Semiempirical Theory of Solid Solubility in Transition Metal Alloys

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A semiempirical theory of solid solubility in transition metal alloys is presented. The theory is based on writing the energy of formation of the solid solution as a sum of several contributions: a) a chemical contribution due to electronic redistribution in forming the alloy, b) an elastic contribution arising from the difference in size between solute and solvent atoms and c) a structural contribution due to the difference in crystal structure between solute and solvent and to the change in average valence when disolving foreign atoms. Special care is taken in evaluating these contributions in the concentrated alloy regime. The influence of charge transfer on the effective atomic volumes of the components in the alloy is also considered and found to be important. The results obtained are in good agreement with experiment.

1. Introduction

The solid part of the phase diagram of a binary alloy formed by metals A and B often contains (although not necessarily) one or several intermediate phases, in addition to terminal solid solutions of A in B and of B in A [1]. In a solid solution the solute atoms occupy substitutional positions in the host lattice, preserving the crystal structure of the host. Interstitial solid solutions also exist but they are less common than substitutional ones. On the other hand an intermediate phase normally has a narrow composition range and a crystal structure different from those of the component metals. Solid solutions and intermediate phases are competitive. Progress in the understanding of the factors governing the occurrence of the different alloy phases has been growing in recent years, but a full theoretical description of phase diagrams, and in particular of solid solutions, is a very difficult task. For this reason, semiempirical treatments, focusing on the fundamental factors which are believed to influence solid solubility, can be of great help. In this paper we present a semiempirical theory of solid solubility and apply it to several types of alloys formed by transition metals. Although the theory is semiempirical, we believe that it contains the key ingredients needed to describe solid solubility correctly. This is supported by the results obtained.

2. Thermodynamic Formulation

The extent of equilibrium solid solubility of a solute metal A in a solvent metal B at temperature T can be calculated from the free energy of formation $\Delta G_s(X_A, X_B; T)$ of the solid solution as a function of composition

$$\Delta G_s(X_A, X_B; T) = G_s(X_A, X_B; T) - X_A G_A(T) - X_B G_B(T), \tag{1}$$

where G_A and G_B are the free energies of the metals and $G_s(X_A, X_B; T)$ is the free energy of the solid solution with atomic concentrations X_A and $X_B = 1 - X_A$. A necessary condition for the thermodynamic stability of the solid solution is

$$\Delta G_s(X_A, X_B; T) < 0 .$$

Nevertheless, this is not a sufficient condition because of the possible existence of competing phases, normally an ordered intermetallic compound of fixed composition $A_\alpha B_\beta$, with free energy of formation ΔG_c. Consequently, the extent of solid solubility is calculated by computing $\Delta G_s(X_A, X_B; T)$ as a function of concentration and comparing it with ΔG_c using the tangent construction [2]. If intermediate phases do not exist, then the competing phase is a solid solution of B in A (if the crystal structures of A and B are different).

The free energy of formation can be separated as

$$\Delta G = \Delta H - T \Delta S, \tag{2}$$

where ΔH is the enthalpy of formation and ΔS is the entropy of formation. The entropy of formation

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of a substitutional solid solution is positive. Its calculation is a difficult matter. The simplest approximation is to consider ideal mixing (strictly speaking, ideal mixing is only valid when the enthalpy of formation is not far from zero). Then the entropy of random mixing [3] can be used to write

$$T\Delta S_s(X_A, X_B) = -k\,T(X_A \ln X_A + X_B \ln X_B), \qquad (3)$$

where k is the Boltzmann constant. More sophisticated approximations can also be used [4] for departures from ideal behavior. For the calculations to be presented below, ideality leads to good results. In contrast, the entropy of formation ΔS_c of ordered intermetallic compounds is normally zero or negative [1, 5–8] (magnetic effects sometimes induce exceptions to this rule [6]). Therefore the entropy term favors the existence of solid solutions.

The next step is to set up an expression for the enthalpy of formation of the solid solution and of competing intermetallic compounds. These points are considered in Sections 3 and 4.

3. Enthalpy of Formation

According to current ideas [9–13], the enthalpy of formation of a substitutional solid solution contains three terms:

$$\Delta H_s = \Delta H_s^c + \Delta H_s^{\text{size}} + \Delta H_s^{\text{str}}. \qquad (4)$$

The first one, ΔH_s^c, is a chemical term due to electron redistribution that occurs when the alloy is formed; it has been extensively studied by Miedema and coworkers [9, 14, 15]. This contribution also exists in liquid alloys. In the case of alloys of two transition metals, ΔH_s^c is equal to the enthalpy of formation in the liquid state (where the other two terms are absent). ΔH_s^{size} is an elastic contribution due to the difference in atomic volume between solute and solvent metals. This term can be computed by using classical elasticity theory [9, 12, 13, 16, 17]. Finally, ΔH_s^{str} is a structural contribution taking into account the difference in valence and crystal structure of solute and solvent [9, 10]. These three contributions are now considered in more detail.

