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Alloying Behavior of Ni_3M-Type Compounds with $D0_a$ Structure

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The atom substitution preference of ternary additions in Ni_3M-type GCP (geometrically close-packed) compounds with $D0_a$ structure was determined from the direction of single-phase region of the GCP phase on the reported ternary phase diagrams. In Ni_3Nb, Co and Cu preferred the substitution for Ni-site, Hf, Ta, Ti, V and W the substitution for Nb-site, and Fe the substitution for both sites. In Ni_3Ta, Co, Cu, Fe, Ir, Mn and Re preferred the substitution for Ni-site, Mo and Nb the substitution for Ta-site, and Al and Cr the substitution for both sites. In Ni_3Mo, Pd and W preferred the substitution for Ni-site, and Al, Nb, Ta, Ti and Zr the substitution for Mo-site. The thermodynamic model, which was based on the change in heat of formation of the host compound by a small addition of ternary solute, was applied to predict the atom substitution preference of ternary additions. The heat of compound formation used in the thermodynamic calculation was derived from Miedema's formula. Good agreement was obtained between the thermodynamic model and the result of the literature search. For Ni_3Mo, with a small negative heat of formation, a weak binding force between the constituent elements is often enhanced by the addition of the ternary elements that substitute for Mo-site. [doi:10.2320/matertrans.M2010386]

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1. Introduction

Among a number of geometrically close-packed (GCP) phases,[1,2] Ni_3M-type GCP phases have various types of structures, e.g., Ni_3Nb, Ni_3Ta, and Ni_3Mo ($D0_a$), Ni_3V ($D0_{22}$), Ni_3Ti ($D0_{24}$), and Ni_3Al, Ni_3Si, and Co_3Ti ($L1_2$) as shown in Fig. 1. The coordination number of atoms is 12 in every structure. These structures are constructed by several stacking sequences of common close-packed plane with combination of a twofold hexagonal layer (h-layer) and a threefold cubic layer (c-layer) (Table 1[3]). In addition, M atoms on the close-packed plane show some ordered arrangements: triangular-type (T-type) and rectangular-type (R-type) in these GCP structures (Table 1). These compounds have a lot of attractive properties as a high-temperature structural material. Therefore these compounds have been used as precipitated phases, i.e., strengtheners in actually used nickel superalloys[4] and as constituent phases of Ni-base multi-phase intermetallic alloys recently developed by the present author's group.[5–10] The addition of third element to these binary Ni_3M-type GCP compounds or alloying element to the constituent Ni_3M phases in Ni-base multi-phase intermetallic alloys might modify not only the mechanical properties but also other properties such as oxidation or corrosion property. Therefore, to study substitution behavior or a solubility limit of alloying element in Ni_3M-type GCP compounds is a critical issue to develop a new type of high-temperature structural material based on intermetallic compounds.

The alloying behavior of $L1_2$-type Ni_3M compound, i.e., whether the addition substitutes exclusively for Ni-site, exclusively for M-site or for both sites, has been investigated and reviewed in Ni_3Al, Ni_3Ga, Ni_3Si, and Ni_3Ge compounds by Ochiai *et al.*[11] The thermodynamic Bragg–Williams model involving the nearest neighbor interactions, i.e., the change in total bonding energy of the host compound by a small addition of ternary solute at stoichiometry has been applied to these $L1_2$-type Ni_3M compounds.[11] The bond energy of each pair was derived from the heat of compound formation by Miedema's formula.[12,13] The agreement for preferable site occupation of the addition between the prediction and the experimental result was found to be excellent. Later, the same treatment has been conducted on $L1_2$-type Co_3Ti compound and was shown to be successful in predicting preferable site occupation of the addition.[14]

Between $L1_2$-type Ni_3M compounds and other Ni_3M-type GCP compounds, the environment of the nearest neighbor atoms is quite same not only for the number of nearest neighbor pairs but also for the kind of nearest neighbor pairs. Ni atom has 8 nearest neighbor pairs with Ni atom and 4 nearest neighbor pairs with M atom while M atom has 12 nearest neighbor pairs with Ni atom. Therefore, the same thermodynamic treatment as that conducted on $L1_2$-type Ni_3M compound may be applicable to other Ni_3M-type GCP compounds. Actually, the alloying behavior of $D0_a$-type Ni_3Nb,[15,16] $D0_{22}$-type Ni_3V[16] and $D0_{24}$-type Ni_3Ti[16] compounds has been investigated and reviewed. Consequently, the agreement for preferable site occupation of the addition between the thermodynamic prediction and the experimental result was found to be excellent. In this paper, we treat three $D0_a$-type Ni_3M compounds of Ni_3Nb, Ni_3Ta, and Ni_3Mo shown in Fig. 1. It is known that these three compounds are Berthollide-type compounds and their structures are stable to the melting points. In an early part of this paper, the alloying behavior is predicted by the thermodynamic model. In a next part of this paper, we collected and reviewed the data for the alloying behavior reported so far. In a last part of this paper, the agreement between the experiment and the modeling is discussed.

