Sc atoms occupy the Ti site irrespective of composition, and the others the Ni and/or Ti site, depending on composition. These results for the Ti-Ni-X alloys are reasonably explained by a parameter D , which is defined by $D = (V_{\text{TiX}} - V_{\text{NiX}})/V_{\text{TiNi}}$, where V_{ij} is pairwise interaction between i and j atoms. Decreases in M_s temperature for the $B2 \rightarrow B19'$ martensitic transformation are discussed in terms of an average number of valence electrons at the specific sites in the parent lattice.

1. INTRODUCTION

Many of parent phases of alloys undergoing martensitic transformations below ambient temperatures are retained once by quenching from elevated temperatures, otherwise decomposed, as typically observed in β phase Cu-based alloys[1,2]. Martensite phases produced from the parent phases upon further cooling are not of thermal equilibrium. These metastable phases are then subject to aging effects even at ambient temperatures[3]. To make clear atomic configurations in both the phases before and after martensitic transformations is thus crucial for understanding origins of marked shifts of the transformation temperatures caused by aging, which are in fact typically observed in some Cu-based shape memory alloys[3]. Exact crystallographic sites or fractions of constituent atoms occupying specific sites in both the parent and martensite lattices in addition to their precise crystal structures may also help us to explore an electronic origin of the transformations. Then, the present authors have extensively studied the problem of occupancy sites in a number of alloys transforming martensitically by means of an electron channeling enhanced microanalysis, called ALCHEMI. In this paper are summarized the results obtained for Ni atoms in Cu-Al-Ni[4], Cu or Zn atoms in Cu-Au-Zn[5,6] and Cu-Zn-Al alloys[7,8], and for third elements X in Ti-Ni-X alloys, where X=3d elements, Pd and Au[9-11]. The stabilization of martensite observed in these Cu-based shape memory alloys are discussed based on the obtained results, and the decreases in M_s temperature for the $B2 \rightarrow B19'$ transformation in nearly equiatomic Ti-Ni alloys due to the above substitution are discussed in terms of an average number of valence electrons at the specific sites in the parent lattice.

ALCHEMI (Atom Location by Channeling Enhanced Microanalysis) developed by Spence and Taftø[12] is a useful technique for site determination, which is in particular powerful and easy to do as well for distinguishing crystallographic sites occupied by constituent atoms with similar atomic scattering factors for X-rays and electrons, e.g., Cu and Ni or Cu and Zn atoms, as in the above Cu-based shape memory alloys, or by those X of small contents as in Ti-Ni-X ternary alloys. Its principle, procedure of analysis and accuracy etc. are described elsewhere[13]. Throughout the present work ALCHEMI was performed at room temperature under the planar channeling condition using a Hitachi H-600FE analytical electron microscope equipped with a field emission type electron gun, operated at 100 kV[14]. The incident electron beam was about 30 nm in diameter, and less than 1.5 mrad in divergence.

