NEW PHACOMP AND ITS APPLICATIONS TO ALLOY DESIGN

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Summary

New PHACOMP was developed from the calculations of electronic structure of alloys by the DV-Xα cluster method. It is based on the first theoretical approach to the solid solubility problem of alloys, both solute and solvent being transition metals. The electron vacancy number that is an important parameter in the current PHACOMP, is not used any more in the New PHACOMP. Instead, a parameter $\bar{M}d$, which is an average energy level of d orbitals of alloying transition metals, was introduced, and used for treating of the phase stability in austenitic (γ) alloys. This parameter correlates with electronegativity and atomic size, being parameters used in the classical approach by Hume-Rothery, and Darken and Gurry. The validity of New PHACOMP was proved by examining about 25 ternary phase diagrams. The constant $\bar{M}d$ line well represents various phase boundaries such as $\gamma/\gamma + \sigma$, $\gamma/\gamma + \mu$, $\gamma/\gamma + \gamma'(Ni_3Al)$, $\gamma/\gamma + \eta(Ni_3Ti)$ and $\gamma/\gamma + \beta(NiAl)$ in austenitic alloys. Our method correctly predicts the occurrence of topological close-packed (TCP) phases in practical superalloys. Several difficulties in the widely used PHACOMP based on the electron vacancy concept, were solved by the present method. New PHACOMP provides a nice tool for better alloy design not only for Ni-base, but also for Co-base and Fe-base superalloys.

Introduction

PHACOMP has been widely used for the development and production of superalloys. According to the review by Barrett (1), up to this year, it has a history for a half century since 1934 when the paper by Hume-Rothery et al was published. Especially in the last two decades since Boesch and Slaney (2) first proposed the idea of PHACOMP based on the electron vacancy concept in 1964, an enormous effort has been made for developing the better PHACOMP. In this method, the tendency of the f.c.c. matrix (called γ phase) to precipitate the undesirable brittle TCP phases (e.g. σ phase) is determined by a magnitude of the average electron vacancy number, $\overline{Nv}$. Here, the electron vacancy number, Nv, is the number of vacancies or electron holes in the metal d band above the Fermi level. In spite of its successful applications to Ni-base superalloys, there still remain some contradictions in it. For instance, it gives an ill-prediction for the occurrence of σ phase in some alloys (e.g. Inconel 713C). It predicts poorly for μ phase. Furthermore, alloy design of Co-base and Fe-base superalloys by PHACOMP has not succeeded satisfactorily yet (3). Most of these problems are inherent in the electron vacancy concept, and hence could not be solved by several modified Nv methods so far proposed.

The purpose of this paper is to propose New PHACOMP to solve these problems. New PHACOMP was developed on the basis of theoretical calculation of electronic structures by the DV(discrete variational)-Xα cluster method.

DV-Xα Cluster Calculations

In the DV-Xα cluster method (4), an exchange correlation between electrons is included by means of a local exchange correlation potential, V_{xc},

$$V_{xc} = -3\alpha \left[\frac{3}{8\pi} \rho(r) \right]^{1/3} . \qquad (1)$$

Here, $\rho(r)$ is the electron density. The parameter α is fixed at 0.7, and the self-consistent charge approximation is used in the calculation.

The electronic structures of Ni_3Al containing transition elements were calculated (5). As shown in Fig.1(a), Ni_3Al has a $L1_2$ type structure. An Al atoms is surrounded by twelve Ni atoms in the first nearest neighbours, and by six Al atoms in the second nearest neighbours. The cluster used in the calculation was $[MNi_{12}Al_6]$, which is shown in Fig.1(b). An Al atom in the center was substituted for the various alloying elements M; M=Ti, V, Cr, Mn, Fe, Co, Ni, Cu (3d elements), Zr, Nb, Mo (4d elements) and Hf, Ta, W, Re (5d elements). This cluster model is also valid for γ phase (f.c.c. Ni). Because, the element which is substituted for Ni in γ phase, is surrounded by twelve Ni atoms in the first nearest neighbours, similarly to $[MNi_{12}Al_6]$ cluster. The first neighbour interactions are most predominant in f.c.c. metals and alloys. In addition, the lattice parameter of Ni_3Al is similar to that of f.c.c. Ni. The electronic structure of Ni_3Al also resembles to that of f.c.c. Ni.