2. Thermodynamic Consideration

This section is devoted to showing whether a simple thermodynamic treatment will serve to account for the atom substitution preference of a third element X in a perfectly

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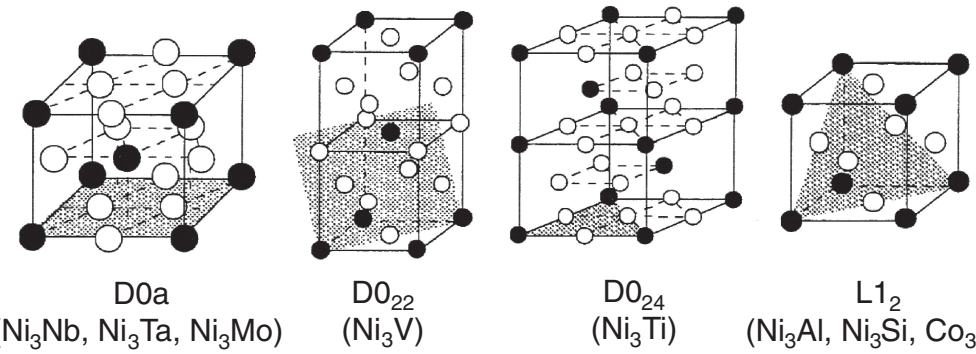

Fig. 1 Crystal structures of Ni_3Nb (or Ni_3Ta, Ni_3Mo) ($D0_a$), Ni_3V ($D0_{22}$), Ni_3Ti ($D0_{24}$), and Ni_3Al (or Ni_3Si, Co_3Ti) ($L1_2$). Open circle and full circle correspond to Ni atom and M atom in Ni_3M-type compounds, respectively. Also, a shaded plane shows closest plane.

Table 1 The crystallographic and thermodynamic feature of various Ni_3M-type GCP compounds. Experimental values for the heat of compound formation, ΔH were referred from Ref. 3).

Crystal structure	Unit cell	Stacking order	Stacking sequence	Hexagonality (%)	Unit mesh	Compound	ΔH_{cal} (kcal·mol^{-1})	ΔH_{exp} [3] (kcal·mol^{-1})
$D0_a$	hcp	AB	hh	100	R	Ni_3Nb	−7.5	−7.7, 298 K −9.6, 1220 K −9.4, 1250 K −5.8, 1273 K
						Ni_3Ta	−7.4	−7.0, 1173–1323 K −4.8, 1220–1320 K
						Ni_3Mo	−1.8	−0.6, 1073–1183 K 1.9, 1323 K
$D0_{22}$	fcc	ABCA′B′C′	cccccc	0	R	Ni_3V	−4.2	data not available
$D0_{24}$	hcp	ABAC	hchc	50	T	Ni_3Ti	−9.1	−8.4, 298 K −13.0, 1100–1300 K −10.6, 1300 K −9.8, 1320 K −10.3, 1513 K −8.4, 298 K
$L1_2$	fcc	ABC	ccc	0	T	Ni_3Al	−7.6	−9.8, 298 K −9.1, 298 K −8.4, 298 K −11.3, 980 K
						Ni_3Si	−8.3	−8.6, 298 K
						Co_3Ti		data not available

ordered stoichiometric $D0_a$ alloys, based on the Bragg–Williams model of nearest neighbor interactions. The only nearest neighbor approximation should be suitable for our purpose, because the second and further distant neighbor interaction energies are likely to be negligible in these Ni_3M-type compounds. $D0_a$ (Cu_3Ti structure type, oP8, space group Pmmn) structure has three crystallographic sites: one site (2b) for M atoms and two sites (2a and 4e) for Ni atoms. In this calculation, the latter two sites are assumed to be equivalent. Comparison will be made on the difference of heat of compound formation between two extreme cases for the substitution of component X. One case is that X atoms replace Ni atoms on Ni-site and the other case is that X atoms replace M atoms on M-site.

In comparison between ΔH (X_3M) and ΔH (Ni_3X) where the former is the change in heat of compound formation in Ni_3M system by a small addition of third element X to Ni-site while the latter is the change in heat of compound formation in Ni_3M system by a small addition of third element X to M-site. The atom substitution preference for a ternary addition of X atoms can be directed by the following expression[11]

$$\Delta H(Ni_3X)/\Delta H(Ni_3M) \lesseqgtr \Delta H(X_3M)/\Delta H(Ni_3M) + P. \quad (1)$$

ΔH is the heat of compound formation calculated by Miedema's formula. If the quantity on the left hand side is smaller, the substitution of X for Ni-site is preferred while if that on the right hand is smaller, the substitution of X for M-site is preferred. Also, P is defined by the following expression