2. Occupancy sites of constituent atoms in Cu-based ternary alloys

2.1 Occupancy site of Ni atoms in the DO_3 parent phase of a Cu-Al-Ni alloy

The atomic configuration in the $Cu_3Al(DO_3)$ type parent phase of a Cu-28Al-4Ni(at.%) alloy and its change upon aging by which M_s temperature for the $DO_3 \rightarrow 2H$ (or $2O$ according to a new notation by Otsuka *et al.*[15]) transformation is raised by several tens of K were investigated by Nakamura *et al.*[16] by means of X-ray diffraction and nuclear magnetic resonance. According to them, before aging excess Al and Ni atoms occupy both the two kinds of Cu sites in the DO_3 lattice, Cu(1) and Cu(2), as defined in Fig.1. Here let the atomic planes consisting of the Cu(1) site only and of the Al and Cu(2) sites, respectively, the α - and β -planes for convenience for ALCHEMI. After aging, in addition to the progress of DO_3 order, a further ordering from DO_3 to $L2_1$ proceeds, *i.e.*, the excess Al and Ni atoms are rearranged into the Cu(2) site. This rearranged configuration, however, was inconsistent with an ordered structure derived from that of a $2H$ martensite identified by Otsuka *et al.*[17] by means of neutron diffraction. That is, according to them, excess Al and Ni atoms occupy the Cu(2) and Cu(1) sites, respectively. In order to solve this discrepancy, Nakata *et al.*[4] examined the occupancy site of Ni atoms in the DO_3 parent lattice by ALCHEMI for a Cu-28.6Al-3.7Ni (at.%) alloy heat-treated in three different ways after betatization: (a) quenching into a 10% NaOH solution at 263 K, (b) quenching into hot water at 363 K, and (c) aging at 523 K for 1 h after the heat-treatment (b). M_s temperature was observed to become higher in the order of these heat treatments, *i.e.*, 158, 185 and 259 K, respectively. A quantitative analysis of ALCHEMI was made following a method developed by Shindo *et al.*[18], assuming Al atoms not to occupy the α -plane. As a result, it was found that the fraction of Ni atoms located at the β -plane was substantially zero for all of these specimens. In other words all of the Ni atoms occupy the Cu(1) site regardless of the heat treatments. This atomic configuration is consistent with that derived by Otsuka *et al.*[17]. It has thus turned out that each Ni atom is surrounded by four of the first nearest neighbor Al atoms. The preferential occupancy of Ni atoms at the Cu(1) site may be due to the strong chemical interaction between Ni and Al atoms. Meanwhile, it was previously shown by Nakata *et al.*[19] by means of a single crystal X-ray diffraction that ordering between the second nearest neighbor atoms in the parent phase of a Cu-Al-Ni alloy was not completed when rapidly quenched, although the ordering between the first nearest neighbor atoms was almost completed. The incomplete second nearest neighbor ordering between Al and Cu atoms occupying the Al and Cu(2) sites was considered to proceed further upon aging. The increase in M_s temperature during aging was thus attributed to the further progress of the second nearest neighbor ordering in the parent phase. A similar correlation between M_s temperature and the second nearest neighbor ordering in parent phase was reported by Suzuki *et al.*[20] for a Cu-Zn-Al alloy.

Figure 1: Atomic configuration in the unit cell of $Cu_3Al(DO_3)$ type lattice.

2.2 Occupancy sites of Cu (or Zn) atoms in the $L2_1$ parent phase of a Cu-Au-Zn alloy

There had been an uncertainty as to occupancy sites of Cu and Zn atoms in the $L2_1$ type parent phase of Cu-Au-Zn alloys near stoichiometric composition $CuAuZn_2$ and hence in the $18R$ (or $6M$ according to a new notation by Otsuka *et al.*[15]) martensite as well. Two crystal structure models had been proposed for the $L2_1$ parent phase: One[21] was that Cu and Zn atoms are located at the Cu(2) and Cu(1) sites, respectively, and the other[22] was that Cu and Zn atoms are located at the Cu(1) and Cu(2) sites, respectively, in the present notation shown in Fig.1; Au atoms occupy the Al site in both the models. The latter model was reduced from the crystal structure of the $18R$ martensite identified. Then, the present authors applied ALCHEMI to this problem[5]. A quantitative analysis of the occupancy site of Cu or Zn atoms in the $L2_1$ parent phase of a Cu-20.7Au-43.8Zn(at.%) alloy was made in the same way as for Ni atoms in the Cu-Al-Ni alloy, assuming that Au atoms do not occupy the α -plane consisting of the Cu(1) site only. The fraction of Cu atoms on the β -plane thus examined was almost unity. Hence it turned out that the atom sites on the β -plane other than those occupied by Au atoms are completely taken over by Cu atoms. This atomic configuration is nothing but the crystal structure model proposed by Duggin and Rachinger[21]. However, the distribution of Cu and Au atoms to the Al and Cu(2) sites on the β -plane remained undetermined by ALCHEMI alone. Then, X-ray diffraction intensities of several reflections from the parent phase were measured and analyzed based on the above result obtained by ALCHEMI. Table 1 shows the results, where I_{obs} and I_{cal} stand for structure factors of hkl reflections observed and calculated for the $L2_1$ parent

Table 1: Result of X-ray diffraction analysis on the degree of order in the $L2_1$ parent phase of a Cu-Au-Zn alloy, based on the results obtained by ALCHEMI.

hkl	type	$ F _{\text{obs}}/ F _{\text{cal}}$
311	nnn	1.22
331		1.16
222		1.17
420	nn	1.19

nnn and nn stand for the second and first nearest neighbor order in the $L2_1$ parent phase, respectively.

