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Calculation of phase diagrams of ternary systems with cluster-variation-method entropy

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Abstract. Phase diagram calculations (isothermal sections) of three ternary alloys (Ti–Al–Mo, Ti–Al–Nb and Ti–Al–W) are performed from a knowledge of experimental binary phase diagrams. The CPA–GPM theory has been used to write the total free energy within the approximation of the CVM for the entropy. The parameters used to calculate the total free energy have been obtained by fitting the binary phase diagrams.

1. Introduction

During the last two decades, many computations of phase diagrams have been made. Most of them make use of the regular or subregular models. These methods have been developed by Kaufman and the Calphad group during the 1970s [1–3]. Murray [4] has recently reviewed many of these calculations on titanium-based alloys. In other contributions, the so-called Bragg–Williams approximation has also been used.

These approaches present some conceptual difficulties. In particular, they do not consider the short-range order (SRO) in the configurational entropy. However, we know that neglect of SRO in the entropy may be a very crude approximation. As an example, the Bragg–Williams approximation, when applied to the FCC lattice with ordering interactions, leads to a phase diagram in complete disagreement with Monte Carlo results which, in principle, are exact [5].

For this reason, the cluster variation method (CVM) [6], which treats the SRO in the entropy explicitly, has become very important nowadays for the purpose of computing phase diagrams.

From another point of view, modern calculations of the electronic structure of alloys have permitted one to evaluate the total energy of formation by means of microscopic quantum-mechanical theories. For example, the so-called coherent potential approximation (CPA)–generalized perturbation method (GPM) theory [7, 8] suggests that this total energy may be conveniently written as the sum of the random energy (the CPA energy) plus an ordering energy contribution expressed in terms of effective pair interactions. The parameters of the CPA energy and the effective pair interactions characterize the energy of formation in a given configuration. As these calculations can be made for many structures, we may use this model even if structural transitions (from FCC to BCC, for example) are present. This quantum-mechanical approach provides explicit values for the effective pair interactions and for the disordering energy parameters. Yet, this treatment may lead to poor estimates for the enthalpies of formation. Hence, following an approach developed in [9–11], we have chosen to obtain all these parameters by fitting the binary phase diagrams.

It is also possible to generalize such a model to ternary alloys. If we make the assumption—which is certainly very rough—that the binary parameters are not changed with the adjunction of a third element, the ternary parameters will be easily expressed in terms of binary parameters. Consequently, following this theoretical background already used in [12–15], we have calculated isotherm phase diagrams of three ternary alloys, starting from the fits of binary phase diagrams.

We have realized these calculations on the BCC structure, at 1273 K. This type of calculation could be really useful in the near future for metallurgical research, particularly in the quest for an A2+B2 field to create a γ - γ' superalloy-type microstructure [16].

2. Binary phenomenological model

We shall consider here only the BCC and HCP structures. For an alloy A–B, the total free energy of a phase ϕ in a structure I can be written, by the use of the CPA–GPM theory [9–11], as

$$F^{\phi,I} = c_A F_A^I + c_B F_B^I + \langle \Delta H_{\text{dis}}^I \rangle + \langle \Delta H_{\text{ord}}^{\phi,I} \rangle - T \Delta S_{\text{conf}}^{\phi,I}. \quad (1)$$

F_A^I and F_B^I are the free energies of the pure A and the pure B elements respectively, in the structure I. $\langle \Delta H_{\text{dis}}^I \rangle$ is the random energy, i.e. the disordering energy analogous to the CPA energy. ($\langle \rangle$ stands for the thermodynamic average.) We can write

$$\langle \Delta H_{\text{dis}}^I \rangle = c_A c_B P(c_A) \quad (2)$$

where P is a polynomial in c_A , for instance

$$P(c_A) = a_0 + a_1 c_A + a_2 (c_A)^2 + a_3 (c_A)^3.$$

$\langle \Delta H_{\text{ord}}^{\phi,I} \rangle$ is the ordering energy:

$$\langle \Delta H_{\text{ord}}^{\phi,I} \rangle = \frac{1}{2} \sum_{\substack{n,m \\ i,j=A,B}} V_{n,m}^{i,j} \langle (p_n^i - c^i)(p_m^j - c^j) \rangle. \quad (3)$$

This ordering energy should also contain, as in any perturbative expansion, triplet interactions, quadruplet interactions, etc (p_n^i is an occupation number which takes the value 1 if the site n is occupied by an atom of type i and 0 otherwise; $c^i = \sum_n p_n^i / N$, where N is the total number of sites). Here, we restrict the summation in the ordering energy to the first and second neighbours pairs. As we can see, $\langle \Delta H_{\text{ord}}^{\phi,I} \rangle$ depends on the nature of the phase ϕ by the product $\langle p_n p_m \rangle$ and on the structure I by the pair interactions. In turn, $\langle \Delta H_{\text{dis}}^I \rangle$ depends only on the structure I by the parameters of the polynomial.

$\Delta S_{\text{conf}}^{\phi,I}$ is the configurational entropy that we treat in the CVM approximation. The reader can refer to standard accounts of the method [5, 8, 17]. Briefly, we just mention that this method consists in factorizing the total probability on partial probabilities, related to finite clusters of the underlying lattice. The CVM approach is therefore a mean-field method that goes beyond the Bragg–Williams and the Bethe approximations. The simplest and currently selected cluster is the tetrahedron: it is regular on the FCC lattice (or the HCP lattice), and irregular on the BCC lattice. It represents the degree of the CVM approximation.

In our study, we have not taken into account the vibrational entropy. Its effects may be taken into account through temperature-dependent parameters that could mask the effects of the configurational parameters.