$$P = 2 - (3/2)(\Delta H_{NiNi} - \Delta H_{MM})/\Delta H(Ni_3M). \quad (2)$$

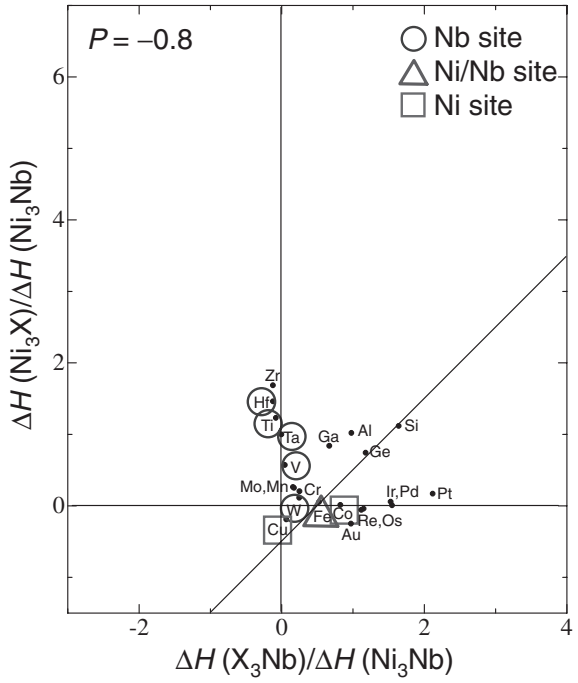

Fig. 2 Substitution behavior of third elements in Ni_3Nb evaluated by ΔH $(Ni_3X)/\Delta H$ $(Ni_3Nb) \lesseqgtr \Delta H$ $(X_3Nb)/\Delta H$ $(Ni_3Nb) + P$. The straight line with the slope of 1 divides third elements into Nb-site and Ni-site elements. Note that the atom substitution preference of elements enclosed by a circle, square and triangular marks were confirmed by literature search, and correspond to the substitution for Nb-site, Ni-site and both sites, respectively.

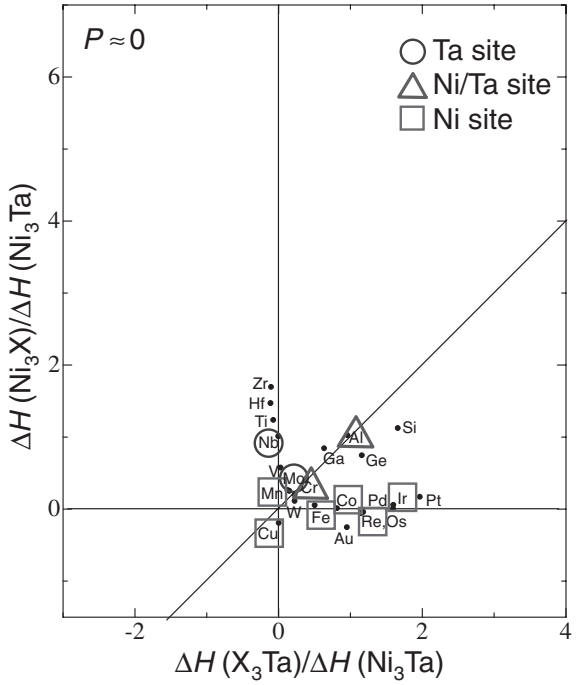

Fig. 3 Substitution behavior of third elements in Ni_3Ta evaluated by ΔH $(Ni_3X)/\Delta H$ $(Ni_3Ta) \lesseqgtr \Delta H$ $(X_3Ta)/\Delta H$ $(Ni_3Ta) + P$. The straight line with the slope of 1 divides third elements into Ta-site and Ni-site elements. Note that the atom substitution preference of elements enclosed by a circle, square and triangular marks were confirmed by literature search, and correspond to the substitution for Ta-site, Ni-site and both sites, respectively.

It is noted that the value of P, which is called as asymmetric index, depends only on the nature of the host compound and has a value between $+1$ and -1. Also, P was suggested to be closely related to the shape of enthalpy curve near the stoichiometric composition and the deviation in the composition range of stability of $D0_a$ phase field.[17)]

Figures 2–4 indicate the correlation between the heat of compound formation ratios of ΔH $(Ni_3X)/\Delta H$ (Ni_3M) and ΔH $(X_3M)/\Delta H$ (Ni_3M) for various third elements with the atom substitution preferences in the three host compounds. Here, the atom substitution behavior determined from the direction of single-phase region of the $D0_a$ phase on the reported ternary phase diagrams, which will be shown in the following section, was taken into consideration to draw a straight line. In all figures, we can successfully draw a straight line with the slope 1, just given by eq. (1). The line drawn bounds the substituting elements into two separate parts with regard to the atom substitution preference in all Ni_3M compounds concerned. The elements situated below the line mostly substitute for Ni-site, and those above the line mostly substitute for M-site and those just close to the line substitute for both sites.

The substitution behavior for transition metals and noble metals is systematic and in this case suggested to be primarily controlled by electronic (or chemical) nature denoted by the number in the periodic table.

In Ni_3Nb (Fig. 2), Ti, Zr, and Hf (4), V and Ta (5), Cr, Mo, and W (6), Mn (7), Cu (11), and Al and Ga (13) where the number in a parenthesis is the group number in a periodic table, shows less preference for the Ni sites but almost neutral

