

Site Preference of The Third Element in TiNi

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To examine the site preference of the third element in TiNi, the electronic structures of the $\text{TiNi}_{1-y}\text{X}_y$ and $\text{Ti}_{1-y}\text{NiX}_y$ alloys were calculated for cases, X=3d, 4d and 5d elements. Then, the concentrations $y=1/9$ for the B2 structure and $y=1/8$ for the B19' structure are assumed as models of alloys containing a small amount of the X atoms. The total energies for a non-magnetic state predict theoretically that the preferential site is the Ni site when the atomic number of the X atom is smaller than one of Ni (Pd or Pt), and the Ti site when the atomic number is larger than one of Ni (Pd or Pt). The predicted preferential sites are in good agreement with experimental results for 3d elements except for Mn.

It was also found that Cr, Mn and Fe atoms carry magnetic moments in TiNi although the other atoms of 3d, 4d and 5d atoms cannot. The energy gains due to the spin polarizations works X atoms to occupy Ti sites.

Key words: site preference, shape memory, titanium nickel (TiNi), electronic structure, B2 structure, B19' structure, third element

1. INTRODUCTION

It is well known that the alloy of titanium nickel (TiNi) exhibits the shape memory effect which is associated with the structural transformation between the B2 (CsCl) structure and the monoclinic B19' structure¹⁾. Experimental results show that a small amount addition of the third element to TiNi causes change of the transition temperature and produces the intermediate phase of the R phase^{2,3)} and/or the orthorhombic B19 phase. If we can control the structural transition temperature, we can use those alloys in wide temperature range.

Nakata et al.⁴⁾ added the 3d transition atoms (hereafter referred as an X atom) to TiNi and examined the site preference of the X atoms in the B2 structure. They reported that all the X atoms prefer the Ni site in the $\text{Ti}_{50}\text{Ni}_{50-y}\text{X}_y$ ($y=2$ for X=Cr, Mn, Fe, Co, and $y=3$ for X=Cu), however, in the $\text{Ti}_{50-y}\text{Ni}_{50}\text{X}_y$, Mn and Cu atoms occupy the Ti site but Fe and Co atoms do the Ni site, and Cr atom does both sites with nearly the same probability.

Thus, it is presumed that the difference in sites and kinds of the X atoms affects the properties of Ti-Ni-X alloys. To examine systematically the effect of the X atoms, 3d, 4d and 5d transition elements are chosen as the X atoms in this paper. Band calculations were carried out self consistently by the linear muffin tin orbital (LMTO) and atomic sphere orbital approximation (ASA) method.⁵⁾ The exchange correlation potential was treated within the framework of the local-spin-density (LSD) approximation.⁶⁾ The site preference of the X atoms is focused and the effect brought from the X atoms is examined on the basis of the electronic structure.

2. CRYSTAL STRUCTURE OF Ti-Ni-X

The alloy TiNi has the B2 (CsCl) structure in the parent phase and the monoclinic B19' structure¹⁾ in the martensitic phase. We cannot use the unit cell of the B2 structure as the unit cell of Ti-Ni-X including a small amount of the X atoms, because there is only one Ti (Ni) atom in the unit cell.

To make possible to replace a small amount of Ti (Ni) atoms by the X atoms, the B2 structure is treated as the P3 structure with 143th group symmetry as treated in a previous paper.⁷⁾ In the P3 structure with the nine times unit cell of the B2 structure, there are five kinds of Ti (Ni) atoms in the unit cell, which are situated at five atomic sites: 1a, 1b, 1c and two kinds of 3d sites. In the nine times unit cell of the B2 structure, one of nine Ti (Ni) atoms can be replaced by an X atom. Thus, we consider $\text{TiNi}_{8/9}\text{X}_{1/9}$ and $\text{Ti}_{8/9}\text{NiX}_{1/9}$ as an example of the alloy with the B2 structure containing a small amount of the X atoms. In the unit cell of $\text{TiNi}_{8/9}\text{X}_{1/9}$, there are nine Ti atoms, eight Ni atoms and an X atom.

In the B19' structure, we devised a unit cell for the two systems of $\text{TiNi}_{7/8}\text{X}_{1/8}$ and $\text{Ti}_{7/8}\text{NiX}_{1/8}$ by considering an eight times unit cell. In the unit cell of $\text{TiNi}_{7/8}\text{X}_{1/8}$, there are sixteen Ti atoms, fourteen Ni atoms and two X atoms.

