

# Atomistic defect structures of $\text{Co}_3\text{Ti}$ containing boron, carbon and beryllium

T. TAKASUGI, M. TAKAZAWA, O. IZUMI

*Institute for Materials Research, Tohoku University, Sendai, Japan*

The lattice properties of the  $\text{L}_{12}$ -type  $\text{Co}_3\text{Ti}$  alloys doped with boron, carbon and beryllium were investigated by the X-ray diffraction analysis. The solubility limits of boron, carbon and beryllium into the  $\text{Co}_3\text{Ti}$  were shown to be 3.0, 0.2, and 0.6 at %, respectively. It was shown that the doping of boron enhanced both of the lattice parameter and the atomic ordering of the alloy, while the doping of carbon or beryllium reduced both of them. Based on these experimental results and the consideration for size (difference) and energetics between the constituent atoms and the additive atoms, it was proposed that boron occupied on the octahedral interstitial site, and carbon and beryllium occupied on the substitutional sites of cobalt and titanium respectively.

## 1. Introduction

The  $\text{Co}_3\text{Ti}$  alloy is the  $\text{L}_{12}$ -type intermetallic compound with attractive properties for structural applications since this alloy shows an increased strength with increasing temperature and sufficient ductility at a wide range of temperatures [1, 2]. A large number of studies for physical and mechanical properties of this alloy have been performed by the present authors. Recently, the alloying behaviour of the ternary additions (whether these substitute for cobalt, titanium or both) has been summarized from the ternary phase diagram [3]. The mechanical properties for some of these ternary  $\text{Co}_3\text{Ti}$  have been studied [4]. However, the studied ternary elements into the  $\text{Co}_3\text{Ti}$  alloys have been limited to the large diameter atoms, i.e. the substitutional atoms.

In the last two decades, some interesting findings have been reported for the effect of the small diameter atoms on the mechanical properties of the  $\text{L}_{12}$ -type  $\text{Ni}_3\text{Al}$  alloys. The additions of a small amount of boron (B) [5] and beryllium (Be) [6] improved the ambient ductility of the  $\text{Ni}_3\text{Al}$  polycrystals, and also the additions of boron and carbon (C) showed a significant solid solution strengthening in the  $\text{Ni}_3\text{Al}$  alloys [7, 8]. Hence, the lattice properties of the  $\text{Ni}_3\text{Al}$  alloys containing these atoms have been investigated by X-ray technique [9-11] and the positron annihilation analysis [12]. It was shown by these experiments that boron [10, 11] and carbon [9, 10] atoms occupy on the body centered site, i.e. the octahedral site of an  $\text{L}_{12}$  unit cell and affected the atomic ordering of the constituent atoms whereas beryllium substitutes for the component atoms of nickel and aluminium [10].

In the present work, the  $\text{Co}_3\text{Ti}$  polycrystals containing a small amount of boron, carbon and beryllium atoms are investigated in terms of the solubility limits and the atomistic defect structure, using the metallographic technique and the X-ray diffraction analysis.

The main objectives are devoted to the determination of the site occupations of the additive atoms and the change of the atomic ordering of the constituent atoms, cobalt and titanium. Obtained results are discussed based on the size term and energetics between the constituent atoms and the dopant atoms. In the subsequent paper [13], the mechanical properties of the  $\text{Co}_3\text{Ti}$  alloys containing these additives will be described. In the last paper [14], the results for the different kind of small diameter atoms, i.e. gaseous atoms of hydrogen (H) and oxygen (O) are reported from the point of view of the environmental effect on the mechanical properties of these ternary alloys.

## 2. Experimental procedures

The starting materials used in this work were cobalt of 99.9 mass %, titanium of 99.8 mass %, crystal boron of 99 mass %, titanium carbide of 99.5 mass % and beryllium of 99.9 mass % in purities. Buttons of about 100 g were prepared by arc-melting in an argon atmosphere using non-consumable electrode. The boron and beryllium were directly doped using their pure metals whereas the carbon was doped using a master alloy of Ti-7.4 mass % carbon which was pre-alloyed from the carbide and pure titanium.