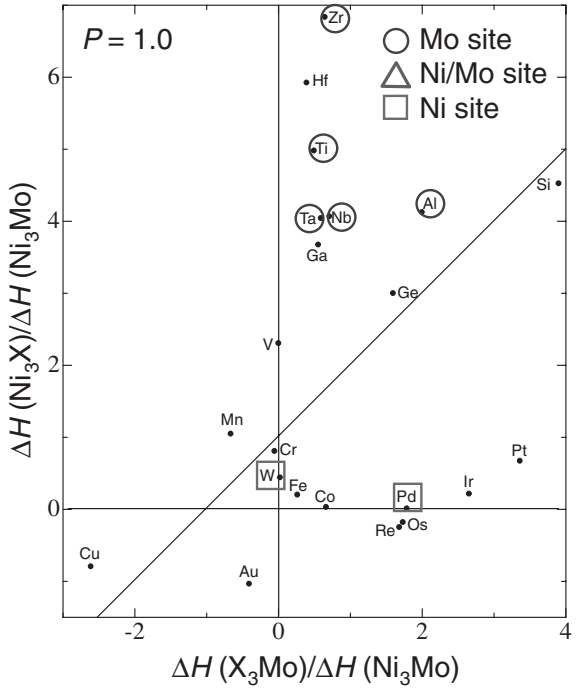

Fig. 4 Substitution behavior of third elements in Ni_3Mo evaluated by ΔH $(Ni_3X)/\Delta H$ $(Ni_3Mo) \lesseqgtr \Delta H$ $(X_3Mo)/\Delta H$ $(Ni_3Mo) + P$. The straight line with the slope of 1 divides third elements into Mo-site and Ni-site elements. Note that the atom substitution preference of elements enclosed by a circle and square marks were confirmed by literature search, and correspond to the substitution for Mo-site and Ni-site sites, respectively.

Table 2 Comparison of the atom substitution preference of alloying elements in Ni_3Nb, Ni_3Ta, and Ni_3Mo. Calculated values for the heat of compound formation, ΔH were listed in the third column.

Eletronic nature (Group number in a peridic table)	Addition element (X)	ΔH_{calc} (Ni_3X) kcal·mol^{-1}	Substitution site					
			Ni_3Nb		Ni_3Ta		Ni_3Mo	
			Prediction	Literature data	Prediction	Literature data	Prediction	Literature data
4	Ti	−9.126	M	M	M		M	M
	Zr	−12.527	M		M		M	M
	Hf	−10.857	M	M	M		M	
5	V	−4.222	M	M	M		M	
	Nb	−7.454			M	M	M	M
	Ta	−7.406	M	M			M	M
6	Cr	−1.476	M		Ni/M	Ni/M	Ni	
	Mo	−1.834	M		M	M		
	W	−0.802	M	M	Ni		Ni	Ni
7	Mn	−1.916	M		M	Ni	M	
	Re	0.463	Ni		Ni	Ni	Ni	
8	Fe	−0.363	Ni/M	Ni/M	Ni	Ni	Ni	
	Os	0.335	Ni		Ni		Ni	
9	Co	−0.050	Ni	Ni	Ni	Ni	Ni	
	Ir	−0.391	Ni		Ni	Ni	Ni	
10	Pd	−0.014	Ni		Ni		Ni	Ni
	Pt	−1.225	Ni		Ni		Ni	
11	Cu	1.462	M	Ni	Ni	Ni	M	
	Au	1.904	Ni		Ni		Ni	
13	Al	−7.559	M		Ni/M	Ni/M	M	M
	Ga	−6.215	M		M		M	
14	Si	−8.291	Ni/M		Ni		Ni	
	Ge	−5.495	Ni/M		Ni		M	

The symbls “Ni”, “M”, and “Ni/M” in the column “Substitution site” mean that ternary element substitutes for Ni-site, M-site, and both sites, respectively.

with Nb atom and are therefore plotted along the vertical axis of ΔH (Ni_3X)/ΔH (Ni_3Nb). In this case, these transition metals substitute for Nb-site. Fe (8) and Ge and Si (14) are almost equivalent in both interactions with Ni atom and with Nb atom, and then tend to substitute for both of Ni-and Nb-sites. On the other hand, Re (7), Os (8), Co and Ir (9), Pd and Pt (10), and Au (11) are attractive with Nb atom but almost neutral with Ni atom and are therefore plotted along the horizontal axis of ΔH (X_3Nb)/ΔH (Ni_3Nb). In this case, these metals substitute for Ni-site.

In Ni_3Ta (Fig. 3), Ti, Zr, and Hf (4), V and Nb (5), Mo (6), Mn (7), and Ga (13) shows less preference for the Ni sites but almost neutral with Ta atom, and are therefore plotted along the vertical axis of ΔH (Ni_3X)/ΔH (Ni_3Ta). In this case, these transition metals substitute for Ta-site. Cr (6) and Al (13) are almost equivalent in both interactions with Ni atom and with Ta atom, and then tend to substitute for both of Ni-and Ta-sites. On the other hand, W (6), Re (7), Fe and Os (8), Co and Ir (9), Pd and Pt (10), Cu and Au (11), and Si and Ge (14) are attractive with Ta atom but almost neutral with Ni atom, and are therefore plotted along the horizontal axis of ΔH (X_3Ta)/ΔH (Ni_3Ta). In this case, these metals substitute for Ni-site.

In Ni_3Mo (Fig. 4), Ti, Zr, and Hf (4), V, Nb, and Ta (5), Mn (7), Cu (11), Al and Ga (13), and Ge (14) shows less preference for the Ni sites but almost neutral with Mo atom, and are therefore plotted along the vertical axis of ΔH (Ni_3X)/ΔH (Ni_3Mo). In this case, these transition metals substitute for Mo-site. On the other hand, Cr and W (6), Re (7), Fe and Os (8), Co and Ir (9), Pd and Pt (10), Au (11), and Si (14) are attractive with Mo atom but almost neutral with Ni atom, and are therefore plotted along the horizontal axis of ΔH (X_3Mo)/ΔH (Ni_3Mo). In this case, these metals substitute for Ni-site.