phase, respectively. $|F|_{\text{cal}}$'s were evaluated by assuming the maximum degree of the $L2_1$ order for a given composition. It is seen from the table that the ratios $|F|_{\text{obs}}/|F|_{\text{cal}}$ are close to unity for both the first and second nearest neighbor orders. This fact indicates that not only the first but also the second nearest neighbor orderings are completed in the alloy during quenching. This result is in contrast with that in the Cu-Al-Ni alloy, as described above, where the second nearest neighbor ordering was incomplete while the first was completed when rapidly quenched. Meanwhile M_s temperature for the $L2_1 \rightarrow 18R$ martensitic transformation of the Cu-Au-Zn alloy was observed to hardly be changed by quenching rate and subsequent aging at room temperature[5]. This is consistent with the result shown in Table 1. Ordering kinetics in the Cu-Au-Zn alloy is thus different from that in a Cu-Zn-Al alloy examined by Suzuki *et al.*[20].

2.3 Occupancy site of Zn (or Cu) atoms in the 18R martensite of a Cu-Zn-Al alloy

β phase Cu-Zn-Al ternary alloys are well known as practical Cu-based shape memory alloys, although prone to aging effects, in particular, in martensitic state[3]. The aging effects in martensite occur as the stabilization of martensite, i.e., rises of the reverse transformation temperature, A_s . The mechanisms proposed so far for the stabilization of martensite occurring before apparent precipitation or decomposition are vacancy-pinning of interfaces [23,24] and disordering or reordering[23,25] causing shifts of T_0 temperature, the thermodynamical equilibrium temperature between parent and martensite phases. However, the vacancy-pinning of interfaces is obviously inconsistent with an experimental fact that the stabilization of martensite occurs even in single crystals of martensites[24]. Delaey *et al.*[26] showed that the orthorhombic distortion in the basal plane of the 18R martensite decreases with increasing aging time. This suggests that the atomic arrangement in martensite changes during aging. But, the detailed atomic configuration had not been made clear. Later Abu Arab and Ahlers[27] suggested that the interchange between neighboring atoms is responsible for the stabilization of the 18R martensite in Cu-Zn-Al alloys. Fig.2 shows the crystal structure of the 18R martensite, where the same notations for atom sites are adopted as those in Fig.1 for the $D0_3$ structure. According to them, disordering between Cu and Zn atoms located at the Cu(1) and Cu(2) sites, respectively, in the present notation takes place upon martensite aging. However, this interchange, even if it had occurred, would be very difficult to be detected by conventional X-ray or electron diffraction techniques, because the atomic scattering factor for Cu atoms is close to that for Zn atoms. Then, Nakata *et al.*[7,8] explored this problem by ALCHEMI directly. They prepared direct- and step-quenched Cu-11.2Zn-17.1Al (at.%) alloy specimens. Although the former did not undergo the reverse transformation up to 473 K, A_s temperature of the latter

Figure 2: Atomic arrangements projected onto the (010) (a) and (100) (b) planes of the 18R martensite, and of the basal plane (c).

increased from the initial value of 380 K to those a few tens of K higher as a function of aging time and temperature. As seen from Fig.2, there are two kinds of atomic planes arranged alternately along the [010] direction: One consists of only the Cu(1) site and the other the Al and Cu(2) sites. These two superlattice planes in the martensite, the α - and β -planes, respectively, consist of the same atom sites as those of {200} in the $L2_1$ parent phase. This atomic configuration is consistent with that in the parent phase recently identified by neutron diffraction[28], where the Al site is occupied by Al and Zn atoms, the Cu(2) site by Cu and Zn atoms and the Cu(1) site fully by Cu atoms. Then, the fraction of Zn atoms on the β -plane, k , in the martensite lattice was examined in a similar way to that in the $L2_1$ parent phase of the Cu-Au-Zn alloy mentioned above as a function of aging time. For a quantitative analysis of ALCHEMI was made an assumption that Al atoms are located on the β -plane for both unaged and aged martensites. The results are shown in Fig.3. It is seen that the value of k changes from about 0.8 to 0.6~0.7 with increasing aging time. This indicates that Zn and Cu atoms initially located on the β - and α -planes, respectively, change their occupancy sites with each other upon aging. It is also to be noted that the martensite formed upon direct quenching, which did not undergo the reverse transformation into the parent phase, exhibited a k value much smaller than that for the specimens aged for prolonged times. It was then concluded that the stabilization of martensite was due to the disordering between Cu and Zn atoms occupying the α - and β -planes, respectively, which are in the first nearest neighbor relation in the $L2_1$ parent lattice, as previously suggested by Abu Arab and Ahlers[27]. Very recently Saule and Ahlers[29] showed by a thermodynamical calculation that an increase in A_s temperature actually observed in a martensitic Cu-Zn-Al alloy is quantitatively accounted for by such disordering that corresponds to k determined by Nakata *et al.*[7] through ALCHEMI.