In our calculation, we can also take into account the liquid phase and complex ordered phases. Following Kaufman *et al* we treat the liquid phase with a regular model, i.e. we write

$$F^{\text{liq}} = c_A F_A^{\text{liq}} + c_B F_B^{\text{liq}} + \Delta E_{\text{exc}}^{\text{liq}} - TS \quad (4)$$

where $\Delta E_{\text{exc}}^{\text{liq}}$ is the excess energy with respect to the ideal model and S is the entropy of mixing:

$$\Delta E_{\text{exc}}^{\text{liq}} = c_A c_B P(c_A)$$

$$S = -k(c_A \ln c_A + c_B \ln c_B).$$

We treat complex ordered phases as stoichiometric compounds; that is, we write

$$F^\alpha = c_A F_A^\alpha + c_B F_B^\alpha + a + bT \quad (5)$$

where α represents the underlying lattice of the complex ordered phase and where a and b are constant parameters that we have to evaluate.

3. Ternary phenomenological model

We extend the binary model to ternary alloys. For an alloy A–B–C, the total free energy of a phase ϕ in a structure I is written as follows:

$$F^{\phi, I} = c_A F_A^\phi + c_B F_B^\phi + c_C F_C^\phi + \langle \Delta H_{\text{dis}}^I \rangle + \langle \Delta H_{\text{ord}}^{\phi, I} \rangle - T \Delta S_{\text{conf}}^{\phi, I} \quad (6)$$

where F_A^ϕ , F_B^ϕ and F_C^ϕ are the free energies of the pure A, B and C elements, respectively, and $\langle \Delta H_{\text{ord}}^{\phi, I} \rangle$ is the ordering term for a ternary system.

We can easily write

$$\langle \Delta H_{\text{ord}}^{\phi, I} \rangle = \frac{1}{2} \sum_{\substack{n, m \\ i, j=A, B, C}} V_{n, m}^{i, j} ((p_n^i - c^i)(p_m^j - c^j)) \quad (7)$$

that generalizes the previous expression.

The configurational entropy $\Delta S_{\text{conf}}^{\phi, I}$ is treated in the CVM framework. The CVM approximation may be readily generalized to ternary or multi-component systems; the only difference is that we have two independent point probabilities per site ($N - 1$ for an alloy of N elements) [18].

In turn, we can make different assumptions for $\langle \Delta H_{\text{dis}}^I \rangle$. The most natural assumption consists in simply writing it as the sum of the three disordering energies, related to the three binary alloys. As noted above, if we suppose as is usually done (see, e.g., [12–15]), that the adjunction of a third element does not disturb the values of the binary parameters, all the parameters of the ternary alloy are known.

4. Determination of the binary parameters

How can we fix the binary parameters? As reported above, we must fit them on the ground of experimental data. The principal difficulties of such an approach is that, in most phase diagrams, order-disorder transitions do not exist. Hence, there is no hope of determining the pair interactions easily.

For a given temperature, a two-phase equilibrium is governed by two equations:

$$\partial F_1(c_1^{\text{equ}})/\partial c_1^{\text{equ}} = \partial F_2(c_2^{\text{equ}})/\partial c_2^{\text{equ}} = \mu \quad (8)$$

$$F_1(c_1^{\text{equ}}) - \mu c_1^{\text{equ}} = F_2(c_2^{\text{equ}}) - \mu c_2^{\text{equ}}. \quad (9)$$

If we know the parameters of the model, these equations lead to c_1^{equ} and c_2^{equ} , the equilibrium concentrations. Inversely, we may use them to evaluate two parameters of the model, starting from knowledge of c_1^{equ} and c_2^{equ} . However, we cannot use this procedure for the ordering energy parameters because we did not know the explicit form of the equilibrium ordering energy (its value is obtained numerically, after minimization). Consequently, using this method, only the parameters of the disordering energy may be evaluated.

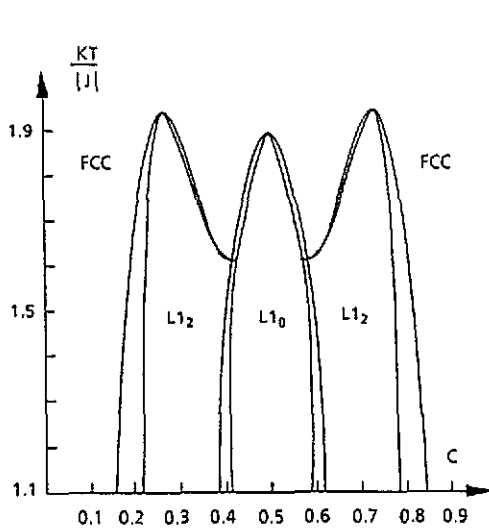


Figure 1. The CVM calculation on the FCC lattice with first-neighbour interactions.

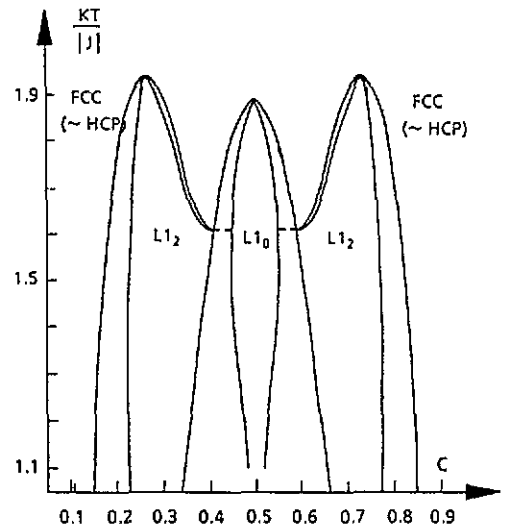


Figure 2. The same CVM calculation with the adjunction of the disordering energy.