All buttons prepared were homogenized for 1 day at 1323 K under a vacuum better than  $6.7 \times 10^{-3}$  Pa and then followed by the furnace cooling. A part of the button was used for the metallographic observation to determine the solubility limit. Also a part of the button was crushed into the small particles by machining and then milling using an agate. Powders consisting of the particle of 250 mesh size were encapsulated into a silica tube and then heat-treated for 1 day at 1123 K under a vacuum better than  $6.7 \times 10^{-3}$  Pa to establish high ordered state of the alloys.

The lattice parameters were measured by the Debye-Scherrer method using the powder samples

TABLE I The solubility limits of boron, carbon and beryllium into Co<sub>3</sub>Ti

	Boron	Carbon	Beryllium
at %	3.0	0.2	0.6
(mass %)	(0.6)	(0.05)	(0.1)

and CuK $\alpha$  or FeK $\alpha$  radiations. Nelson-Riley extrapolation technique was used to determine the precise lattice parameters.

The structure analysis by the X-ray diffraction was performed by measuring the integrated intensity of reflection peaks of fundamental (200) and superlattice reflection (100) peaks, respectively. For the X-ray diffraction, CrK $\alpha$  radiation was used under the condition of an accelerating voltage of 35 kV and a current density of 20 mA. Counting of intensity of reflection peaks was done at every interval of  $2\theta = 0.05^\circ$  of reflection angle. Counting time at each reflection angle was for 400 sec for (100) peak and for 100 sec for (200) peak, respectively.

### 3. Results

#### 3.1. Solubility limits

The nominal compositions of the alloys performed in this work were prepared based on the formula as



where X is the ternary additives and  $x$  is the mass % (or at %) of the additives.

The results obtained for the solubility limits of the dopants into the Co<sub>3</sub>Ti alloy are shown in Table I. It was shown that the solubility limits of the dopant used in this work were larger in the sequence of boron > beryllium > carbon.

#### 3.2. Lattice parameters

Based on the above results for the solubility limits, the nominal compositions shown in Table II were used for the measurements of the lattice parameter and the structural analysis by the X-ray diffraction. All of these alloys are in a single phase of L1<sub>2</sub> structure and no second phases. In the Table II, it is noted that the chemical compositions of last two alloys were prepared based on the formula as



where X is again the ternary additives and  $x$  is the at % of the additives. This alloying method was per-

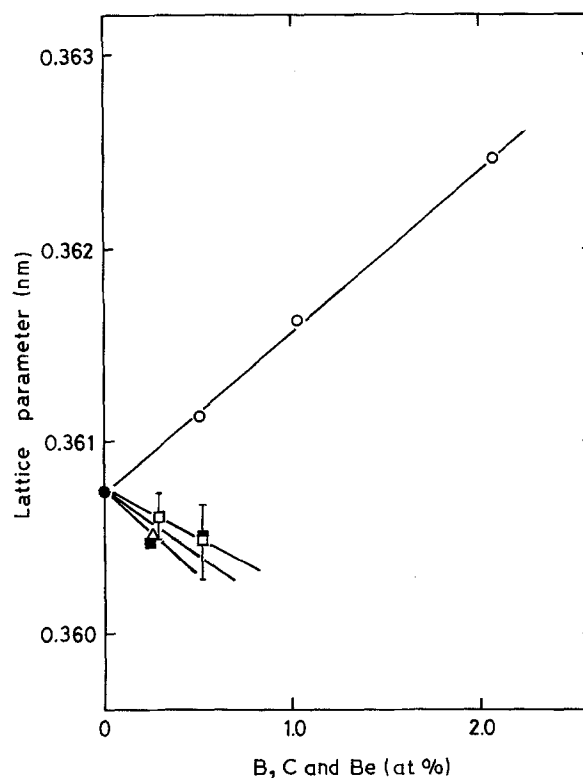


Figure 1 Variations of the lattice parameters of the Co<sub>3</sub>Ti alloys with the concentrations of the additive elements. (○) B, (Δ) C, (□) Be (int.), (■) Be (sub.).

formed on an assumption that the additives would substitute for the component atoms, titanium. In contrast to this, the alloying method by Formula 1 assumes that the additives occupy on the interstitial sites, independent of the mother lattice sites.