Meanwhile, it is well known that β phase Cu-Au-Zn alloys with compositions near CuAuZn_2 , when aged in martensitic state, come to exhibit the rubber-like behavior instead of shape memory effect before aging, as clearly demonstrated by Miura *et al.*[30]. But, what happens in the martensite phase during aging had remained unclear. Then, the present authors examined atomic configuration in the stabilized 18R martensite of a Cu-26Au-45Zn (at.%) alloy by ALCHEMI[6]. As a result, the fraction of Cu atoms occupying the β -plane was found to be almost unity. This means that the sites on the β -plane other than those occupied by Au atoms are completely filled with Cu atoms. Such an ordered structure was consistent with a crystal structure model formerly proposed by Duggin and Rachinger[21]. In other words the atomic configuration in the stabilized martensite is the same as that directly derived from the $L2_1$ parent phase. However, the distribution of Cu and Au atoms on the β -plane to the Al and Cu(2) sites in the present notation was undetermined by ALCHEMI alone. Then, X-ray diffraction was made to examine the ordered structure of the stabilized martensite, based on the results obtained by ALCHEMI. As a result, while the degree of order between Au and Cu atoms on the α -plane and Zn atoms on the β -plane was almost unity, that between Au atoms at the Al site and Cu atoms at the Cu(2) site on the β -plane was less than unity, *i.e.*, about 0.8. As mentioned above, both the first and second nearest neighbor ordering in the $L2_1$ parent phase was completed in a Cu-Au-Zn alloy even when rapidly quenched[5]. The perfect order in the $L2_1$ parent phase should be inherited to the 18R martensite because of the diffusionless nature of the martensitic transformation. Nevertheless it was found that in the martensite the ordering corresponding to the second nearest neighbor ordering in the $L2_1$ parent phase is imperfect. This disordering was thus considered to have occurred during aging in martensitic state and as a result to bring about a change in the relative stability between the $L2_1$ parent and 18R martensite phases.

However, whether the change in atomic arrangement which is supposed to be responsible for the stabilization of martensite is disordering or ordering, or whether it does occur or not, is controversial at present. Very recently, Ohba *et al.*[31] explored crystal structure change upon martensite aging by means of single crystal X-ray diffraction, if any, of the 18R martensite of a Cu-Au-Zn alloy with the same composition as that of the alloy examined by the present authors. It was then revealed that no significant change occurs in intensity of superlattice reflections related to the ordering between Au and Cu atoms located at the Al and Cu(2) sites, respectively. The discrepancy between the results obtained by Ohba *et al.*[31] and the present authors[6] is an open question at present. No indication was found for disordering or reordering,

Figure 3: The fraction k of Zn atoms occupying the β -plane in the 18R martensite of a Cu-Zn-Al alloy as a function of aging time.

nor for atomic shift after prolonged aging for 2H martensites of a Cu-27.14Al-3.64Ni (at.%) [32] and a Au-Cd alloy [33] by thorough crystal structure analyses. Gui *et al.* [34], however, showed theoretically by means of the embedded-atom method based on a density-functional theory that ordering in martensite is energetically more favorable than disordering in Cu-Zn-Al and Cu-Al-Ni alloys. Meanwhile, Tsuchiya *et al.*, obtaining an activation energy of 87 kJ/mol for the disordering in martensite of a Cu-Zn-Al alloy [35], indicated that if this value is adopted, the time necessary for a detectable change in long range order to occur is about 5×10^6 s at room temperature, and that no significant change in the long range order should be expected during room temperature aging of the order of 10^4 s, by which a rise in A_s temperature as large as about 100 K is in fact brought about [36]. Therefore they concluded that the rise in the transformation temperature or the observed change in yield stress after aging cannot be caused by the change in the long range order, suggesting that the change in the short range ordered structure seems to be responsible for the rubber-like behavior and the stabilization effect at room temperature. However, another interesting result to be noted was previously reported for the 18R martensite of a Cu-Al-Ni alloy by Van Humbeeck *et al.* [37]: According to them, angular splitting between the 122 and 202 reflections of 18R structure were different among the martensites as-quenched, stabilized and destabilized although no indication for atomic rearrangement was found for the stabilized 2H martensite of the same alloy system. Such being the case, the origin for the stabilization of martensite is confused in the crystal-structural point of view at present.