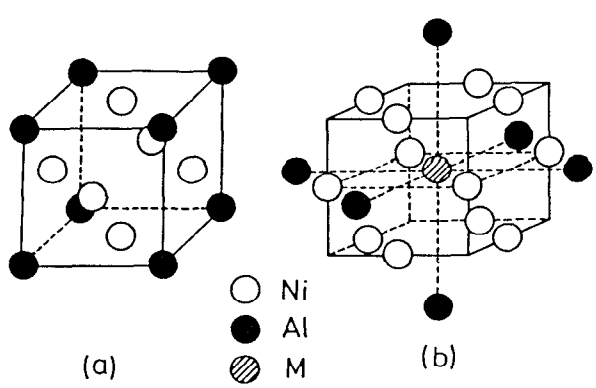

Fig.1 (a) Crystal structure of Ni_3Al, and (b) cluster model used in the calculation.

Electronic Structures of Alloyed Ni_3Al

The results of level structures are shown in Fig.2. In pure Ni_3Al, the levels of $13a_{1g}$ to $15e_g$ are mainly originated from Ni 3d orbitals, namely, Ni 3d band where the Fermi level (E_f) lies. The lower energy levels of $12a_{1g}$ to $9t_{2g}$ and the upper energy levels of $15a_{1g}$ to $14t_{2u}$ are the mixed states of Al 3s, 3p and Ni 4s, 4p as well as Ni 3d. The calculated density of states agrees well with the results of band calculations.

In alloyed Ni_3Al with transition elements, new energy levels due to the d orbitals of alloying elements, appear above the Fermi level. For instance $16e_g$ and $14t_{2g}$ which are drawn by dotted levels in Fig.2, correspond to these levels. Similarly, for the 4d and 5d transition elements such new levels appear and change systematically with the order in periodic table of the elements. These metal-d levels (Md) correlate with electronegativity as shown in Fig.3. The values of electronegativity are taken from Watson and Bennett (6). Following Mulliken, the eigenvalues of energies obtained by the DV-Xα calculation may represent electronegativity, although for a cluster the covalency between the neighbouring atoms somehow modifies this idea for a free atom. In addition, the Md levels are related to the metallic radius of element M, as shown in Fig.4. The metallic radii are taken from the values of closed packed metals with CN=12, reported by Teatum et al (7). The energies of both e_g and t_{2g} levels increase with metallic radius of M, independently of 3d, 4d or 5d elements. This is understood primarily as due to the electron binding energy that decreases with an average radius <r> of d orbital and also with metallic radius, resulting in the higher energy of Md levels for a larger element.