Suppose, for example, that the parameters of the ordering and disordering energies of a first phase are known, and that only the pair interactions of the second phase are known. If we note that

$$\langle \Delta H_{\text{dis}2}^I(c) \rangle = c(1-c)(a_0 + a_1c)$$

and

$$F_2^* = F_2 - \langle \Delta H_{\text{dis}2}^I \rangle$$

we have the explicit relations

$$\begin{aligned} \partial F_1(c_1^{\text{equ}})/\partial c_1 &= \partial F_2^*(c_2^{\text{equ}})/\partial c_2 + \partial \langle \Delta H_{\text{dis}2}^1(c_2^{\text{equ}}) \rangle / \partial c_2 = \mu \\ F_1(c_1^{\text{equ}}) - \mu c_1^{\text{equ}} &= F_2^*(c_2^{\text{equ}}) + \langle \Delta H_{\text{dis}2}^1(c_2^{\text{equ}}) \rangle - \mu c_2^{\text{equ}}. \end{aligned}$$

It is easy to invert such a system. We find a_0 and a_1 , the disordering parameters, for one temperature T . However, numerical difficulties arise here which make the task of fitting phase diagrams problematic. In fact, we have to determine a set of disordering energy parameters valid for all the temperatures of the two-phase region. The first possible way of achieving this is to express these equations simultaneously for several temperatures and to use a least-squares procedure. In fact, if we take many two-phase equilibria, the form used for $\Delta H_{\text{dis}2}^1(c_2^{\text{equ}})$ is too crude and the least-squares procedure is consequently not very efficient. Another possibility would be to introduce $2N$ parameters for the disordering energy with the purpose of reproducing the two-phase equilibria for N temperatures. Obviously, this approach is not physically justified and must be rejected. The last solution would be to introduce temperature-dependent parameters, but this would be equivalent to considering the vibrational entropy, with a polynomial treatment. We have excluded this approach.

Table 1. The Ti–Al system results (in units of $\mathbf{C} = 91.64$ meV); see equations (2) and (3) with $c_{\text{Al}} = c_{\text{Al}}$.

	V_1	V_2	a_0	a_1	a_2	a_3
BCC	1	0	-17.27	16.47	-71.42	117.30
HCP	4	—	-16.67	17.08	-17.08	—
Liquid	—	—	-9.40	-6.19	—	—

Table 2. Enthalpies of formation for the liquid phase in the TiAl system at 2000 K: experimental [19] and calculated.

c_{Al}	0.2	0.25	0.3	0.4	0.5	0.6	0.7	0.75	0.8
Experimental value (kJ mol^{-1})	-15.06	-18.41	-21.13	-25.94	-29.71	-29.50	-26.78	-24.48	-21.55
Theoretical value (kJ mol^{-1})	-15.02	-18.11	-20.88	-25.15	-27.57	-27.78	-25.44	-23.22	-17.49

For all these reasons, there is no simple way to fit phase diagrams. We must first estimate the 'good' pair interactions and then find the 'good' two-point equilibria, to reproduce the most important part of the two-phase region.

5. Study of the binary systems Ti–Al, Ti–Mo, Ti–Nb, Ti–W, Al–Mo, Al–Nb, Al–W

As explained in the introduction, we look for a two-phase regime of the A2+B2 type. We have chosen to mix two binary alloys which are ordered (but metastable) on the BCC lattice, and one which is segregated. With these requirements, we may hope to observe, for the ternary system on the BCC lattice, a two-phase field in stable equilibrium.

In the present case, it is easy to determine the pair interactions for just the binary alloys which segregate (Ti–Mo, Ti–Nb, Ti–W), but not for the alloys which order (Ti–Al, Mo–Al, W–Al and Nb–Al). More precisely, for the first set of alloys, the tops of the miscibility

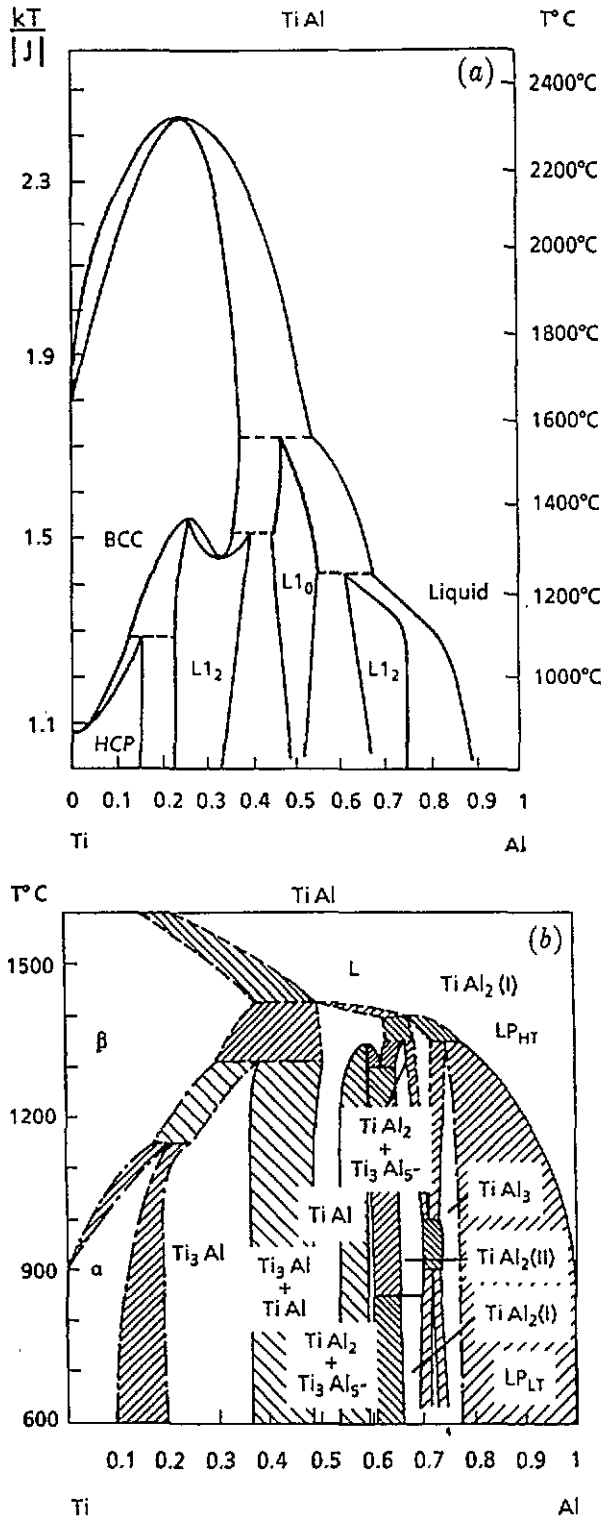


Figure 3. The Ti-Al system: (a) calculated; (b) observed [28]; (c) observed [4].