3. Occupancy sites of the third elements X added to nearly equiatomic Ti-Ni alloys

It is well known [3] that the martensitic transformation in nearly equiatomic Ti-Ni alloys is significantly affected by the addition of third elements with respect to transformation temperatures and also crystal structure of martensite. The R phase appears in the alloys containing Fe [38], Cr [39] or Al [40,41], while the B19 phase appears in those containing Au [42], Cu [43,44], Pd [45], prior to the $B2 \rightarrow B19'$ martensitic transformation. These intermediate phases do not appear in solution-treated binary alloys. When a third element X is added to the Ti-Ni alloy in a chemical formula, $Ti_{0.5}Ni_{0.5-x}X_x$ or $Ti_{0.5-x}Ni_{0.5}X_x$, one may expect the atoms X to occupy the Ni or Ti site, respectively. But, these are not necessarily confirmed experimentally. There is a possibility that an element which has strong interaction with Ni may occupy the Ti site even in the composition of $Ti_{0.5}Ni_{0.5-x}X_x$, and *vice versa*. Consequently, the site occupancy of the third elements depends on not only the chemical composition but also other factors such as chemical interaction between the third and the host elements. The variations of martensite phases and transformation temperatures may originate likely from those in electronic structure caused by the addition of third elements. Since the electronic structure would depend strongly on the location of third elements, it is crucial to examine which of the Ni and Ti sites a third element is located at. Then, occupancy sites of many third elements X, where $X = 3d$ elements, Pd and Au, in Ti-Ni-X ternary alloys have been systematically investigated by the present authors by means of ALCHEMI [9-11]. The compositions have been varied in the following chemical formulae: (a) $Ti_{0.5-x}Ni_{0.5}X_x$, (b) $Ti_{0.5-x/2}Ni_{0.5-x/2}X_x$, (c) $Ti_{0.5}Ni_{0.5-x}X_x$ with x less than 0.05.

ALCHEMI was carried out for the B2 parent phase of the Ti-Ni-X alloys in the same way as mentioned above for the Cu-based alloys, since the {100} superlattice planes in the B2 phase consist of two kinds of planes, *i.e.*, one containing Ni atoms and the other Ti atoms. To do this, however, the followings were taken into account for these alloys.

Letting the chemical composition of a ternary alloy $Ti_aNi_bX_c$ and the fraction of X atoms occupying the Ni site k , the distribution of the constituent atoms to the Ti and Ni sites are expressed as shown in Table 2. Here, z denotes a fraction of wrong atoms which occupy the Ni or Ti site, even if there are vacant sites at the Ni and Ti sites to be occupied by right atoms. But, since Ti-Ni alloys near equiatomic composition exhibits a high critical temperature T_c for the order-disorder transformation [46], it was assumed that the state $z \approx 0$ is usually attained upon quenching. Although the concentration of each atom at each site can vary, depending

Table 2: Fractions of Ti, Ni and X atoms located at the Ti and Ni sites in $Ti_aNi_bX_c$.

	$Y > 0$		$Y < 0$	
	Ti site	Ni site	Ti site	Ni site
Ti	$a-z$	z	$1/2-(1-k)c-z$	$1/2-b-kc+z$
Ni	$1/2-a-(1-k)c+z$	$1/2-kc-z$	z	$b-z$
X	$(1-k)c$	kc	$(1-k)c$	kc

Table 3: Occupancy fractions of third elements X located at the Ni site determined by ALCHEMI.

X	Ti _{0.5-c} Ni _{0.5} X _c	Ti _{0.5-c/2} Ni _{0.5-c/2} X _c	Ti _{0.5} Ni _{0.5-c} X _c
Sc	0.01 ± 0.08	-0.08 ± 0.11	0.04 ± 0.09
V	0.13 ± 0.10	0.54 ± 0.06	0.78 ± 0.06
Cr	0.51 ± 0.12	0.50 ± 0.11	0.89 ± 0.05
Mn	0.24 ± 0.07	0.55 ± 0.11	0.66 ± 0.09
Fe	0.91 ± 0.08	0.89 ± 0.07	—
Co	1.01 ± 0.06	1.00 ± 0.07	—
Cu	0.34 ± 0.23	0.52 ± 0.18	1.11 ± 0.13
Pd	0.92 ± 0.06	0.94 ± 0.06	0.90 ± 0.08
Au	0.14 ± 0.07	0.55 ± 0.07	0.64 ± 0.06

Table 4: Occupancy fractions of Mn and Cr atoms located at the Ni site after annealing at 773 K for 10 min.