Solid Solubility and Md Parameter

The solid solubility problem is one of old but important problems in

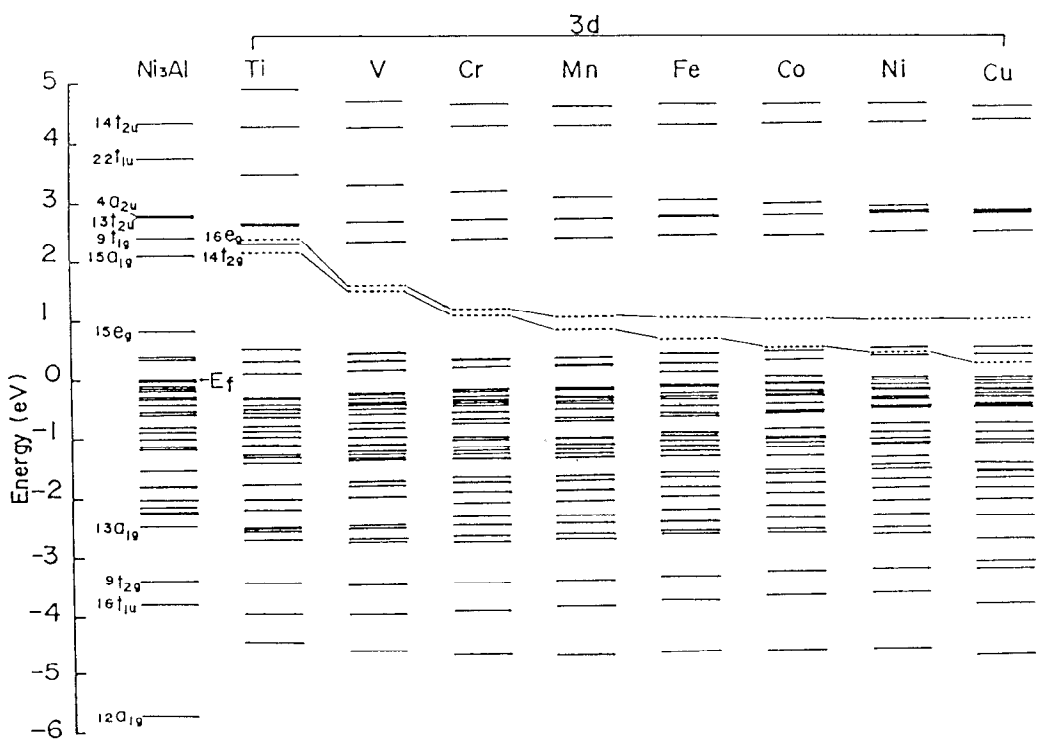

Fig.2 Energy level structures of pure and alloyed Ni_3Al with 3d transition elements.

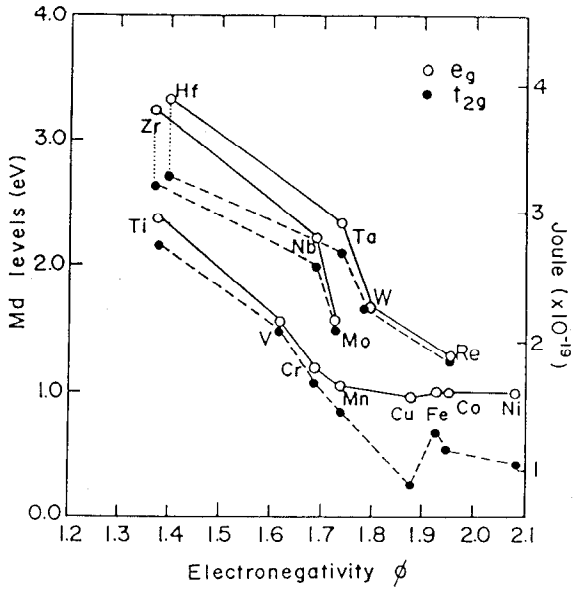

Fig.3 Correlation of Md levels with electronegativity.

Table 1 List of Md for various elements.

Element		Md level, eV	Element		Md level, eV
	Ti	2.271		Zr	2.944
	V	1.543	4d	Nb	2.117
	Cr	1.142		Mo	1.550
	Mn	0.957		Hf	3.020
3d	Fe	0.858	5d	Ta	2.224
	Co	0.777		W	1.655
	Ni	0.717		Re	1.267
	Cu	0.615		Al	1.900
				Si	1.900

physical metallurgy. Recently, Chelikowsky (8) proposed a new approach for divalent alloys (e.g. Zn and Cd), following the Miedema's semi-empirical model (9). But, there has been no solid theory so far developed to treat of alloys, both solute and solvent being transition metals. In this case, anisotropic interactions due to d electrons may be dominant rather than isotropic ones stressed by Miedema, and hence the Miedema-Chelikowsky scheme may be no longer valid for treating of the present problem. The electron vacancy concept has been used empirically for this, but it is less accurate. As described before, the Md levels physically correlate with electronegativity and metallic radius of elements, both of which are parameters used in the classical approach by Hume-Rothery (10) and Darken and Gurry (11). Therefore, the Md has a great possibility of dealing with the present solubility problem. The values of Md for various transition metals and Cu, Al and Si are listed in Table 1. Each Md is the average value of e_g and t_{2g}. As the reference, the zero level was set to the Fermi level of Ni_3Al.