The atomic concentration of the X atoms is 5.56 atomic percent in the systems of $\text{TiNi}_{8/9}\text{X}_{1/9}$ and $\text{Ti}_{8/9}\text{NiX}_{1/9}$ and 6.25 atomic percent in the systems of $\text{TiNi}_{7/8}\text{X}_{1/8}$ and $\text{Ti}_{7/8}\text{NiX}_{1/8}$. Although their concentrations are larger than 2-3 atomic percent of the X atoms in the samples used by Nakata et al., we use four systems described above as systems Ti-Ni-X containing a small amount of the X atoms.

In the systems $\text{TiNi}_{1-y}\text{X}_y$ ($\text{TiNi}_{8/9}\text{X}_{1/9}$ and $\text{TiNi}_{7/8}\text{X}_{1/8}$), we consider two cases: one is a case where the X atoms (X(at Ni)) occupy the empty Ni sites and the other is a case where Ti atoms (Ti(at Ni)) move to the empty Ni sites and the X atoms (X(at Ti)) occupy the Ti sites.

In the systems $\text{Ti}_{1-y}\text{NiX}_y$ ($\text{Ti}_{8/9}\text{NiX}_{1/9}$ and $\text{Ti}_{7/8}\text{NiX}_{1/8}$), we also consider two cases: one is a case where the X atoms (X(at Ti)) occupy the empty Ti sites and the other is a case where Ni atoms (Ni(at Ti)) move to the empty Ti sites and the X atoms (X(at Ni)) occupy the Ni sites.

As described above, we consider two cases of the X atoms at Ti sites and at Ni sites. Comparing total energies of the two cases in $\text{TiNi}_{1-y}\text{X}_y$ and $\text{Ti}_{1-y}\text{NiX}_y$, we will judge the site preference of the X atoms in Ti-Ni-X systems.

3. RESULTS AND DISCUSSION

3.1 Total energy

The total energy per unit cell was calculated as a function of the lattice constant. For example, the curve for $\text{TiNi}_{8/9}\text{Fe}_{1/9}$ with the B2 structure is shown in Fig. 1. In this figure, the curve shown by a broken line is of the lattice constant dependence for the case that Fe atoms occupy Ti sites. Another curve shown by a solid line is of one for the case that Fe atoms occupy Ni sites. From these results, the theoretical value of the lattice constant is defined by that where the total energy becomes minimum. Then, the difference between the minimum value of the case of Fe at Ti sites and one of Fe at Ni sites is defined by the symbol ' ΔE ' which is shown in Fig. 1. That is, Fe atoms prefer Ni sites if ΔE is positive and Ti sites if ΔE is negative.

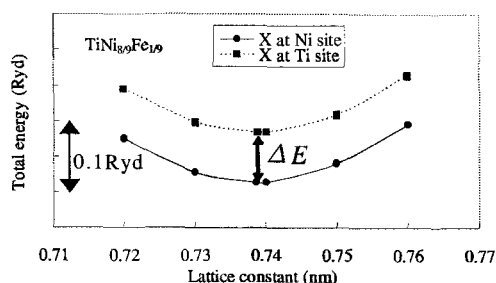


Fig. 1 Lattice constant dependence of total energies of $\text{TiNi}_{8/9}\text{Fe}_{1/9}$ with the B2 structure. The curves shown by a broken and a solid line indicate the cases that Fe atoms occupy Ti sites and Ni sites, respectively.

The same calculations were also done for the cases where the X atoms are other transition atoms in the $\text{TiNi}_{1-y}\text{X}_y$ and $\text{Ti}_{1-y}\text{NiX}_y$ alloys with the B2 and B19' structures. The ΔE for $\text{TiNi}_{8/9}\text{X}_{1/9}$ and $\text{Ti}_{8/9}\text{NiX}_{1/9}$ with the B2 structure are plotted for 3d, 4d and 5d X atoms in Fig. 2(a) and (b), and those for $\text{TiNi}_{7/8}\text{X}_{1/8}$ and $\text{Ti}_{7/8}\text{NiX}_{1/8}$ with the B19' structure in Fig. 2(c) and (d), respectively. It is seen that the differences have a maximum at VIIA element and, after that, decrease gradually as the number of the valence electron of the X atoms increases, and that ones become nearly negative when the X atoms are IB elements such as Cu. That is, the tendency that the X atoms occupy Ti sites is gradually strengthened as the number of the valence electron of the X atoms increases.