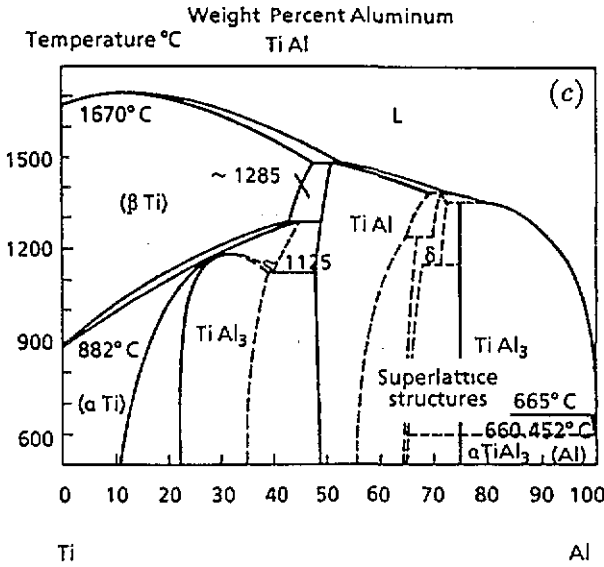


Figure 3. (Continued)

Table 3. Enthalpies of formation for the solid solution in the Ti–Al system: experimental [19] (at $T = 600\text{--}1010\text{ K}$) and calculated (at $T = 0\text{ K}$). (We used the energy difference between FCC and HCP Al given in [4] because the heats of formation are measured experimentally from HCP Ti and FCC Al.)

c_{Al}	0.25	0.50	0.75
Experimental value (kJ mol^{-1})	-25.5	-36.4	-36.6
Theoretical value (kJ mol^{-1})	-34.1	-42.3	-31.4

Table 4. Disordering and ordering energies of the Ti–Al system on the FCC lattice. We compare our results with those in [23].

c_{Al} (phase)	ΔH_{dis} (kJ mol^{-1})		ΔH_{ord} (kJ mol^{-1})	
	[23]	Present work	[23]	Present work
0.25 ($L1_2$)	-17.9	-22.3	-14.4	-13.2
0.5 ($L1_0$)	-27.5	-27.4	-18.0	-17.7
0.75 ($L1_2$)	-25.2	-22.3	-15.7	-13.2

Table 5. The results on the Ti–Mo system (in units of $C = 91.64\text{ meV}$); see equations (2) and (3) with $c_A = c_{Ti}$.

	V_1	V_2	a_0	a_1	a_2	a_3
BCC	-0.33	-0.33	2.30	—	—	—
HCP	-0.33	—	49.10	-46.16	—	—
Liquid	—	—	1.72	0.59	—	—

Table 6. The Ti-Nb system (in units of $C = 91.64$ meV); see equations (2) and (3) with $c_A = c_{Ti}$.

	V_1	V_2	a_0	a_1	a_2	a_3
BCC	-0.10	-0.10	0.69	—	—	—
HCP	-0.10	—	40.11	-40.64	—	—
Liquid	—	—	0.17	—	—	—

Table 7. The Ti-W system (in units of $C = 91.4$ meV); see equations (2) and (3) with $c_A = c_{Ti}$.

	V_1	V_2	a_0	a_1	a_2	a_3
BCC	-0.49	-0.49	3.42	—	—	—
HCP	-0.49	—	678.97	-681.72	—	—
Liquid	—	—	0.92	3.60	—	—

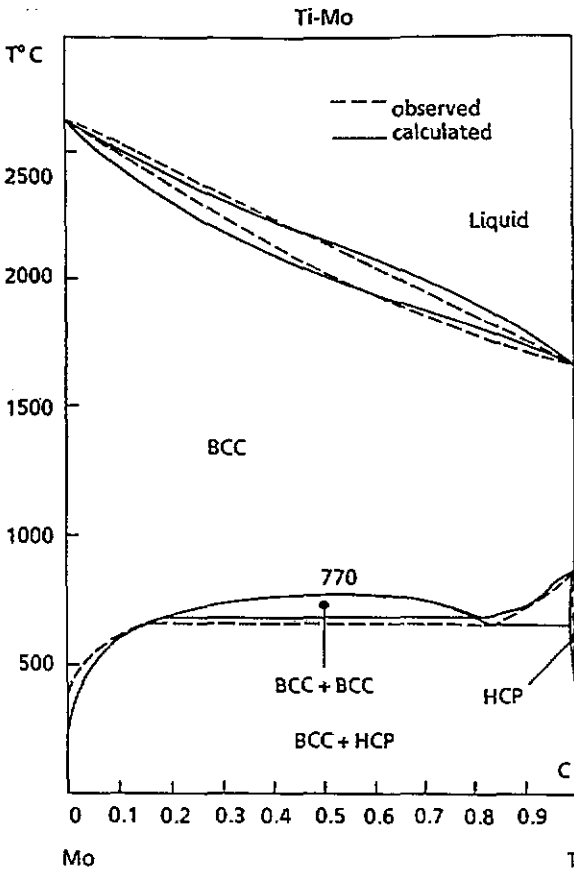


Figure 4. The Ti-Mo system: observed and calculated.

gaps occur before the melting point and, for the second set, the binary alloys remain ordered up to the melting point.