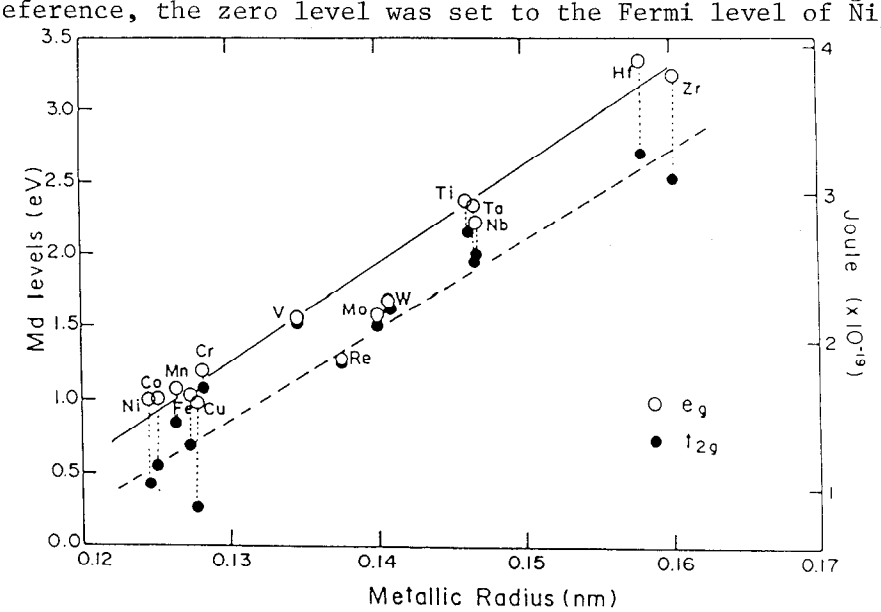

Fig.4 Correlation of Md levels with metallic radius.

New PHACOMP

We define the average value of Md in alloys by taking the compositional average and denote $\bar{M}d$ as follows,

$$\bar{M}d = \sum_{i=1}^{n} X_i \, (Md)_i \quad . \qquad (2)$$

Here, X_i is the atomic fraction of component i in the alloy, and $(Md)_i$ is the Md value for component i in Table 1. The summation is taken over all the components, i=1,2....,n.

We assume that when the $\bar{M}d$ becomes larger than a certain value, the phase instability takes place and the second phase occurs in a γ matrix. In other words, such a critical $\bar{M}d$ determines the solubility limit of γ matrix. The critical $\bar{M}d$ value depends on a type of second phase, because the solubility limit is determined by the tangent to the Gibbs free energy vs composition curves of matrix and second phase. As a solid solubility changes with temperatures, it should depend on temperatures, too. Such a critical value for $\bar{M}d$ was determined by fitting the solubility line in phase diagrams by a constant $\bar{M}d$ line, as explained in the next section. It is noted that Eq.(2) is analogous to the equation for the average electron vacancy number, $\bar{N}v$.

Solid Solubilities in Ternary Alloys

To verify our New PHACOMP, the three phase boundaries were mainly examined. They are 1) $\gamma/\gamma + \sigma$, 2) $\gamma/\gamma + \mu$ and 3) $\gamma/\gamma + \gamma'$. The σ and μ phase are TCP (topological close-packed) phase, and $\gamma'(Ni_3Al)$ is a GCP (geometrically close-packed) phase. All of them are important phases in superalloys.

$\gamma/\ \gamma + \sigma$ Phase Boundaries. The two typical phase diagrams are shown in Fig.5(a) Ni-Co-Cr and (b) Ni-Cr-Mo. In each figure, an iso $\bar{M}d$ line of 0.925 (eV) is drawn with an iso $\bar{N}v$ line of 2.49, which is the critical $\bar{N}v$ for Ni base alloys (12). In both systems, the iso $\bar{M}d$ line well represents $\gamma/\gamma + \sigma$ phase boundary, whereas the iso $\bar{N}v$ line is far away from the boundary. Barrows and Newkirk (13) introduced the idea of critical electron vacancy number, N_V^C to improve this mismatching. They estimated N_V^C from the solid solubilities in binary phase diagrams, and included both temperature and compositional dependence on it. They inferred that σ phase tends to occur if $N_V^C < \bar{N}v$. Their modification may be physically in problem since compositional and temperature factors are involved in a purely electronic parameter Nv. Their model, however, seemed to lead to a considerable improvement in estimating $\gamma/\gamma + \sigma$ phase boundaries. But, their model still falls short in the prediction for the occurrence of σ phase in Inconel 713C alloys. Wallace (14) gave a further modification for solving this problem, but there exists a definite limitation in the electron vacancy concept, probably owing to the lack of atomic size concept in it.

In Fig.5(a) and (b), the line of equi-atomic size is also shown by $\bar{R}$. This was obtained by taking the compositional average of metallic radii of elements (7). In Ni-Co-Cr, the $\bar{R}$ line coincides with the phase boundary, but it does not in Ni-Cr-Mo. This clearly indicates the importance of atomic size effect in determining solubilities of transition metal base alloys, and also the occurrence of atomic size adjustments in alloys, probably by a charge transfer between atoms.