The discrepancies between the nominal and analysed chemical compositions were mostly small, as shown in Table II; for the contents of titanium, the analysed values were slightly smaller than the nominal values (usually less than 0.5 at %) and for the contents of the dopants, the analysed values were almost identical to the nominal values.

The variations of the lattice parameters with the concentrations of the additive elements are summarized in Fig. 1. The lattice parameter of the alloys doped with boron increased linearly with increasing concentration of boron whereas the lattice parameter of the alloys containing carbon and beryllium decreased with increasing concentration of these elements. Also, it is noted in this figure that the variations of the lattice

TABLE II Alloy compositions used for the X-ray measurement

Alloy	Analysed composition at % (mass %)			
	Titanium	Boron	Carbon	Beryllium
Co23Ti	22.73			
Co23Ti-0.1 mass % boron	22.53	0.51(0.10)		
Co23Ti-0.2 mass % boron	22.43	1.03(0.20)		
Co23Ti-0.4 mass % boron	22.24	2.07(0.40)		
Co23Ti-0.05 mass % carbon	22.57		0.26(0.06)	
Co23Ti-0.05 mass % beryllium	22.69			0.25(0.04)
Co23Ti-0.1 mass % beryllium	22.63			0.52(0.08)
Co22.7Ti-0.3 at % beryllium	22.35			0.25
Co22.4Ti-0.6 at % beryllium	22.18			0.52

TABLE III Approximate equation of the lattice parameters with the concentrations of the additive elements

Additive element	Equation (nm)
Boron	$a = 8.42 \times 10^{-2} \times + 0.36073$
Carbon	$a = -8.81 \times 10^{-2} \times + 3.6073$
Beryllium(int)*	$a = -5.04 \times 10^{-2} \times + 3.6073$
Beryllium(sub)†	$a = -6.62 \times 10^{-2} \times + 3.6073$

\*The alloy composition was prepared by Formula 1.

†The alloy composition was prepared by Formula 2.

parameter of the alloys containing beryllium were almost the same, regardless of the alloying methods by Formula 1 or 2. Table III represents the approximate equations of the lattice parameter changes with the concentrations of the additives obtained by a least square fitting. Here, it is noted that the lattice parameter change,  $da/dx$ , obtained for the boron addition into the  $\text{Co}_3\text{Ti}$  alloy was almost identical to the values obtained for the boron addition into the  $\text{Ni}_3\text{Al}$  alloys ( $8.08 \times 10^{-2} \text{ nm/at \%}$  [15],  $9.90 \times 10^{-2} \text{ nm/at \%}$  [16] and  $7.28 \times 10^{-2} \text{ nm/at \%}$  [10]).

### 3.3. Crystal structure

As the possible occupation sites of a small diameter atom in a unit cell of the Al (f c c) structure, three sites might be considered; an octahedral, a tetrahedral and a triangular occupations. Among these sites, an octahedral site is most likely to provide the occupation site of small atoms because of its largest volume of occupation. When the constituent atoms of the  $\text{Co}_3\text{Ti}$  order, i.e. if cobalt atoms and titanium atoms occupy on the face centred site and corner site, respectively, an octahedral site can be distinguished into two non-equivalent sites, as shown in Fig. 2. The site I offers larger occupation volume than site II in the  $\text{Co}_3\text{Ti}$  since the volume of titanium atom is larger than that of cobalt atom. On the other hand, an occupation of atoms in site I provides six pairs with cobalt atoms while an occupation of atoms in site II does four pairs with cobalt atoms and two pairs with titanium atoms.