For the ordered systems, we proceeded as follows: we have chosen to consider first the Ti-Al alloy and to evaluate the pair interactions for the BCC and FCC lattices, as well as for the liquid phase, for which they are some thermodynamic estimations of the enthalpies of

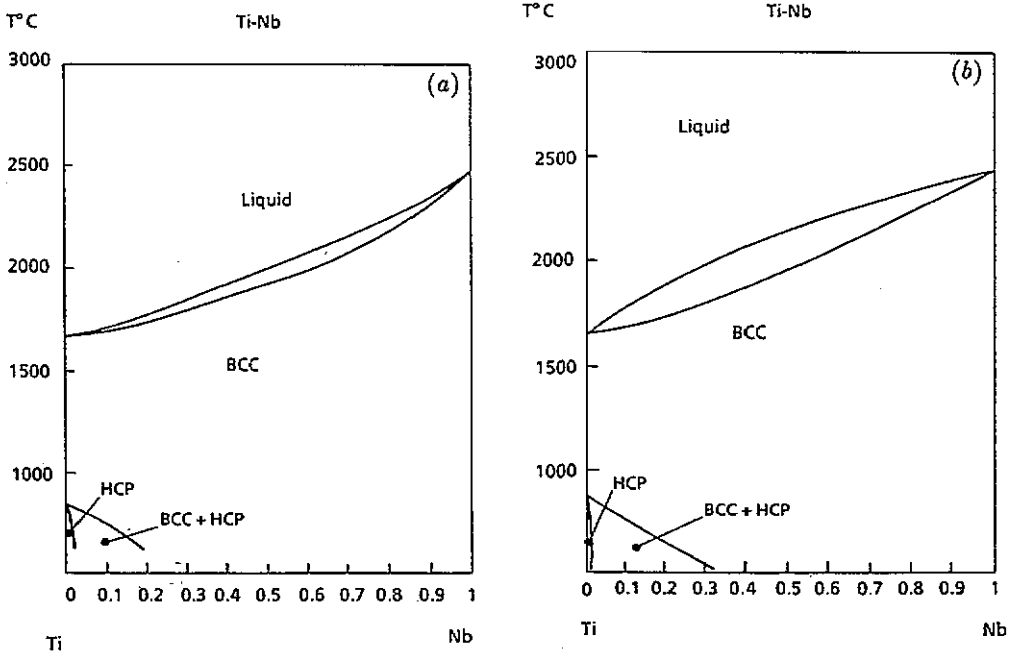


Figure 5. The Ti-Nb system: (a) calculated; (b) observed [2-4].

formation [19]. Then, we have assumed that the value for the pair interactions obtained—for the BCC lattice—was approximately the same in the Mo-Al, Nb-Al and W-Al alloys. This can be justified by electronic structure considerations. Nevertheless, this constitutes an important approximation.

We have first studied the Ti-Al system [4,28]. We preliminarily note that the experimental phase diagram given in [28], which was chosen for the fit, has some features in common with that calculated by the CVM, with first-neighbour interactions only, in the tetrahedron approximation on the FCC lattice.

In this approximation, the HCP disordered phase α is equivalent to the FCC disordered phase δ ; the α_2 (or DO_{19}) ordered phase is equivalent to $L1_2$. Then, except for the long-period structures around the stoichiometry $TiAl_3$, we may consider that the main features of the FCC and HCP parts of the Ti-Al phase diagram will be well reproduced within the CVM, by considering only one underlying lattice, namely the FCC lattice. More precisely, if we consider only first-neighbour interactions and a CVM entropy based on the regular tetrahedron, as has been done in the past [9-14], the free-energy differences between the FCC and HCP lattices are, for any concentration and temperature, exceedingly small. Consequently, the corresponding phase diagrams are almost indistinguishable [20,21]; the HCP phase diagram is similar to the FCC phase diagram and may be obtained by replacing the FCC-based $L1_2$ and $L1_0$ by the HCP-based phases DO_{19} and B_{19} , respectively. Of course, this approach is fully justified for a specific system if it can be shown that the ordered FCC compounds and the corresponding HCP compounds have similar enthalpies of formation.

In recent studies of the Ti-Al system [22-25], the enthalpies of formation of FCC and HCP-based ordered compounds have been calculated, using *ab initio* electronic structure methods, such as the full-potential linear muffin-tin orbital and full-potential linearized augmented-plane-wave methods. It is found that the HCP-based structure DO_{19} (Ti_3Al) is