Ti ₅₀ Ni ₄₈ Mn ₂	Ti ₄₈ Ni ₅₀ Mn ₂	Ti ₄₈ Ni ₄₈ Cr ₂
0.90 ± 0.09	0.03 ± 0.14	0.60 ± 0.09

on the existence of vacancies even for a fixed value of k , it was verified by the present authors through measurements of density and lattice parameters[47] that there are no significant amounts of vacancies in the Ti-Ni-X alloys. It is also to be noted in Table 2 that there are two cases for Y , where $Y=b+kc-1/2$. When $Y>0$, i.e., the sum of the fraction of Ni atoms b and that of the third element kc exceeds the fraction of the Ni site $1/2$, a part of the Ni atoms should move to the Ti site, and when $Y<0$, a part of Ti atoms should move to the Ni site.

Results of quantitative analysis of k for the Ti-Ni-X alloys are summarized in Table 3. It is seen from the table that the third elements added to Ti-Ni alloy are divided into the following three groups with respect to occupancy site:

- (i) occupy the Ni site, irrespective of composition: Fe, Co and Pd.
- (ii) occupy the Ti site, irrespective of composition: Sc.
- (iii) occupy the Ni or Ti site, depending on composition: Cr, Mn, Cu, Au and V.

The third elements of the groups (i) and (ii) exhibit preferential occupancy of either of the two sites, and those of the group(iii) have a tendency to occupy the vacant sites in the Ti or Ni site. To be noted in the group (iii) k does not become unity or zero, but it takes in-between values. Cr atoms are located at the Ni site in Ti_{0.5}Ni_{0.5-x}X_x, but they are at both the sites with almost equal fractions in Ti_{0.5-x}Ni_{0.5}X_x. The reason for the fact that the third elements of the group(iii) do not exhibit preferential occupancy for one side may be that the alloy specimens are in as-quenched state from high temperature. In order to confirm this point, ALCHEMI was done on the alloy specimens annealed at 773 K for 600 s subsequently after quenching. Results for Ti-Ni-Mn alloys are shown in Table 4. It is then seen that Mn atoms exhibit preferential occupancy after annealing in both the compositions Ti_{0.5-x}Ni_{0.5}X_x and Ti_{0.5}Ni_{0.5-x}X_x. But, the value of k for Cr atoms was not varied so remarkably by annealing.

These site occupancies of the third elements thus determined experimentally are expected to be related to chemical bonding between Ti and X, and Ni and X. Then the observed sites of the third elements have been examined in terms of chemical bonding based on statistical thermodynamics. The calculation of occupancy sites indicated that the fraction k of X atoms located at the Ni site can be evaluated as a function of a parameter, D , defined as follows:

$$D = (V_{TiX} - V_{NiX}) / V_{TiNi}$$

Here, V_{ij} is pairwise interaction between i and j atoms, and it is expressed by the following equation,

$$V_{ij} = (U_{ii} + U_{jj}) / 2 - U_{ij}$$

where U_{ij} 's stand for bonding energies between i and j atoms. Figs.4(a), (b) and (c) show relations between

k and D calculated for $\text{Ti}_{0.48}\text{Ni}_{0.5}\text{X}_{0.02}$, $\text{Ti}_{0.49}\text{Ni}_{0.49}\text{X}_{0.02}$ and $\text{Ti}_{0.5}\text{Ni}_{0.48}\text{X}_{0.02}$ alloys, respectively, at various temperatures, T/T_c , where T_c denotes the order-disorder transition temperature. According to Honma *et al.* [46], T_c is 1363 K. The values of D are estimated by assuming that V_{ij} is equal to ΔH_{ij} , the enthalpy change associated with the formation of an equiatomic compound or alloy from pure metals i and j [48]. That is,