The phase diagram of Fe-Ni-Cr is given in Fig.5(c). The critical value of $\bar{M}d$ changes with temperatures. It is 0.900 (eV) at 1073K, lower than 0.925 at 1477K in (a) and (b).

$\gamma/\gamma + \mu$ Phase Boundaries. The phase diagram of Co-Ni-Mo is shown in Fig.5(d). The critical $\bar{M}d$ is 0.900 for μ phase, which is smaller than that for σ phase (see Fig.5(a) and (b)). This is probably due to the difference in stability of σ and μ phases relative to γ phase, arising from the difference in their crystal structure.

$\gamma/\gamma + \gamma'$ Phase Boundaries. The phase diagrams of Ni-Al-Ti and Ni-Cr-Ti are given in Fig.5(e) and (f), respectively. The γ' phase is Ni_3Al and the η phase is Ni_3Ti. Because of resemblance in their structure, these phases can be treated by the same $\bar{M}d$ value.

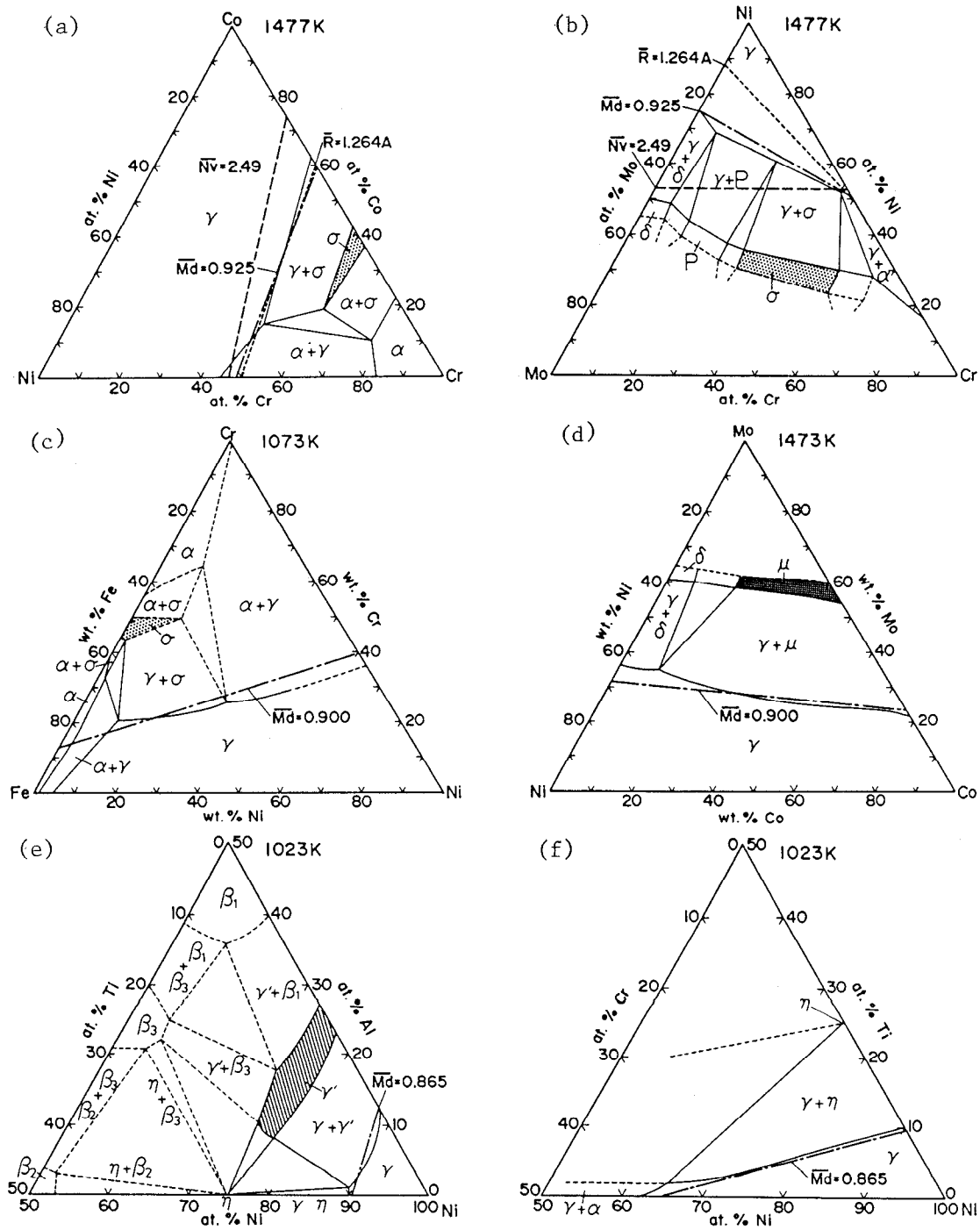

Fig.5 Ternary phase diagrams, (a) Ni-Co-Cr, (b) Ni-Cr-Mo, (c) Fe-Ni-Cr, (d) Co-Ni-Mo, (e) Ni-Al-Ti and (f) Ni-Cr-Ti.

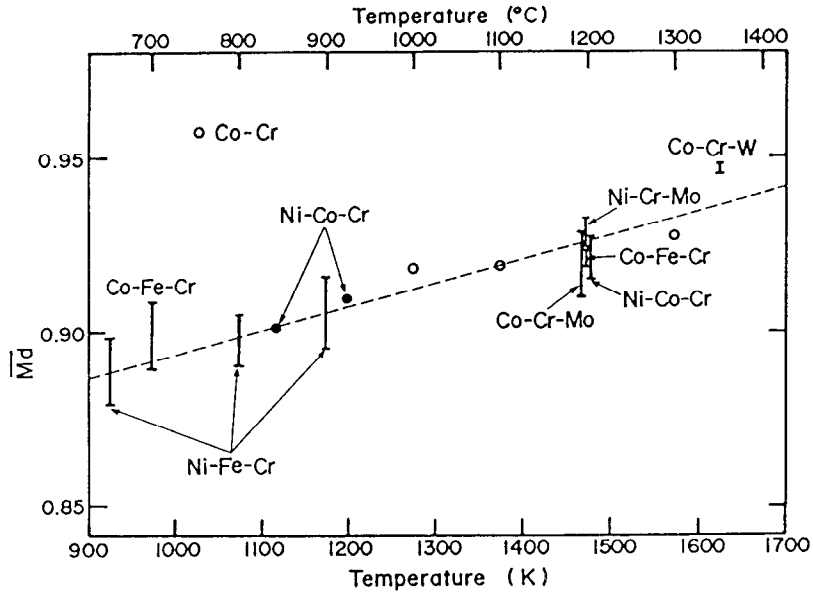

Fig.6 Temperature dependence of critical $\bar{M}d$ for σ phase.

Besides these, $\gamma/\gamma + \beta$(NiAl) phase boundary in Ni-Fe-Al system is also traced by iso $\bar{M}d$ line, for instance, $\bar{M}d$=0.930 at 1323K. The present method is applicable to the TCP phases other than σ or μ phase. For example, the critical $\bar{M}d$ for Laves phase seems to be smaller than that for σ phase.

The temperature dependence of critical $\bar{M}d$ for σ phase is shown in Fig.6. It may be expressed approximately by the equation,