Structural analysis for the  $\text{Co}_3\text{Ti}$  alloy containing the additives was performed on the integrated intensity ratio  $I_{200}/I_{100}$  of the fundamental to the superlattice reflections, based on the following equation:

$$S^2 \frac{I_{200}}{I_{100}} = \frac{|F_{200}|^2 (LP)_{200} (e^{-2M})_{200} (m)_{200}}{|F_{100}|^2 (LP)_{100} (e^{-2M})_{100} (m)_{100}} \quad (3)$$

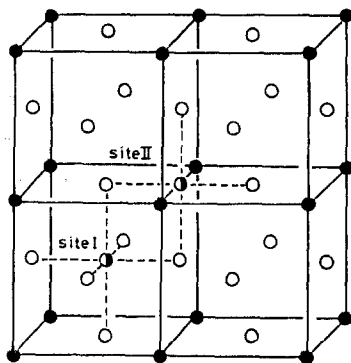


Figure 2 Two different octahedral sites in  $\text{Li}_2 \text{Co}_3\text{Ti}$  structure. (○) Co, (●) Ti, (○) X.

where  $S$  is the long-range order parameter,  $F$  the structural factor,  $(LP)$  the Lorentz-polarization factor,  $(e^{-2M})$  the temperature factor and  $(m)$  the multiplicity factor. The subscripts (200) and (100) refer to the fundamental reflection of (200) and the superlattice reflection of (100), respectively. Here,  $m$  is given to be equal, i.e. 6 for two reflections. The structure factor  $F$  for the crystal structure at which the additive atoms occupy on site I can be expressed as follows:

$$F_{200} = 3f_{\text{Co}} + f_{\text{Ti}} + xf_x \quad (4a)$$

$$F_{100} = (f_{\text{Ti}} - f_{\text{Co}}) - xf_x \quad (4b)$$

where  $x$  is the fraction of the additive atoms occupying on the site I in each unit cell, and  $f$  is atomic scattering factor of each atom. Next, the structure factor  $F$  corresponding to site II can be expressed as follows:

$$F_{200} = 3f_{\text{Co}} + f_{\text{Ti}} + xf_x \quad (5a)$$

$$F_{100} = (f_{\text{Ti}} - f_{\text{Co}}) + (1/3) xf_x \quad (5b)$$

On the other hand, the structural factor of the alloys expressed by Formula 2, i.e. the alloys prepared on an assumption that berylliums occupy on the Ti sites, can be described as,

$$F_{200} = 3f_{\text{Co}} + (1-x)f_{\text{Ti}} + xf_x \quad (6a)$$

$$F_{100} = (1-x)f_{\text{Ti}} + xf_x - f_{\text{Co}} \quad (6b)$$

In the calculations of Equation 3 through Equation 6, the values of  $(LP)$  and  $f$  were taken from tables in [17, 18].

In order to evaluate the long-range order parameter  $S$  in the alloys doped with the additives, the observed intensity ratios  $I_{200}/I_{100}$  and the calculated structure factors (Equations 4, 5 or 6) were thus substituted into Equation 3. Here, the temperature factor was not taken into the calculation. In fact, the structural factors  $F$  calculated by Equation 4 (i.e. for site I) and Equation 5 (i.e. for site II) were not distinguishable because of the small values of atomic scattering factor and small concentration of the additive atoms (B, C and Be). This means that the site occupation of these additive atoms whether site I or site II is not determined from the experimentally obtained integrated intensity ratio  $I_{100}/I_{200}$ . Only the atomic ordering of the constituent atoms could be evaluated.