The preferential sites of the X atoms deduced from

the calculations are summarized in Table I. From this table, we can guess that the preferential site of the X atoms is the Ni site when the atomic number of the X atom is smaller than one of Ni (Pd or Pt) for 3d (4d or 5d) transition elements. On the other hand, it seems that the preferential site is the Ti site when the atomic number is larger than one of Ni (Pd or Pt).

Comparing the results of calculations with those of experiments for 3d elements in the B2 structure, their results agree except for Cu in $\text{TiNi}_{1-y}\text{X}_y$ and Mn in $\text{Ti}_{1-y}\text{NiX}_y$. Thus, theoretical results are roughly consistent with the experimental ones for 3d transition elements observed by Nakata et al., but there are no experimental data for 4d and 5d transition elements.

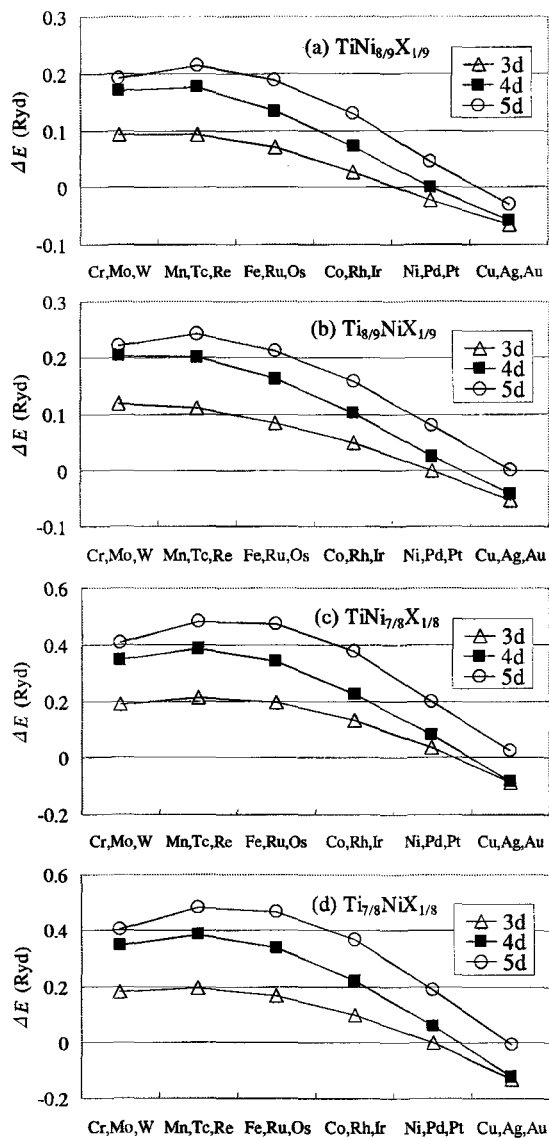


Fig. 2 Total energy differences plotted for 3d, 4d and 5d X atoms in $\text{TiNi}_{8/9}\text{X}_{1/9}$ (a), $\text{Ti}_{8/9}\text{NiX}_{1/9}$ (b), $\text{TiNi}_{7/8}\text{X}_{1/8}$ (c) and $\text{Ti}_{7/8}\text{NiX}_{1/8}$ (d).

3.2 Density of states

The alloy TiNi is non-magnetic, so we performed calculations for a non-magnetic state and the results were described in the previous section. However, we

could not obtain the good result about the site preference of Mn atoms in $Ti_{1-y}NiX_y$. Considering magnetic states in this section, we examine possibility that Mn atoms occupy Ti sites.

At first, we pay attention to the density-of-states (DOS) of a non-magnetic state. The local DOS of the X atoms in $Ti_{1-y}NiX_y$ are shown in Fig.3 for the B2 structure. The solid and the broken line indicate the DOS for X at Ti sites and at Ni sites, respectively. It is found that there is a high peak at the Fermi level in the DOS for Cr at Ti sites, while the DOS at the Fermi level is low for Cr at Ni sites. Therefore, we guess from Stoner's condition for ferromagnetism that Cr atoms in $Ti_{8/9}NiX_{1/9}$ may carry magnetic moments at Ti sites but not at Ni sites. The peak of DOS near the Fermi level moves to the low energy range with increasing atomic number of the X atom. In $Ti_{8/9}NiX_{1/9}$, similar features were also obtained for 3d X atoms but the peak near the Fermi level is lower. These features motivate us to examine energy gains due to spin polarizations.