The positions of the data points plotted about various ternary elements are almost identical in Fig. 2 (Ni_3Nb) and Fig. 3 (Ni_3Ta). However, there is a discrepancy in the prediction of the atom substitution preference between Ni_3Nb and Ni_3Ta as shown in Table 2. In Ni_3Nb, the number of the ternary elements that substitute for Nb-site is higher than the number of the elements that substitute for Ni-site. By contrast, in Ni_3Ta, the number of the ternary elements that substitute for Ni-site is higher than the number of the elements that substitute for Ta-site. The difference is caused by the values of the intercepts, P, depending on the nature of the host compounds. The values of P are following the order of P (Ni_3Nb) $< 0 \cong P$ (Ni_3Ta), as shown in Figs. 2 and 3.

Figure 4 (Ni_3Mo) differs from other figures, Fig. 2 (Ni_3Nb) and Fig. 3 (Ni_3Ta) in the positions of the data points. The data points in Fig. 2 (Ni_3Nb) and Fig. 3 (Ni_3Ta) are somehow converged around the origins, while those in

Table 3 The reported substitution behavior of ternary additions in Ni_3Nb ($D0_a$).

Element [Ref.]	Authors	Year	Temperature (K)	Solid solubility (at%)	Substitution site
Al[15]	Sugimura *et al.*	2010	1473	Ni(0) Nb(0)	indeterminable
Al[15,16]	Sugimura *et al.*	2010			Nb
Co[18]	Panteleimonov *et al.*	1982	1253	Ni (7), Nb (1)	Ni
Co[19]	Gupta *et al.*	1990	1348	Ni (5), Nb (0)	Ni
Co[15]	Sugimura *et al.*	2010	1473	Ni(5) Nb(0)	Ni
Co[15,16]	Sugimura *et al.*	2010	1473		Ni
Cr[20]	Kodentsov *et al.*	1986	1475	Ni (3), Nb (1)	Ni
			1473	Ni (0), Nb (0)	indeterminable
			1448	Ni (0), Nb (0)	indeterminable
Cr[21]	Gupta	1990	1446	Ni (0), Nb (0)	indeterminable
			1433	Ni (0), Nb (0)	indeterminable
			1373	Ni (0), Nb (0)	indeterminable
Cr[22]	Svechnikov *et al.*	1960	1373	Ni (0), Nb (0)	indeterminable
Cu[23]	Kodentsov *et al.*	1988	1175	Ni (11), Nb (1)	Ni
Fe[24]	Raghavan	1992	1173	Ni (6), Nb (8)	Ni/Nb
Hf[15]	Sugimura *et al.*	2010	1473	Ni(0) Nb(2)	Nb
Hf[15,16]	Sugimura *et al.*	2010			Nb
Si[15]	Sugimura *et al.*	2010	1473	Ni(0) Nb(0)	indeterminable
Si[15,16]	Sugimura *et al.*	2010			Ni/Nb
Ta[15]	Sugimura *et al.*	2010	1473	Ni(0) Nb(4)	Nb
Ta[15,16]	Sugimura *et al.*	2010			Nb
Ti[25]	Gupta	1991	1273	Ni (0), Nb (6)	Nb
Ti[26]	Pryakhina *et al.*	1966	1273	Ni (0), Nb (6)	Nb
			1173	Ni (0), Nb (3)	Nb
Ti[15]	Sugimura *et al.*	2010	1473	Ni(0) Nb(2)	Nb
Ti[15,16]	Sugimura *et al.*	2010			Nb
V[27]	Gupta	1991	1323	Ni (4), Nb (13)	Nb
W[28]	Gupta	1991	1273	Ni (3), Nb (4)	Ni/Nb
			1173	Ni(3), Nb (4)	Ni/Nb
W[29]	Tikhankin *et al.*	1976	1273	Ni (1), Nb (5)	Nb
			1173	Ni (1), Nb (5)	Nb

The symbols "Ni", "Nb", and "Ni/Nb" in the column "Substitution site" mean that third element substitutes for Ni-site, Nb-site and both sites, respectively. The numerical values expressed in the parentheses in the column "Solid solubility" mean deficit (expressed by at%) of each element from the stoichiometric composition of Ni_3Nb.

Fig. 4 (Ni_3Mo) are scattered widely, especially in a vertical direction. It means that for Ni_3Mo, with a small negative heat of formation, a weak binding force between the constituent elements is often enhanced by the addition of the ternary elements that substitute for Mo-site. The heats of formation of the host compounds have been calculated to be -7.454 kcal/mol in Ni_3Nb, -7.406 kcal/mol in Ni_3Ta, and -1.834 kcal/mol in Ni_3Mo by Miedema's formula.

The substitution behavior for group 13-14 elements is peculiar and not so simple. It is evident that group 13-14 elements fall on the first quadrant in Figs. 2–4 because both interactions with Ni atom and M atom are equally attractive. Consequently, group 13-14 elements are separated by a straight line into a different two region, depending on the relative values of two interaction energies.

Here it is interesting to note the difference of substitution behavior between compounds studied previously (Ni_3Al, Ni_3Ga, Ni_3Si, and Ni_3Ge)[11] and compounds of this study (Ni_3Nb, Ni_3Ta, and Ni_3Mo). In the former compounds, group 13-14 elements lay on the second quadrant and then substituted exclusively for M-sites while the transition metals substituted for Ni-site or for M-site, depending on the relative value of two heat of compound formation. In the latter compounds, both of the transition elements and group 13-14 elements have two possibilities, i.e., the case of substitution for Ni-site or the case for M-site, depending on the relative value of two heat of compound formation.