$$\text{Critical } \bar{M}d = 6.25 \times 10^{-5}\ T + 0.834, \qquad (3)$$

where, T is the absolute temperature (K). The temperature coefficient can be compared with the coefficient of thermal energy, $kT = 8.62 \times 10^{-5}$ T (eV), where k is the Boltzmann constant.

In Fig.6, the two solid circles of Ni-Co-Cr at 1118K and 1198K are due to the study by Kirby et al (15). They investigated the effects of the addition of Cr, Mo and W on the occurrence of σ phase. The solid circle with no error bar means that a single value of $\bar{M}d$ describes well $\gamma/\gamma + \sigma$ phase boundary. However, Kirby et al analyzed their results following the electron vacancy concept, and adjusted the electron vacancy number for Mo and W to be about 8.6, which is about twice as large as the usual one, 4.66. In contrast to this, no such adjustments in parameters are needed in our Md method.

Thus, the validity of New PHACOMP was confirmed through the examination of a variety of phase diagrams more than about twenty-five (16).

Applications of New PHACOMP to Alloy Design

Ni-Base Alloys

The prediction for the occurrence of σ phase was carried out using the results of compositions of γ phase, analyzed by Kriege and Baris (17) and Mihalisin and Pasquine (18). The calculated results are given in Fig.7(a) $\bar{M}d$ and (b) $\bar{N}v$. As reported by Barrows and Newkirk (13), either calculation of $\bar{N}v$ or N_v^c-$\bar{N}v$ does not give a right prediction in IN 713C and IN 713LC.