The obtained effects of 4d and 5d elements as a third element are similar to those of 3d elements, although the peaks near the Fermi level are lower than those of 3d elements.

Table I List of the preferential site. The experimental results are put in the parentheses.

X	$Ti_{1-y}NiX_y$		$Ti_{1-y}NiX_y$	
	B19'	B2	B19'	B2
3d				
Cr	Ni	Ni(Ni)	Ni	Ni(Ni,Ti)
Mn	Ni	Ni(Ni)	Ni	Ni(Ti)
Fe	Ni	Ni(Ni)	Ni	Ni(Ni)
Co	Ni	Ni(Ni)	Ni	Ni(Ni)
Ni	—	—	—	—
Cu	Ti	Ti(Ni)	Ti	Ti(Ti)
4d				
Mo	Ni	Ni	Ni	Ni
Tc	Ni	Ni	Ni	Ni
Ru	Ni	Ni	Ni	Ni
Rh	Ni	Ni	Ni	Ni
Pd	Ni	Ni	Ni	Ni
Ag	Ti	Ti	Ti	Ti
5d				
W	Ni	Ni	Ni	Ni
Re	Ni	Ni	Ni	Ni
Os	Ni	Ni	Ni	Ni
Ir	Ni	Ni	Ni	Ni
Pt	Ni	Ni	Ni	Ni
Au	Ni	Ti	Ti	Ni

3.3 Ferromagnetic state

As mentioned in the previous section, Stoner's condition and non-magnetic electronic structures suggest that a ferromagnetic state may appear for the case where the X atoms are the VIA, VIIA elements and Fe atom in the $Ti_{1-y}NiX_y$ and $Ti_{1-y}NiX_y$ alloys with the B2 and B19' structures.

Then, to examine appearance of ferromagnetism, calculations were carried out again, assuming finite

magnetic moments on the X atoms at the initial step in the self-consistent process. As a result of the calculations, ferromagnetism appears for the cases where the X atoms are Cr, Mn and Fe atoms at Ti sites in the $Ti_{1-y}NiX_y$ and $Ti_{1-y}NiX_y$ alloys with the B2 and B19' structures, but doesn't for the other cases. Thus, Cr, Mn and Fe atoms surrounded by Ni atoms carry magnetic moments.