The systems of Ni with Cu, Co, Fe, Ir, Mn, Os, Pd, Pt, and Re form continuous solid solutions of f.c.c. phase. In these systems the deviation from the ideal solution is considered to be relatively small and then ΔH (Ni_3X) is close to zero, as indicated in Figs. 2–4, so that most of these elements will substitute for Ni-site. However, the prediction by this concept is not applicable to the cases of Cu, Fe, and Mn. The situations of Cu, Fe, and Mn are critical since both ΔH (Ni_3X) and ΔH (X_3M) are so small in comparison with ΔH (Ni_3M).

3. Reported Works

In this paper, the atom substitution preference for various third elements (X) in the unit cell of a host Ni_3M-type compound is determined from the direction of single-phase region in an isothermal section of a ternary phase diagram

Table 4 The reported substitution behavior of ternary additions in Ni_3Ta ($D0_a$).

Element [Ref.]	Authors	Year	Temperature (K)	Solid solubility (at%)	Substitution site
Al[30]	Nash *et al.*	1979	1273	Ni (0.8) Ta (0.8)	Ni/Ta
			1523	Ni (1.3) Ta (1.3)	Ni/Ta
Al[31]	Kaufman	1991	1800	Ni (0) Ta (0)	indeterminable
			1600	Ni (0) Ta (0)	indeterminable
			1400	Ni (0) Ta (0)	indeterminable
Al[32]	Zakharov	1993	1273	Ni (0.9) Ta (0.9)	Ni/Ta
			1523	Ni (1.5) Ta (1.3)	Ni/Ta
Al[33]	Hong *et al.*	1989	1300	Ni (1.9) Ta (0.6)	Ni
Al[34]	Willemin *et al.*	1986	1523	Ni (2.5) Ta (1.6)	Ni/Ta
Co[35]	Nesterenko *et al.*	1980	1273	Ni (15.4) Ta (2.6)	Ni
Cr[36]	Schittny *et al.*	1985	1273	Ni (3.5) Ta (2.2)	Ni/Ta
Cu[31]	Kaufman	1991	1573	Ni (4.8) Ta (0)	Ni
			1673	Ni (7.8) Ta (0)	Ni
Cu[37]	Gupta	1990	1573	Ni (18.7) Ta (0)	Ni
			1573	Ni (19.1) Ta (0)	Ni
Cu[23]	Kodentsov *et al.*	1988	1473	Ni (7.8) Ta (0)	Ni
Fe[38]	Uskova *et al.*	1991	1273	Ni(10.0) Ta (0)	Ni
Ir[39]	Bernard *et al.*	1973	1173	Ni (2.2) Ta (0.6)	Ni
Mn[40]	Slyusarenko *et al.*	1997	1225	Ni (19.1) Ta (8.7)	Ni
Mo[31]	Kaufman	1991	1700	Ni (0) Ta (5.7)	Ta
			1173	Ni (0) Ta (25.0)	Ta
			1600	Ni (0) Ta (17.4)	Ta
Mo[41]	Gupta	1991	1173	Ni (0) Ta (25.0)	Ta
			1523	Ni (4.8) Ta (6.1)	Ta
Mo[42]	Chakravorty *et al.*	1983	1273	Ni (0) Ta (10.9)	Ta
			1523	Ni (0) Ta (10.4)	Ta
			1273	Ni (0) Ta (10.0)	Ta
Nb[43]	Gupta	1991	1073	Ni (0) Ta (25.0)	Ta
			1473	Ni (0) Ta (25.0)	Ta
Nb[44]	Kornilov *et al.*	1956	1473	Ni (0) Ta (25.0)	Ta
Re[45]	Slyusarenko *et al.*	1998	1425	Ni (1.7) Ta (1.7)	Ni/Ta
Re[46]	Ametov *et al.*	1990	1425	Ni (3.9) Ta (2.0)	Ni

The symbols "Ni", "Ta", and "Ni/Ta" in the column "Substitution site" mean that third element substitutes for Ni-site, Ta-site and both sites, respectively. The numerical values expressed in the parentheses in the column "Solid solubility" mean deficit (expressed by at%) of each element from the stoichiometric composition of Ni_3Ta.

that have been reported so far. The unit cell of Ni_3M lattice involves two types of site, which are defined as Ni-site and M-site. A ternary addition which occupies mostly Ni-site has a single-phase region lying in parallel to Ni–X edge in an isothermal section, an addition which occupies mostly M-site has a lobe lying in parallel to M–X edge, and an addition which substitutes for both sites has a lobe extending in a direction almost bisecting the quasi-binary section Ni_3M–Ni_3X and Ni_3M–X_3M.

A relatively large number of ternary Ni–Nb–X phase diagrams have been published. Table 3 summarizes the results. Reported temperatures range between 1173 and 1473 K. The table shows the direction and the extent of solubility limit for each solute element. Fe[24] substitutes for both sites, Co[15,16,18,19] and Cu[23] mostly for Ni-site, and Hf,[15,16] Ta,[15,16] Ti,[15,16,25,26] V,[27] and W[28,29] mostly for Nb-site. The ternary systems with Al,[15,16] with Cr,[20–22] and with Si[15,16] did not provide a clear indications of substitution behavior in Ni_3Nb because of very small solid solubility. The reported results on the solid solubility of various kinds of solutes in Ni_3Nb are summarized in Fig. 5.