On the other hand, the Md method of (a) predicts rightly even in these alloys. All the alloys of σ-prone have a higher $\overline{Md}$ value than about 0.915. The reason for the ill-prediction for TRW 1900 by both Md and Nv methods is unknown.

Co-Base Alloys

Following the Sims method (3), the tendency for the precipitation of TCP phases in six Co alloys was examined. The results are given in Fig.7(c) $\overline{Md}$ and (d) $\overline{Nv}$. Sims assigned the critical $\overline{Nv}$ for Co base alloys to be about 2.70. However, TCP (μ) phases occur in L-605 at $\overline{Nv}$=2.48, which is considerably lower than the critical $\overline{Nv}$. In the Md method there is a clear splitting in alloys, denoted by open and solid circles, and L-605 lies near $\overline{Md}$= 0.90, in close to the critical $\overline{Md}$ for μ phase.

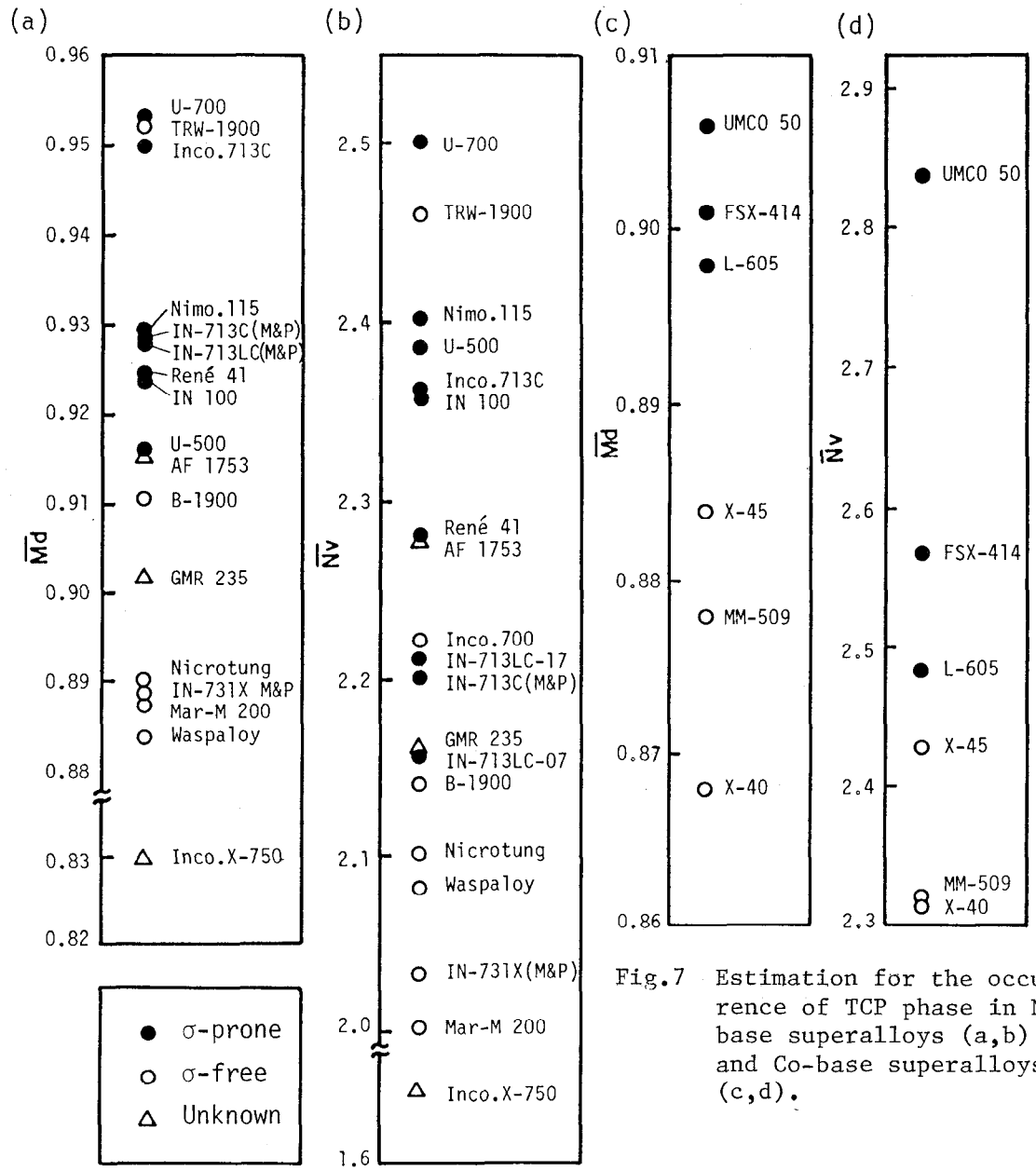

Fig.7 Estimation for the occurrence of TCP phase in Ni-base superalloys (a,b) and Co-base superalloys (c,d).

Fe-Base Alloys

The phase stability of a variety of HK-40 type alloys (Fe-25%Cr-20%Ni) was examined by aging them at 1073K for 3000 hours (19). The boundary of whether σ phase is prone or free, ranges from 2.6-2.7 in $\overline{N}v$, while it exists near 0.90 in $\overline{M}d$, in agreement with the estimate from the phase diagram of Fe-Ni-Cr ternary alloy at 1073K (see Fig.5(c)).

Thus, it is greatly expected that the NEW PHACOMP provides a nice tool for a systematic alloy design of Ni-base, Co-base and Fe-base superalloys.

Discussions