Fig. 3 represents the variations of the long-range order parameter  $S$  with the concentrations of the additive atoms. The long-range order parameter  $S$  of the alloy doped with boron increased with increasing concentrations of boron whereas the long-range order parameter  $S$  of the alloys doped with carbon and beryllium decreased with increasing concentration of these elements although the long-range order parameter  $S$  in the latter alloys tended to increase again at higher concentrations. Also, it is noted in this figure that the variations of the long-range order parameter  $S$  of the alloys containing beryllium were almost similar, regardless of the alloying methods by Formula 1 or Formula 2.

Thus, this result implies that the addition of boron into the  $\text{Co}_3\text{Ti}$  alloy promoted the atomic ordering of the constituent atoms whereas the additions of carbon

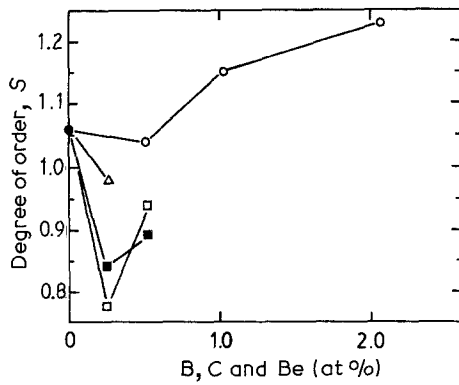


Figure 3 Variations of the long-range order parameter  $S$  with the concentrations of the additives. (O) B, ( $\Delta$ ) C, ( $\square$ ) Be (int.), ( $\blacksquare$ ) Be (sub.).

and beryllium reduced the atomic ordering of the constituent atoms.

#### 4. Discussion

Table IV shows that the atomic diameters of the constituent atoms and the additives, and the vacant sizes for the possible interstitial sites (site I and site II). From this table, it is clearly suggested that if the additive atoms occupy on the interstitial sites, a unit cell of the mother lattice must be expanded, alternatively if the additive atoms occupy on the sites of the constituent atoms, a unit cell must be shrunk. It was shown in Fig. 1 that the lattice parameter change with the concentration of the additives indicated a positive slope for the boron addition whereas those did negative slopes for the carbon and beryllium additions. This result simply suggests that boron occupies on the interstitial site whereas carbon and beryllium occupies on the substitutional sites of the constituent atoms. However, it must be described here that carbon atom which is smaller than boron atom did not occupy on the interstitial site but on the substitutional site.

In general, the site occupation of the atoms depends on two factors; the atomic size (difference) and the chemical bond nature between neighbouring atoms. Table V describes the nearest neighbour (NN) bonds with cobalt and titanium atoms in  $L1_2$  structure (i.e. the undoped state) and in two doped  $L1_2$  structures (i.e. for site I and site II), respectively. When the additive atoms (X) occupy on the body centred site in  $L1_2$  structure, the NN bond between the constituent atom and X atom occurs at a distance of  $a/2$  which is much closer than  $\sqrt{2}/2 a$ , i.e. the NN bond between the constituent atoms of cobalt and titanium, where  $a$  is the lattice parameter. Thus, the NN bond between the additive atoms and the constituent atoms is suggested to be dominant factor determining the energetic stability of  $L1_2$  structure doped with the addi-

TABLE IV Atomic diameters and vacant sizes for occupation sites of the additive atoms (nm)

Atomic diameter (nm)		Vacant size (nm)			
Constituent atom	Additive atom	Site I	Site II		
Co	Ti	B	C	Be	
0.250	0.294	0.18	0.154	0.226	0.111 0.067

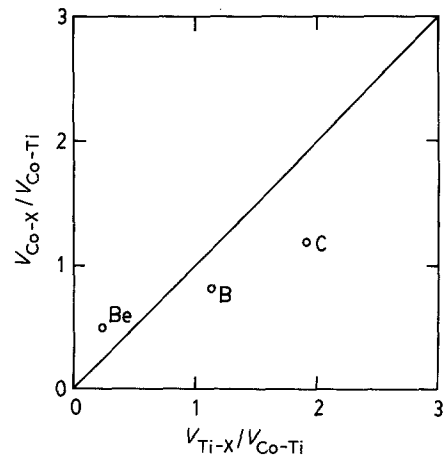


Figure 4 Correlation between the interaction energy (parameter) ratios of  $V_{Ti-X}/V_{Co-Ti}$  and  $V_{Co-X}/V_{Co-Ti}$  for the additive atoms, X.