$$V_{ij} \approx \Delta H_{ij}.$$

ΔH_{ij} 's can be evaluated from the data book by de Boer *et al.* [49]. For the third elements X of which ΔH_{TiX} and/or ΔH_{NiX} are unknown, semiempirical values calculated by Miedema *et al.* [50] were adopted. The D values obtained in this way are shown in the row(a) of Table 5. Although the alloy specimens were quenched from 1273 K, the temperature of the specimens, T/T_c , was assumed roughly to lie between 0.2 and 0.6. Then, the fractions k of the third elements actually measured for the ternary alloys are reproduced in the calculated k versus D curves. In particular, the variation of k for Mn observed upon annealing is reasonably accounted for as due to that of temperature T/T_c roughly from 0.4 to 0.2. However, although the D value for the Ti-Ni-V system is close to -1, V does not exhibit clearly a tendency of preferential occupancy of the Ti site; moreover, although the D value of Au for the Ti-Ni-Au system is larger than unity, Au atoms do not occupy preferentially the Ni site, rather occupy both the sites with nearly equal fractions. These discrepancies may arise likely from the assumption, $V_{ij} \approx \Delta H_{ij}$.

The bonding energy U_{ij} , by which V_{ij} is defined, is a function of the atomic distance, r , between i and j atoms. Here $U_{ij}(r)$ is evaluated from the Lennard-Jones potential:

$$U_{ij}(r) = U_{ij}^a \left\{ \frac{m}{n-m} \left(\frac{r_{ij}^a}{r} \right)^n - \frac{n}{n-m} \left(\frac{r_{ij}^a}{r} \right)^m \right\},$$

where m and n are 4 and 8, respectively, following Sanchez *et al.* [50]. $U_{ij}(r)$ can be evaluated if two parameters, U_{ij}^a and r_{ij}^a , are known, and it becomes minimum, $-U_{ij}^a$, at $r=r_{ij}^a$. When $i=j$, U_{ii}^a and r_{ii}^a are evaluated by cohesive energy for element i , H_i , and the atomic distance of pure element i , r_i , respectively. When $i \neq j$, U_{ij}^a and r_{ij}^a are evaluated by the following equations,

$$U_{ij}^a = (H_i + H_j)/2 - \Delta H_{ij},$$

and

$$r_{ij}^a = (r_i + r_j)/2.$$

Thus, U_{ij} for Ti-Ni-X alloy systems can be calculated by substituting the first nearest atomic distance, 0.261 nm, for r . The values of D thus calculated are shown in the row(b) of Table 5. It is seen that D 's for the Ti-Ni-Au and Ti-Ni-V alloys are considerably close to zero, compared with those shown in the row(a). The fact

Figure 4: Relation between k and D for $\text{Ti}_{0.48}\text{Ni}_{0.50}\text{X}_{0.02}$ (a), $\text{Ti}_{0.49}\text{Ni}_{0.49}\text{X}_{0.02}$ (b) and $\text{Ti}_{0.50}\text{Ni}_{0.48}\text{X}_{0.02}$ (c).

Table 5: Values of a parameter D evaluated by using enthalpy change (a) and Lennard-Jones potential (b) for the third elements X .

	Sc	V	Pd	Au	Cr	Mn	Fe	Co	Cu
(a)	-2.0	-0.76	2.2	2.30	0.50	-0.03	0.68	1.3	0.47
(b)	-2.8	0.06	0.71	0.22	0.83	0.08	0.93	1.1	0.69

Figure 5: Amount of decrease in M_s , ΔM_s , due to addition of 3d elements to the TiNi alloy per 1 at. %.

that the D 's for the Ti-Ni-Au and Ti-Ni-V alloys are nearly zero indicates that the sites occupied by Au and V atoms depend on the alloy compositions. Then, this prediction agrees in fact with the experimental results. Thus, it is seen that the atom locations of the third elements X can be evaluated reasonably from the parameter D , which is defined by using pairwise interaction V_{ij} .

Fig.5 shows the amounts of decrease in M_s temperature for the B2 to B19' transformation, ΔM_s , as a function of the added element per 1 at.%. It is to be noted that whenever an average number of valence electrons on either of the Ti and Ni sites is varied, M_s temperature decreases, and that the amount of decrease is large when the variation in average number of valence electron is large. Moreover, when Au atoms were substituted for Ni, ΔM_s was found to differ only by about 5 K from that for Cu. This implies that M_s temperature is more sensitive to the change in valence electron than the difference in atomic size. In fact, according to a very recent calculation by Nakata *et al.*[52] for the electronic structure of the B19' martensite of an equiatomic TiNi alloy, the density of state exhibits a deep valley in the vicinity of the Fermi level, suggesting that the total energy of the B19' martensite is sensitive to the change in number of valence electrons; in the case of the equiatomic TiNi alloy the total density of state at the Fermi level significantly decreases in the B19' martensite, compared with that of the B2 parent phase, indicating a higher stability of the B19' martensite adopted.