3.1 Chemical Contribution

According to Miedema and coworkers, the chemical part of the heat of solution of a transition metal A in a transition metal B can be expressed as

$$\Delta h_s^c(\text{A in B}) = \frac{2(V_A^0)^{2/3}}{(n_A)^{-1/3} + (n_B)^{-1/3}} \cdot [-P(\Phi_A - \Phi_B)^2 + Q(n_A^{1/3} - n_B^{1/3})^2]. \qquad (5)$$

This equation contains two terms: an ionic-like term which accounts for the electronegativity difference $(\Phi_A - \Phi_B)$, and a term related to the difference in electron density n at the boundary of bulk atomic cells. V_A^0 is a measure of the atomic volume of metal A in the alloy *(at infinite dilution)*, and P and Q are empirical constants [15]. At finite solute concentration the chemical part of the heat of formation $\Delta H_s^c(X_A, X_B)$ of a disordered solid solution is

$$\Delta H_s^c(X_A, X_B) = X_A(1 - X_A^s)\left[\frac{V_A}{V_A^0}\right]^{2/3} \Delta h_s^c(\text{A in B}), \qquad (6)$$

where X_A^s is an atomic cell surface area concentration of metal A in the alloy, defined by

$$X_A^s = \frac{X_A V_A^{2/3}}{X_A V_A^{2/3} + X_B V_B^{2/3}}, \qquad (7)$$

and V_A, V_B are the atomic volumes of A and B in the alloy. By using pure metal atomic volumes V_A^m, V_B^m in (5), (6) and (7) one ignores the changes in atomic volume that arise upon alloying due to charge transfer. Therefore Miedema and coworkers have introduced the approximate correction [18]

$$V_A^{2/3}(\text{alloy}) = (V_A^m)^{2/3}[1 + a(1 - X_A^s)(\Phi_A - \Phi_B)]. \qquad (8)$$

That is, the relative volume change depends on the difference of electronegativity $(\Phi_A - \Phi_B)$ and on the degree to which A atoms are surrounded by dissimilar neighbours, that is $(1 - X_A^s)$. a is a constant which depends on the valence of the solute metal. This formula gives a volume between the pure metal and the fully corrected volume. This is a reasonable choice to use in (5) or (6). Let us notice that at infinite dilution (8) becomes

$$(V_A^0)^{2/3} = (V_A^m)^{2/3}[1 + a(\Phi_A - \Phi_B)]. \qquad (9)$$

Since X_A^s is a function of V_A and V_B (relation (7)), the calculation of $V_A^{2/3}$ (alloy) in principle requires an iteration procedure. In this paper we have introduced three steps.

3.2 Size Mismatch Contribution

The atomic volume of the solute metal is normally different from that of the solvent. Then the substitution of a solvent atom by a solute atom generates elastic tensions in the host lattice. Eshelby used classical continuum elasticity to prove that the contribution to the heat of solution from atomic size mismatch is approximately [17]

$$\Delta h_{\text{s}}^{\text{size}}(\text{A in B}) = \frac{2\mu_{\text{B}}}{3+4\chi_{\text{B}}\mu_{\text{B}}}\,\frac{(V_{\text{A}}-V_{\text{B}})^2}{V_{\text{B}}}, \tag{10}$$

where μ_{B} is the shear modulus of the host and χ_{A} is the compressibility of the solute metal. Eshelby also computed the size-mismatch part of the heat of formation in the case of a small solute concentration

$$\Delta H_{\text{s}}^{\text{size}}(X_{\text{A}}, X_{\text{B}}) = X_{\text{A}}\left[1 - X_{\text{A}}\frac{(\gamma-1)\,\gamma}{(\gamma^*-1)\,\gamma^*}\right]\Delta h_{\text{s}}^{\text{size}}(\text{A in B}), \tag{11}$$

where

$$\gamma = 1 + \frac{4\mu_{\text{B}}}{3\chi_{\text{B}}}, \quad \gamma^* = 1 + \frac{4\mu_{\text{B}}}{3\chi_{\text{A}}}. \tag{12a, b}$$