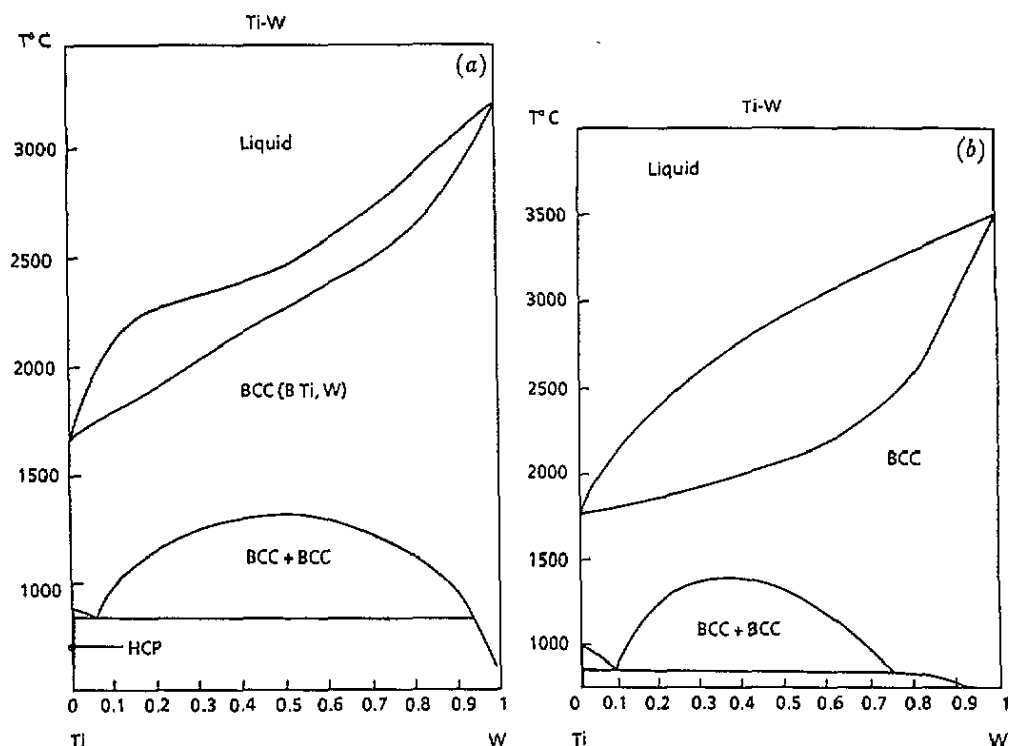


Figure 6. The Ti-W system: (a) calculated; (b) observed [2-4].

stable with regard to $L1_2$ only by less than 1 kJ mol^{-1} (the enthalpies are found to be $-28.7 \text{ kJ mol}^{-1}$ and $-27.8 \text{ kJ mol}^{-1}$, respectively). We may then replace the stable DO_{19} by the metastable $L1_2$ compound. Additionally, experimental evidence for a metastable $L1_2$ has been reported [26]. On the other hand, around the composition $TiAl_3$, the FCC-based DO_{22} phase is stable together with long-period superlattice structures (LPSS) [27], which can be described as consisting of one-dimensionally conservatively antiphased $L1_2$ unit cells.

The existence of these LPSS can be understood as being the result of a competition between the $L1_2$ and DO_{22} phases, whose enthalpies of formation should be very close. This is confirmed by the *ab initio* electronic structure calculations [22-24]; DO_{22} is stable with regard to $L1_2$ only by 2 kJ mol^{-1} (the enthalpies of formation are found to be $-41.9 \text{ kJ mol}^{-1}$ and $-39.6 \text{ kJ mol}^{-1}$, respectively). Hence, as the purpose of this paper is to reproduce the main features of the Ti-Al phase diagram, we may ignore the LPSS and replace the DO_{22} phase by the $L1_2$ phase.

As a result, the ordering effects of the Ti-Al system on the HCP and FCC lattices may be reproduced, to a good level of approximation, by considering only the FCC lattice, with a CVM entropy based on the regular tetrahedron. The CVM phase diagram with first-neighbour interactions is shown in figure 1.

The CVM calculation leads to a two-phase field $L1_0$ - $L1_2$ area narrower than the experimental area. Then, in a first step, we have enlarged this regime with an appropriate symmetric disordering energy (see figure 2).

In a second step, we have estimated $(V_1)_{\text{HCP}}$, by considering the best fit for all the two-phase domains. Finally, we have fitted the parameters for the other structures. The

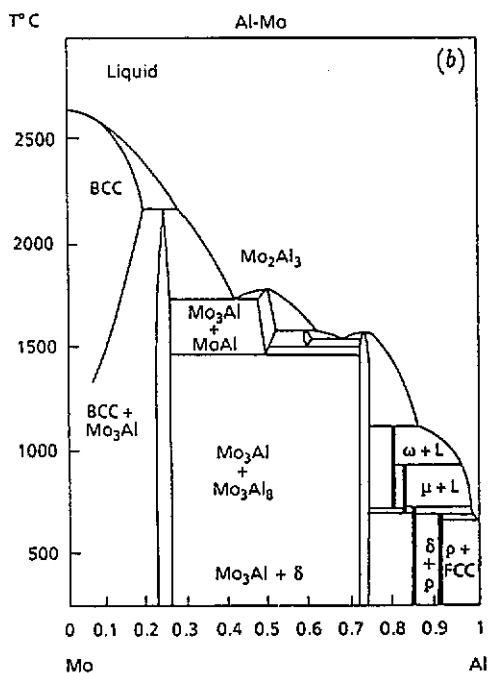
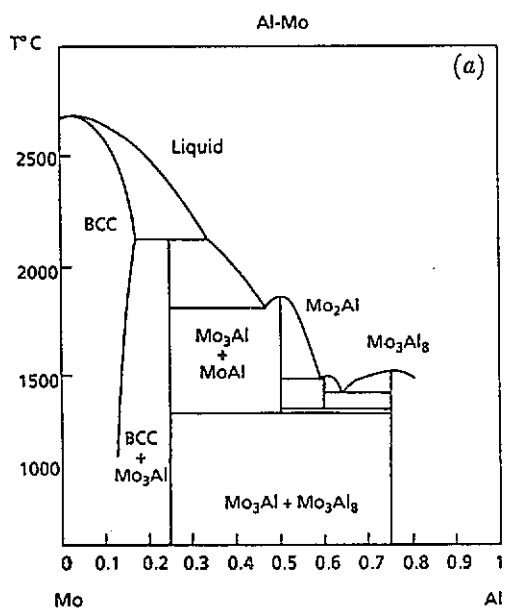


Figure 7. The Al-Mo system: (a) calculated; (b) observed [3-29].