The value of Nv is given by the expression, Nv=10.66 - e/a (e/a: the ratio of valence electrons to atoms). Therefore, for instance, the element Cr, Mo and W belonging to the VIa group in periodic table, have the same Nv value of 4.66. However, recalling that there is a large difference in the atomic (or metallic) radius among these elements (see Fig.4), we may see the lack of atomic size facor in Nv. This is a shortcoming as a parameter exhibiting a solid solubility. For this, the values of Mo and W have been sometimes assigned to be 9.66. No such an ambiguity in parameters exists in New PHACOMP, in which the parameter Md is determined by the calculations of electronic structure of alloys from the first principle. In Fig.8, Md is compared with Nv. In the 3d series, Nv changes linearly with the atomic number Z, but Md does not. The slope of Nv vs Z line around Fe, Co and Ni is rather steep, compared to that in Md vs Z curve. Further, the Nv's for non-transition elements Al and Si are too large. These are probably main reasons for the existence of various contradictions in Nv PHACOMP.

Not only the Md, but also the other two parameters showing the alloying effect of elements were obtained by the DV-Xα cluster calculations (5). They are the ionicity and the bond order of alloying elements. These show the strength of ionic and covalent bonds between elements in alloys, and hence correlate with the physical and mechanical properties of alloys. The knowledge of these is very helpful for the developements of superalloys.

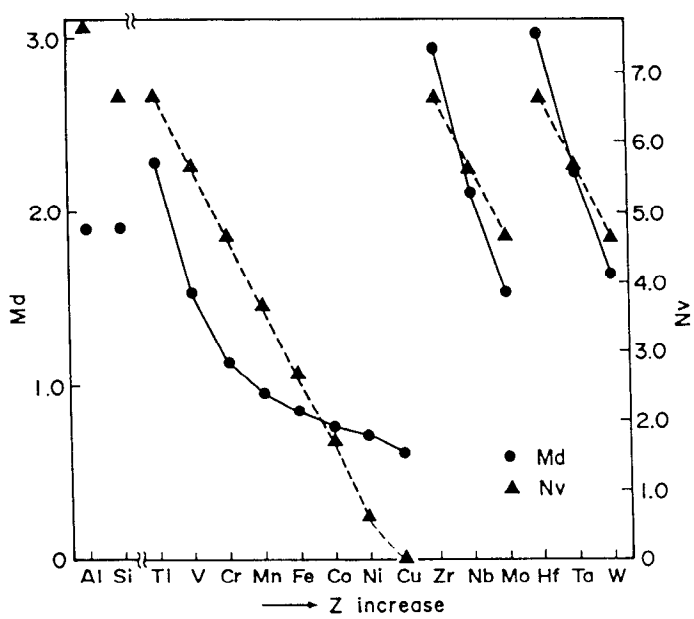

Fig. 8 Comparison of Md with Nv of elements.

Conclusions

New PHACOMP that is superior in many aspects to the widely used PHACOMP, was developed. It can predict the occurrence of various TCP and GCP phases in Ni-base, Co-base and Fe-base superalloys.

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