Due to the limited validity of (11) we have extended the theory to concentrated alloys in a previous paper [13]. Here we simply outline the method. The formation of a substitutional solid solution of finite solution concentration X_{A} can be divided into several steps. In the first step a very dilute alloy is formed, and (11) is used to calculate the corresponding elastic energy. At this point, the dilute alloy is considered as an effective pure metal with atoms having atomic volume and elastic constants conveniently averaged between those of solute and solvent (see [13] for details). Then, in a second step a few more solute atoms are added to this effective host. The elastic energy cost in this second step is again computed from (11), taking into account that the host is not the pure B metal but the effective metal. The process is continued in the same way and any arbitrary concentration can be reached after a sufficient number of steps. It was also observed that the results of the multi-step calculation can be accurately reproduced by the interpolation formula [13]

$$\Delta H_{\text{s}}^{\text{size}}(X_{\text{A}}, X_{\text{B}}) = \frac{X_{\text{A}}X_{\text{B}}\,\Delta h_{\text{s}}^{\text{size}}(\text{B in A})\,\Delta h_{\text{s}}^{\text{size}}(\text{A in B})}{X_{\text{A}}\,\Delta h_{\text{s}}^{\text{size}}(\text{A in B}) + X_{\text{B}}\,\Delta h_{\text{s}}^{\text{size}}(\text{B in A})}. \tag{13}$$

In [13] the pure metal volumes V_{A}^{m}, V_{B}^{m} were used for V_{A}, V_{B} in (10). But, as pointed out above, the volumes should be corrected for charge transfer effects. Niessen and Miedema [9] have proposed to use, instead of V_{A}^{m}, V_{B}^{m}, the following solute and hole volumes:

$$V_{\text{A}}^* = V_{\text{A}}^{\text{m}} + \frac{\alpha}{n_{\text{A}}}(\Phi_{\text{B}} - \Phi_{\text{A}}), \tag{14a}$$

$$V_{\text{B}}^* = V_{\text{B}}^{\text{m}} + \frac{\alpha}{n_{\text{B}}}(\Phi_{\text{B}} - \Phi_{\text{A}}), \tag{14b}$$

where

$$\alpha = \frac{-\,1.5\,V_{\text{A}}^{2/3}(\text{alloy})}{n_{\text{A}}^{-1/3} + n_{\text{B}}^{-1/3}}. \tag{15}$$

These corrected solute and hole volumes will be used in the present paper. The difference between V_{A}(alloy) of (8) and V_{A}^* of (14) should not be surprising since these represent slightly different quantities.

3.3 *Structural Contribution*

The crystal structure of the two pure metals also influences the extent of solid solubility. A substitutional solid solution preserves the crystal structure of the host. Clearly complete solid solubility (from $X_{\text{A}} = 0$ to $X_{\text{A}} = 1$) can only occur if the crystal structure of the two pure components is the same. Miedema and Niessen [9, 10] have studied the structural contribution to the enthalpy of solution of alloys of two transition metals. This contribution reflects the fact that there exists a preference for the transition metals to crystallize in one of the main crystallographic structures bcc, fcc and hcp, depending on the number Z of valence (s + d) electrons per atom. This preference has been quantified by these authors, who combined experimental and theoretical data for the energy differences $(E_{\text{bcc}} - E_{\text{fcc}})$ and $(E_{\text{hcp}} - E_{\text{fcc}})$ between bcc, fcc and hcp structures and then derived the variation of the absolute stability $E_\sigma(Z)$ ($\sigma =$ bcc, fcc, hcp) of each of the main crystal structures along the transition metals series. Their results are shown in Fig. 1, where the reference state is the average of the close-packed structures and the looser packed bcc lattice:

$$\frac{E_{\text{hcp}}(Z) + E_{\text{fcc}}(Z)}{2} + E_{\text{bcc}}(Z) = 0. \tag{16}$$

Strictly speaking, Fig. 1 is only valid for 4d and 5d transition metals. The stable crystal structure of the 3d metals Mn, Fe and Co deviates from the trend shown by the 4d and 5d metals. But, except for those three particular metals, we expect that Fig. 1