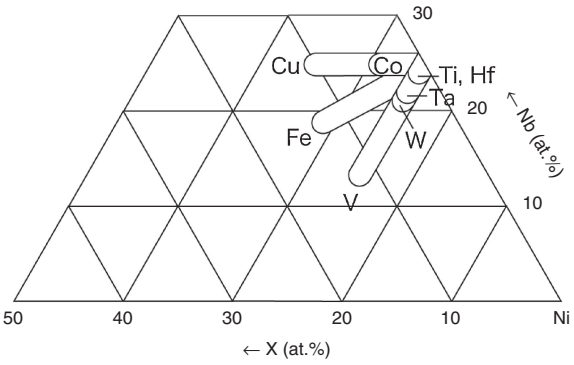

Fig. 5 Semischematic depiction of the single-phase regions of ternary Ni_3Nb phase for various elements. Data for the systems with Fe[24] and W[29] at 1273 K, Cu[23] at 1175 K, V[27] at 1323 K, and Co,[15] Hf,[15] Ta,[15] and Ti[15] at 1473 K are taken from literatures.

A large number of ternary Ni–Ta–X phase diagrams have been published. Table 4 summarizes the results taken from the existing ternary phase diagrams. Reported temperatures range between 1073 and 1800 K. Al[30–34] and Cr[36] substitute

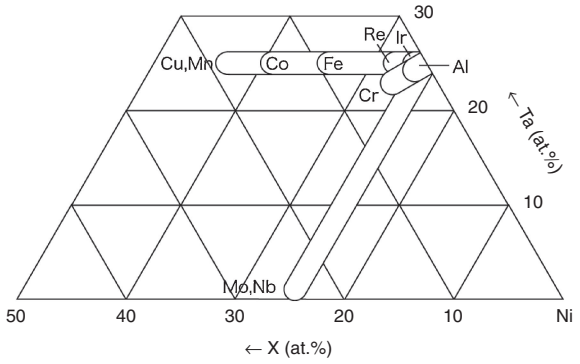

Fig. 6 Semischematic depiction of the single-phase regions of ternary Ni_3Ta phase for various elements. Data for the systems with Ir[39] and Mo[31] at 1173 K, Mn[40] at 1225 K, Co,[35] Cr,[36] and Fe[38] at 1273 K, Re[46] at 1425 K, Nb[43] at 1473 K, Al[34] at 1523 K, and Cu[37] at 1573 K are taken from literatures.

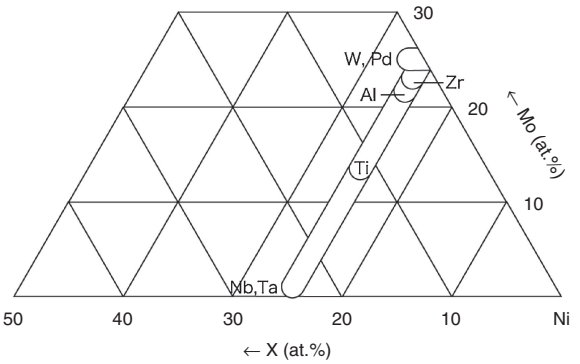

Fig. 7 Semischematic depiction of the single-phase regions of ternary Ni_3Mo phase for various elements. Data for the systems with W[54] and Pd[59] at 973 K, Al[47] at 1153 K, and Ti,[52] Nb,[57] Zr,[56] and Ta[41] at 1173 K are taken from literatures.

Table 5 The reported substitution behavior of ternary additions in Ni_3Mo ($D0_a$).

Element [Ref.]	Authors	Year	Temperature (K)	Solid solubility (at%)	Substitution site
Al[47]	Maslenkov *et al.*	1988	1153	Ni (0) Mo (4.4)	Mo
Al[48]	Markiv *et al.*	1969	1073	Ni (0) Mo (0)	indeterminable
Al[49]	Kubaschewski	1993	973	Ni (0) Mo (3.1)	Mo
Cr[50]	Turchi *et al.*	2006	573	Ni (0) Mo (0)	indeterminable
			773	Ni (0) Mo (0)	indeterminable
			893	Ni (0) Mo (0)	indeterminable
			973	Ni (0) Mo (0)	indeterminable
Ti[51]	Eremenko *et al.*	1984	1173	Ni (0) Mo (14.0)	Mo
Ti[52]	Gupta	1991	1173	Ni (0) Mo (12.5)	Mo
W[53]	Meshkov *et al.*	1985	973	Ni (2.5) Mo (1.9)	Ni/Mo
W[54]	Gupta	1991	973	Ni (2.5) Mo (0.9)	Ni
Nb[55]	Kaufman *et al.*	1974	1625	Ni (0) Mo (2.5)	Mo
			1525	Ni (0) Mo (13.1)	Mo
			1173	Ni (0) Mo (25.0)	Mo
Nb[56]	Virkar *et al.*	1969	1173	Ni (0) Mo (25.0)	Mo
Nb[57]	Gupta	1991	1173	Ni (0) Mo (25.0)	Mo
Zr[56]	Virkar *et al.*	1969	1173	Ni (0) Mo (3.1)	Mo
Zr[58]	Prime *et al.*	1991	1173	Ni (0) Mo (0)	indeterminable
Ta[41]	Gupta	1991	1173	Ni (0) Mo (5.6)	Mo
			1173	Ni (0) Mo (25.0)	Mo
Pd[59]	Raevskaya *et al.*	1984	973	Ni (2.5) Mo (0)	Ni