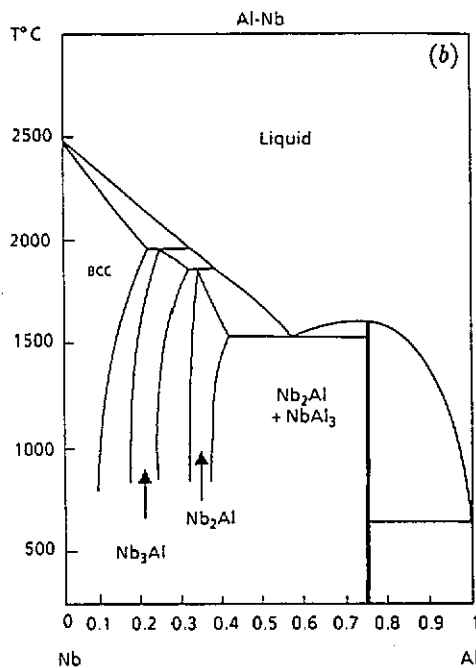
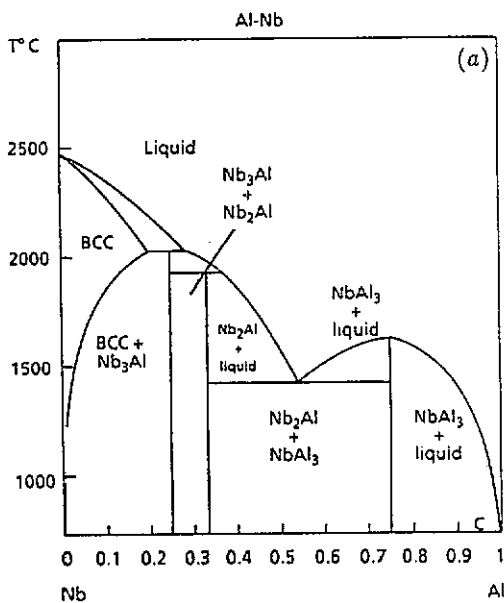


Figure 8. The Al-Nb system: (a) calculated; (b) observed [3-30].

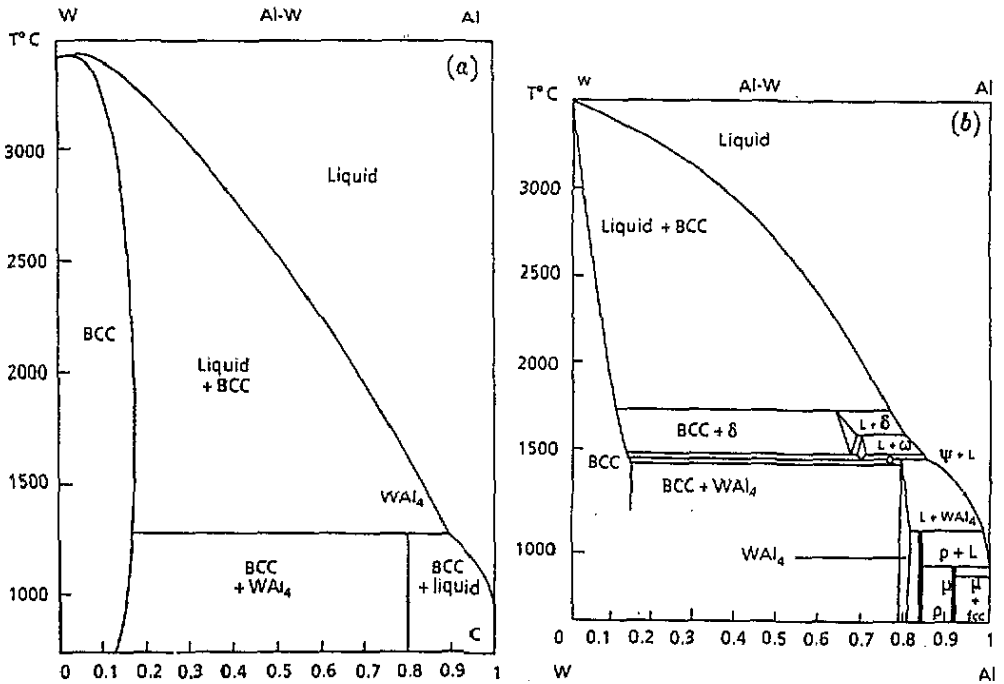


Figure 9. The Al-W system: (a) calculated; (b) observed [3].

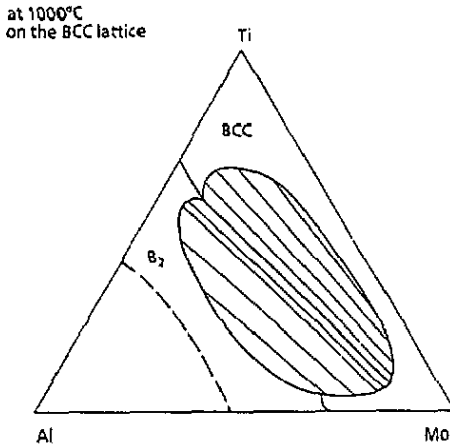


Figure 10. The Ti-Al-Mo system: calculated.

results are presented in table 1 and figure 3(a).

We now discuss our results for the Ti-Al system on the FCC lattice. We compare enthalpies of formation with experimental data for the liquid and for the solid phase in tables 2 and 3. The result is relatively good. Using the values in table 1, we may compute the disordering energies (equation (2)) and ordering energies (equation (3)) of ordered phases. We compare our results with those obtained using *ab-initio* electronic structure calculations by Asta *et al* [23] (table 4). The agreement between the two sets is very good, more especially as no information on structural energies has been used to fit the parameters of Ti-Al in the solid phases. This gives some confidence in the simplified approach used in

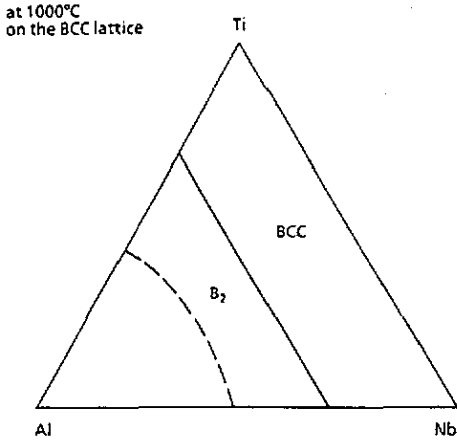


Figure 11. The Ti-Al-Nb system: calculated.