tives. Here, the bond energies can be evaluated by Miedema's semiempirical formula regarding the formation energy of intermetallic compounds [19, 20]. Fig. 4 plots the correlation between the interaction energy (parameter) ratio of  $V_{Ti-X}/V_{Co-Ti}$  and  $V_{Co-X}/V_{Co-Ti}$  for the additive atoms, X. Here,  $V_{ij}$  is defined as  $H_{ij} - (H_{ii} + H_{jj})/2$  where  $H_{ii}$ , etc. is the bond energy for  $ii$  pairs.

First, let us consider the site occupation of carbon. Fig. 4 clearly shows that the interaction between titanium atom and carbon atom is much stronger than the interaction between the other constituent atom, cobalt and carbon atom. This leads that carbon atoms occupy on the interstitial position of site II, or on the substitutional position of cobalt since both occupations create the C-Ti pair in the NN neighbour. However, the former occupation is geometrically impossible because of much small vacant size, as shown in Table IV. Instead, it is suggested that the latter occupation occurs, thereby reducing the lattice parameter of the  $Co_3Ti$  alloy. Corresponding to this occupation, it is assumed that carbon atoms are rejected into the wrong site of cobalt atoms, i.e. titanium sites, therefore resulting in the atomic disordering of the constituent atoms (Fig. 3).

Next, concerning the site occupation of boron, the result for the lattice parameter change (Fig. 1) suggested that boron behaved as the interstitial atom. We must determine which site (site I or site II) could be occupied by boron. However, in this case, the site II is again excluded for the consideration because of its small vacant size. Here, boron atoms which occupied on site I are considered to bring about two actions; first is that boron atoms may attract titanium atoms in the NN neighbour more than cobalt atoms by the chemical effect (Fig. 4). Second is that boron atoms may repel titanium atoms wrongly occupied on the cobalt sites by the size effect (Table IV). The former action produces the atomic disordering of the constituent atoms whereas the latter action produces the atomic ordering of the constituent atoms. Experimental result shown in Fig. 3 reveals that boron atoms on site I repelled the wrongly occupied Ti atoms rather than they attracted titanium atoms from their correct sites, thereby enhancing the long-range order

TABLE V Nearest neighbour (NN) atom relationship for  $L1_2$  structure and two doped  $L1_2$  structures (site I and site II)

Structure	NN relation		
	Co	Ti	X
$L1_2$	Co	$8(\sqrt{2}/2a)$	$4(\sqrt{2}/2a)$
	Ti	$12(\sqrt{2}/2a)$	
$L1_2$ (site I)	Co		$6(a/2)$
	Ti	$12(\sqrt{2}/2a)$	
$L1_2$ (site II)	Co		$4(a/2)$
	Ti		$2(a/2)$

The value in the parenthesis is an interatomic distance and  $a$  is the lattice parameter.

parameters of the  $Co_3Ti$  alloy. Indeed, the fact that two values of the interaction parameter,  $V_{Ti-B}$  and  $V_{Co-B}$  shown in Fig. 4 are not so anisotropic suggests that the chemical effect was not dominant in this phenomenon.

Fig. 1 indicated that beryllium atoms substituted for the constituent atoms, regardless of alloying methods. Fig. 4 (the chemical effect between the constituent atoms) suggests that beryllium atoms prefer to occupy on the titanium site rather than the cobalt sites and then create the wrong atoms, resulting in the atomic disordering as shown in Fig. 3.

In the present work, the site occupations of these additives in the  $L1_2$   $Co_3Ti$  structure were proposed based on the indirect technique by the X-ray diffraction. Of course, more reliable conclusion would be given based on the direct measurement such as an electron channelling technique.