The symbols "Ni", "Mo", and "Ni/Mo" in the column "Substitution site" mean that third element substitutes for Ni-site, Mo-site and both sites, respectively. The numerical values expressed in the parentheses in the column "Solid solubility" mean deficit (expressed by at%) of each element from the stoichiometric composition of Ni_3Mo.

for both sites, Co,[35] Cu,[23,31,37] Fe,[38] Ir,[39] Mn,[40] and Re[45,46] mostly for Ni-site and Mo,[31,41,42] and Nb[43,44] mostly for Ta-site. Fig. 6 summarizes the single-phase regions of ternary Ni_3Ta phase. This figure shows that Ni_3Ta forms continuous solid solutions with Ni_3Nb and Ni_3Mo. It can be said that Nb and Mo substitute for Ta-site in Ni_3Ta because of similar electronic configuration to Ta.

There have been some data for ternary Ni–Mo–X phase diagrams as listed in Table 5. Reported temperatures range between 573 and 1625 K. Pd[59] and W[53,54] substitute mostly for Ni-site, and Al,[47–49] Nb,[55–57] Ta,[41] Ti,[51,52] and Zr[56,58] mostly for Mo-site. The ternary systems with Cr[50] did not provide a clear indication of substitution behavior in Ni_3Mo because of very small solid solubility. Figure 7 summarizes the reported results on the substitution behavior in Ni_3Mo. Ni_3Mo is completely miscible with Ni_3Nb and Ni_3Ta.

There are strong indications to show that the substitution behavior is not as simple as was thought. As for the atom substitution preference of W in Ni_3Nb and Al in Ni_3Ta, there are discrepancies between the data from various sources. This would, then, suggest that the addition of the fourth element undoubtedly affects the atom substitution preference of the third element, and vice versa. In instances where a solute element lies close to the boundary defined by eq. (1), the atom substitution preference would become sensitive to the

addition of an impurity. This may occur in the cases of W in Ni_3Nb and Al in Ni_3Ta. The extension of the theoretical treatment to quaternary system is a future problem and further experimental work is needed to enable us to get a firm conclusion. In many respects, the present concept is however regarded as the quantitative description of the Guard and Westbrook rules in Ni_3Al;[60] the elements most like Ni in electronic configuration will substitute for Ni-site and those like Al will substitute for Al-site.

4. Comparison between the Prediction and the Reported Works

Summarizing the results for three host compounds (Figs. 2–4), the agreement for atom substitution preference between the prediction and the experimental work is fairly good. If mentioning disagreement, in Ni_3Nb, it has been reported that Fe substitutes for both Ni-site and Nb-site. We can draw the straight line with the slope 1 which passes through the point plotted about Fe, and the point about Cu substituted mostly for Ni-site should be below the line. In Ni_3Ta, Al and Cr substitute for both Ni-site and Ta-site. We can draw the straight line with the slope 1, which passes close to the points plotted about Al and Cr. The point about Mn substituted mostly for Ni-site should be below the line. So, it remains possible that the intercept of the straight line P may not be accurate in the cases of both Ni_3Nb and Ni_3Ta. We should actually do some experiments for determination of the value of P.

As far as ternary phase diagrams with Ni and Mo we could obtain, no element substitutes for both Ni-site and Mo-site. Accordingly, we drew the straight line with the slope 1 which bounds the substituting elements into two separate parts with regard to the atom substitution preference of the literature search result in such a way that P has a value between -1 and $+1$.

5. Conclusion

The atom substitution preference of various kinds of ternary additions in $D0_a$-type Ni_3Nb, Ni_3Ta, and Ni_3Mo GCP compounds was determined from the direction of single-phase regions of the GCP phases on ternary phase diagrams, and also predicted by the thermodynamic consideration involving the nearest neighbor interactions. The following conclusion was obtained from the present study.

From the reported experimental works, we determined the atom substitution preference of ternary additions. In Ni_3Nb, Co and Cu preferred the substitution for Ni-site, Hf, Ta, Ti, V and W the substitution for Nb-site, and Fe the substitution for both sites. In Ni_3Ta, Co, Cu, Fe, Ir, Mn, and Re preferred the substitution for Ni-site, Mo, and Nb the substitution for Ta-site, and Al and Cr the substitution for both sites. In Ni_3Mo, Pd and W preferred the substitution for Ni-site, Al, Nb, Ta, Ti, and Zr the substitution for Mo-site.

From the thermodynamic argument for Ni_3Mo, with a small negative heat of formation, it was found that a weak binding force between the constituent elements is often enhanced by the addition of the majority of ternary elements that substitute for Mo-site.

In the compounds (Ni_3Nb, Ni_3Ta, and Ni_3Mo) treated in this study, both of the transition elements and group 13-14 elements have two possibilities, i.e., the case of substitution for Ni-site or the case of substitution for M-site, depending on the relative value of two heat of compound formation, in contrast to the compounds (Ni_3Al, Ni_3Ga, Ni_3Si, and Ni_3Ge) consisting of group 13-14 elements and Ni atoms.

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