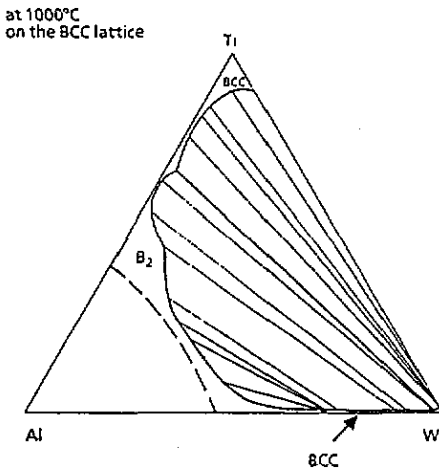


Figure 12. The Ti-Al-W system: calculated.

this paper.

For all the other systems that we shall consider, the HCP and FCC lattices will be treated as for the Ti-Al system, i.e. as equivalent structures.

We have reported in figures 4-6 and in tables 5-7 the results of our fits for the Ti-Mo, Ti-Nb and Ti-W systems, respectively. For these systems, as noted above, we can easily determine the pair interactions and also fit the disordering parameters. The calculated pair interactions are reasonable and leads to satisfactory phase diagrams.

For the Al-Mo, Al-Nb and Al-W alloys, we used Kaufman's [2,3] work for the determination of the parameters of the complex phases treated as stoichiometric compounds (see the results in figures 7-9, and in tables 8-13. Then we fitted the interaction and disordering parameters. Although the diagrams are really simplified, the result is qualitatively correct.

We refer the reader to [2-4, 28-30] for all the experimental phase diagrams. The free energies of the pure elements that we used for this work are reported in table 14.

Table 8. The results on the Al–Mo system (in units of $C = 91.64$ meV); see equations (2) and (3) with $c_A = c_{Al}$.

	V_1	V_2	a_0	a_1	a_2	a_3
BCC	1	0	-9.97	19.22	—	—
Liquid	—	—	-5.21	—	—	—

Table 9. The Al–Mo system [3] (in units of $C = 91.64$ meV).

Stoichiometric compounds	A	B (in kT/C)
Mo_3Al	-1.69	-0.33
$MoAl$	-0.28	-1.41
$Mo_{0.4}Al_{0.6}$	-0.30	-1.45
$Mo_{0.273}Al_{0.727}$	-1.88	-0.50

Table 10. The results on the Al–Nb system (in units of $C = 91.64$ meV); see equations (2) and (3) with $c_A = c_{Al}$.

	V_1	V_2	a_0	a_1	a_2
BCC	1	0	-6.94	2.47	—
Liquid	—	—	$-23.7 + 8.16kT/C$ if $T < 2300$ K; -6.04 otherwise	—	—

Table 11. The system Al–Nb [3] (in units of $C = 91.64$ meV).

Stoichiometric compounds	A	B (in kT/C)
$Nb_{0.75}Al_{0.25}$	-5.16	1.24
$Nb_{0.667}Al_{0.333}$	-6.33	1.58
$Nb_{0.25}Al_{0.75}$	-8.12	2.27

Table 12. The Al–W system (in units of $C = 91.64$ meV); see equations (2) and (3) with $c_A = c_{Al}$.

	V_1	V_2	a_0	a_1	a_2	a_3
BCC	1	0	-3.19	16.10	—	—
Liquid	—	—	0.80	—	—	—

6. Study of the ternary systems: Ti–Al–Mo, Ti–Al–Nb and Ti–Al–W

We are now able to use these values as input data for the ternary model. We have calculated, on the basis of our previous fits, the phase diagrams (isothermal sections) of three ternary systems, on the BCC structure: Ti–Al–Mo, Ti–Al–Nb and Ti–Al–W. The results, at 1273 K, are represented, in figures 10–12, respectively.

We now discuss them.

6.1. The Ti–Al–Nb alloy

We do not observe any two-phase field (B2–BCC or BCC–BCC) in this system. This seems to have been noticed already experimentally [31]. This can be understood easily; the binary

Table 13. The Al-W system [3] (in units of $C = 91.64$ meV).

Stoichiometric compounds	A	B (in kT/C)
$W_{0.2}Al_{0.8}$	-1.18	0.02

Table 14. Free energies of the pure elements.

	F_{Al}	F_{Ti}	F_{Mo}	F_{Nb}	F_W
BCC	$-628 + 6.694T$	$-16234 + 8.368T$	$-24267 + 8.368T$	$-22928 + 8.37T$	$-30543 + 8.266T$
HCP	$-5230 + 9.707T$	$-20585 + 12.134T$	$-15899 + 8.368T$	$-16652 + 11.72T$	$-22175 + 8.266T$
Liquid	0	0	0	0	0

Ti-Nb alloy segregates at too low a temperature (less than 400 K according to Murray [4]). Thus, at 1273 K, it does not show any two-phase field in the ternary system.

6.2. The Ti-Al-Mo alloy

We obtain a very instructive result. For the binary Ti-Mo, the top of the miscibility gap lies at 1043 K. Therefore, at 1273 K, there is no segregation on the Ti-Mo line of the ternary isotherm. Nevertheless, we note a two-phase field and a segregation in the inner part of the isotherm. This can be explained because ordering effects from the other binary alloys (Ti-Al and Al-Mo) strengthen the segregation tendency. Obviously, to observe such an effect, the temperature must be close to the top of the miscibility gap of the Ti-Mo system.

6.3. The Ti-Al-W alloy

The Ti-W binary system segregates at a higher temperature than the Ti-Mo alloy. Consequently, the widths of the two-phase fields in the ternary phase diagram will be larger at 1273 K. The Ti-W binary system also segregates at this temperature.

7. Conclusions

The calculations that we have developed here may be very fruitful in the future, with a view to making some predictions on the nature of multi-component systems. Our approach, which goes beyond the regular or subregular models, is also more physical than the Calphad approach, but serious difficulties do exist in evaluating the model parameters, as we have noted above.

It might be useful to evaluate them with accurate microscopic quantum studies. The linear muffin-tin orbital method [32-34] seems to be a very good candidate for realizing such calculations. Utilization of this method will be presented in a forthcoming publication.

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