## 5. Conclusions

The atomistic defect structure of the  $Co_3Ti$  alloys doped with boron, carbon and beryllium was evaluated by the X-ray diffraction analysis. The following results were obtained.

1. By the metallographic observation, it was shown that the solubility limits of the additive elements were larger in the sequence of boron (3.0 at %), beryllium (0.6 at %) and carbon (0.2 at %).

2. The lattice parameter change with the concentration of the additive elements showed a positive slope for the alloy doped with boron whereas those showed negative slopes for the alloys doped with carbon and beryllium.

3. From the structural analysis by the X-ray diffraction, it was shown that the doping of boron enhanced the atomic ordering of the constituent atoms whereas the dopings of carbon and beryllium reduced them.

4. The geometric (size) and energetic considerations between the constituent atoms and additive atoms

were performed on these results. It was proposed that boron occupied on the interstitial site, i.e. the octahedral site where six pairs of the nearest neighbour between boron and cobalt occur. On the other hand, carbon and beryllium were shown to occupy on the substitutional site of cobalt and on the substitutional site of titanium, respectively.

## Acknowledgement

Research was partly supported by Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials-Design, Preparation and Control, The Ministry of Education, Science and Culture.

## References

1. T. TAKASUGI and O. IZUMI, *Acta Metall.* **33** (1985) 39.
2. *Idem, ibid.* **34** (1986) 607.
3. Y. LIU, T. TAKASUGI and O. IZUMI, *Metall. Trans.* **17A** (1986) 1433.
4. Y. LIU, T. TAKASUGI, O. IZUMI and H. SUENAGA, *J. Mater. Sci.* **24** (1989) 4458.
5. K. AOKI and O. IZUMI, *Nippon Kinzoku Gakkaishi* **43** (1979) 1190.
6. T. TAKASUGI, N. MASAHASHI and O. IZUMI, *Scripta Metall.* **20** (1986) 1845.
7. S. C. HUANG, A. I. TAUB and K. M. CHANG, *Acta Metall.* **32** (1984) 1703.
8. N. MASAHASHI, T. TAKASUGI and O. IZUMI, *ibid.* **36** (1988) 1823.
9. K. H. HAN and W. K. CHOO, *Scripta Metall.* **17** (1983) 281.
10. N. MASAHASHI, T. TAKASUGI and O. IZUMI, *Acta Metall.* **36** (1988) 1815.
11. I. BAKER, B. HUANG and E. M. SCHULSON, *ibid.* **36** (1988) 493.
12. A. DASGUPTA, L. C. SMEDSKJAER, D. G. LEGNINI and R. W. SIEGEL, *Mater. Lett.* **3** (1985) 457.
13. T. TAKASUGI, M. TAKAZAWA and O. IZUMI, *J. Mater. Sci.* **25** (1990) 4231.
14. T. TAKASUGI, M. TAKAZAWA and O. IZUMI, *J. Mater. Sci.* **25** (1990) 4239.
15. L. J. HEUTTER and H. H. STADELMAIER, *Acta Metall.* **6** (1958) 367.
16. C. L. BRIANT and S. C. HUANG, *Metall. Trans. A* **17A** (1986) 2084.
17. International Tables for X-ray Crystallography, Vol. II, (Kynoch Press, Birmingham, 1959) (Table 5.2.5.B; p 270).
18. *ibid.* Vol. III (Kynoch Press, Birmingham, 1962) (Table 3.3.1.A; p 201).
19. A. R. MIEDEMA, R. BOOM and F. R. de BEER, *J. Less-common Metals* **4** (1975) 283.
20. A. R. MIEDEMA and P. F. de CHATEL, "Theory of Alloy Phase Formation" edited by L. H. Benett, (Metallurgical Society AIME, 1980) pp. 304-389.

Received 13 March  
and accepted 30 August 1989