Table 6 shows variations in T_R , the B2→R transformation temperature, ΔT_R , and in M_s , ΔM_s , by the addition of the third elements for the compositions $\text{Ti}_{0.5-x}\text{Ni}_{0.5}\text{X}_x$ and $\text{Ti}_{0.5}\text{Ni}_{0.5-x}\text{X}_x$. It seems that there is a tendency for the R phase to appear for such substitution that the number of valence electron at the Ni site is reduced, although the replacement of Ni by Sc is exceptional, because, as mentioned above, Sc atoms always occupy the Ti site preferentially irrespective of composition and there does not exist such an alloy with composition $\text{Ti}_{0.5}\text{Ni}_{0.5-x}\text{Sc}_x$. However, it seems that the R phase is not present in most of the $\text{Ti}_{0.5-x}\text{Ni}_{0.5}\text{X}_x$ alloys and also that the B19 phase appears when the average number of valence electrons at the Ni site is increased. The B19 phase is in fact observed to appear in the $\text{Ti}_{0.5}\text{Ni}_{0.5-x}\text{Cu}_x$ alloys when x exceeds about 10 at. %[43,44,55,56]: when $x < 7.5$ at.% the B2→B19' transformation takes place upon cooling, when $x > 7.5$ at.% the successive transformation B2→B19→B19' occurs, and at $x = 20$ at.% only the B2→B19

Table 6: Amounts of decrease in M_s and T_R , ΔM_s and ΔT_R , respectively, due to addition of third elements X to Ti-Ni alloy in chemical formulae, $\text{Ti}_{0.5-x}\text{Ni}_{0.5}\text{X}_x$ and $\text{Ti}_{0.5}\text{Ni}_{0.5-x}\text{X}_x$.

	$\text{Ti}_{0.5-x}\text{Ni}_{0.5}\text{X}_x$		$\text{Ti}_{0.5}\text{Ni}_{0.5-x}\text{X}_x$	
	ΔT_R	ΔM_s	ΔT_R	ΔM_s
Sc	—	25	*	*
Ti	0	0	*	*
V	—	20	15	50
Cr	—	140	25	90
Mn	105	120	25	85
Fe	—	215<	20	75
Co	—	215<	15	20
Ni	—	215<	0	0
Cu	—	110	—	25
Pd	—	215<	25	40
Au	—	215<	—	30

—: The B2→R transformation does not occur

*: Alloying is impossible.

<: The M_s temperature is below 123 K, which is the lowest temperature attainable in DSC measurement.

transformation occurs. Then the variations of T_R , M_s and M_s' (for the $B2 \rightarrow B19$ transformation) temperatures, and thus of the relative stability among the $B2$, R , $B19$ and $B19'$ phases due to the replacement of Ni and Ti by third elements are likely to correlate with that of the average number of valence electrons at each atom site. In order to investigate the effects thoroughly the electronic structures before and after the transformations should be made clear. Recently an extensive study on the effect of alloying by $3d$, $4d$ and $5d$ transition elements on the martensitic transformations of the Ti-Ni alloys has been reported by Kolomytsev[57], but in his study are not specified experimentally crystallographic sites of the third elements in the $B2$ matrix. It appears that precise information on them is necessary for the consideration about an electronic origin of the alloying effects.

4. Closing

Occupancy sites of certain constituent atoms in some β phase Cu-based and of several third elements in Ti-Ni-based ternary alloys have been made clear experimentally by means of ALCHEMI. Those in the latter alloys are shown to be reasonably accounted for by statistical thermodynamics. But, for occupancy sites of constituent atoms in stabilized martensites of some Cu-based alloys, there exist discrepancies at present with respect to the occurrence of site interchange between constituents and its nature, *i.e.*, ordering or disordering. Further intensive studies are no doubt necessary to be made to solve them. A systematic study on the effects of the addition of third elements on the relative stability among the phases concerned in the Ti-Ni alloys is now in progress by the present authors by means of ALCHEMI and band calculation.

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