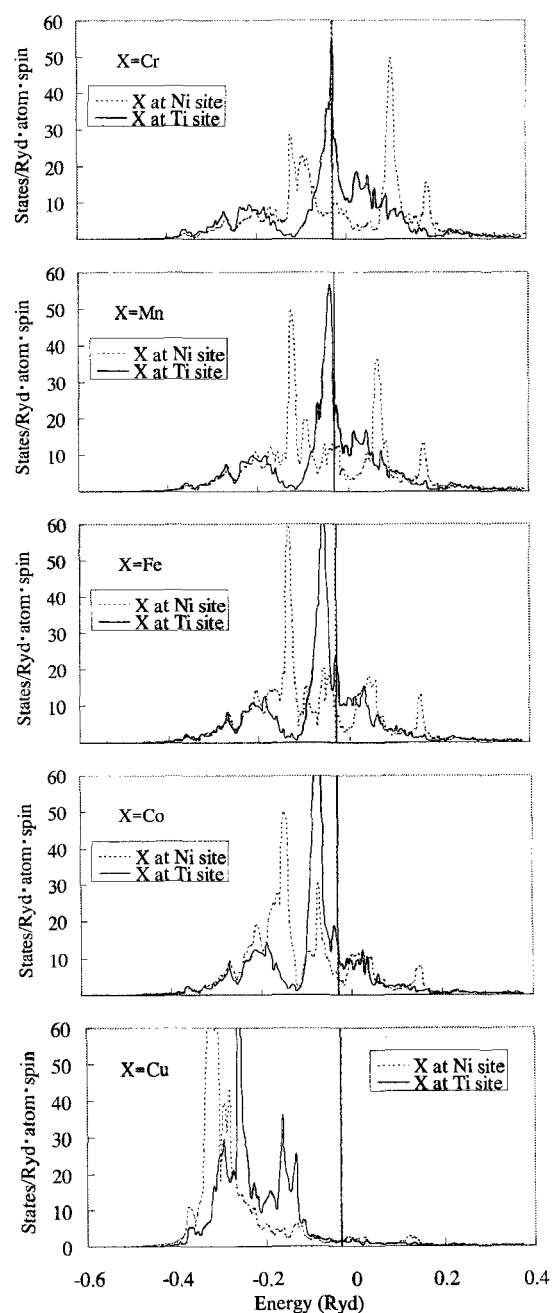


Fig.3 Local DOS of the X atoms in $Ti_{8/9}NiX_{1/9}$ with the B2 structure. The local DOS are shown for the cases of X=Cr, Mn, Fe, Co and Cu, respectively. A solid and a broken line indicate the cases of X at Ti sites and X at Ni sites, respectively. The vertical lines show the Fermi levels.

The energy difference ΔE between the cases of two X sites was also calculated for a ferromagnetic state. The differences are plotted against 3d transition elements in

Fig.4(a) and (b) which correspond to Fig.2(a) and (b). From these figures, it is found that the differences ΔE are smaller than those of the case where the X atoms are non-magnetic. The energy gain of ΔE due to spin polarizations is large in the order of Mn, Cr and Fe. That is, the spin polarizations of the X atoms work the X atoms to occupy Ti sites. The effect is large in the order of Mn, Cr and Fe. This tendency corresponds to that of the experimental result that Mn atoms prefer Ti sites, Cr atoms occupy both sites of Ti and Ni, and Fe atoms prefer Ni sites.

For the case of the 4d and 5d atoms as the X atoms, ferromagnetic states could not appear even if the spin polarizations on the X atoms were assumed at the initial step of the self-consistent calculations. That is, the energy gains due to the spin polarizations were not obtained because the peaks of the non-magnetic DOS near the Fermi level are low, compared with those of 3d atoms.

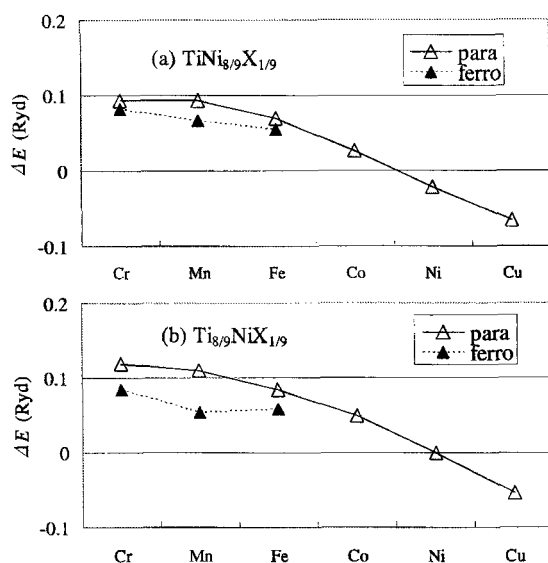


Fig.4 Total energy differences plotted against 3d X atoms in TiNi_{8/9}X_{1/9} (a) and Ti_{8/9}NiX_{1/9} (b). The curves for the case that the X atoms at Ti sites carry magnetic moments are shown by a broken line.

4. SUMMARY

To examine the site preference of the third element in TiNi, the electronic structures of the TiNi_{1-y}X_y and Ti_{1-y}NiX_y alloys were calculated for cases, X=3d, 4d and 5d elements. Then, the concentrations y=1/9 for the B2 structure and y=1/8 for the B19' structure are assumed as models of alloys containing a small amount of the X atoms. The total energies for a non-magnetic state were calculated for two cases of X at Ti sites and X at Ni sites. It was found from the energy difference (ΔE) between the two cases that the obtained preferential sites of the X atoms are in good agreement with experimental results for 3d elements except for Mn. It was predicted theoretically that the preferential site is the Ni site when the atomic number of the X atom is smaller than one of Ni (Pd or Pt), and the Ti site when the atomic number is larger than one of Ni (Pd or Pt).

It was also found that Cr, Mn and Fe atoms carry

magnetic moments in TiNi although the other atoms of 3d, 4d and 5d atoms cannot. The energy gains due to spin polarizations of these three atoms strengthened the tendency that the X atoms occupy Ti sites. However, concerning the preferential site of Mn, agreement with the experimental result was not obtained, even if we took account of the spin polarization. To obtain the good agreement, we may have to consider the other factor such as entropy except for the total energy.

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