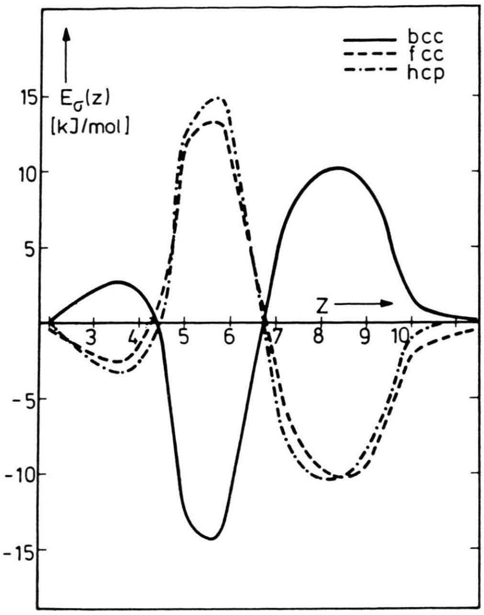

Fig. 1. Structural energy of 4d and 5d metals in the main crystal structures as a function of the number Z of valence electrons using the reference state defined by (16). The curves have been drawn by Miedema and Niessen by smoothly interpolating between the points for integer Z given in Fig. 2 of [9] (private communication by A. K. Niessen and A. R. Miedema).

describes well the rest of the 3d metals and will be used in this paper since we do not treat alloys containing Mn, Fe or Co. It is then reasonable to assume that also structure dependent energies in transition metal solid solutions will vary systematically with the average number of valence electrons per atom if the two metals form a common d-band. Consequently, disolving metal A into the host B changes the energy that stabilizes the crystal structure of the matrix metal. The structural contribution to the enthalpy of solution of metal A (with crystal structure σ) in B (with structure σ') can be written as

$$\Delta h_s^{\mathrm{str}}(\mathrm{A}_\sigma \text{ in } \mathrm{B}_{\sigma'}) = E_{\sigma'}(Z(\mathrm{B})) - E_\sigma(Z(\mathrm{A})) + (Z(\mathrm{A}) - Z(\mathrm{B})) \left.\frac{\mathrm{d}E_{\sigma'}(Z)}{\mathrm{d}Z}\right|_{Z=Z(\mathrm{B})}. \tag{17}$$

$\Delta h_s^{\mathrm{str}}$ contains two terms: The first one comes from the difference in structural energy of the two pure metals. The second one is the change of structural stability of the σ' structure due to the change in average valence. Niessen and Miedema have computed $\Delta h_s^{\mathrm{str}}$ for all combinations of two transition metals (excluding the 3d-group) [9].

The structural contribution to the heat of formation of a substitutional solid solution of concentration X_{A} can be calculated from Figure 1. Let us consider the alloy as an effective monatomic crystal with a crystal structure σ', the structure of the solvent, and with an effective valence

$$Z(\text{alloy}) = X_{\mathrm{A}}\, Z(\mathrm{A}) + (1 - X_{\mathrm{A}})\, Z(\mathrm{B}). \tag{18}$$

Then the structural contribution to the heat of formation can be written as

$$\Delta H_s^{\mathrm{str}}(X_{\mathrm{A}}, X_{\mathrm{B}}) = E_{\sigma'}(Z(\text{alloy})) - X_{\mathrm{A}}\, E_\sigma(Z(\mathrm{A})) - (1 - X_{\mathrm{A}})\, E_{\sigma'}(Z(\mathrm{B})), \tag{19}$$

where $E_{\sigma'}(Z(\text{alloy}))$, $E_\sigma(Z(\mathrm{A}))$ and $E_{\sigma'}(Z(\mathrm{B}))$ are obtained from Figure 1. Of course, this equation is consistent with (17).

4. Results

4.1 Extensive Solid Solutions

First we apply the model to alloys which show complete solid solubility in their phase diagram [5]. The alloys considered are Sc Y, Sc Zr, Sc Hf, Ti HF, V Cr, V Nb, V Mo and V W. The computations have been performed at $T = 1000$ K. The results are similar for all systems: in agreement with [13] and with experiment, the solid solution is the stable phase over the whole concentration range at that temperature.

The free energy of formation of the solid solution has been plotted in Figs. 2–5 for the systems Sc Zr, V Nb, V Mo and Sc Y. The free energy of formation calculated in [13] has also been plotted for comparison. Two differences between the calculations of the present paper and those of [13] must be pointed out. First, structural contributions were not included in [13]. Second, charge transfer corrections to the atomic volumes in the alloy (see (8) and (14) of the present paper) were neglected in [13]. These two effects are rather important. Since structural contributions are absent in the alloys V Nb and Sc Y, the effect of the charge transfer corrections to the atomic volumes is responsible for the differences in free energy of formation of these two alloys.

Quantitative information also exists for the heat of formation of equiatomic Cr V [1]. The experimental

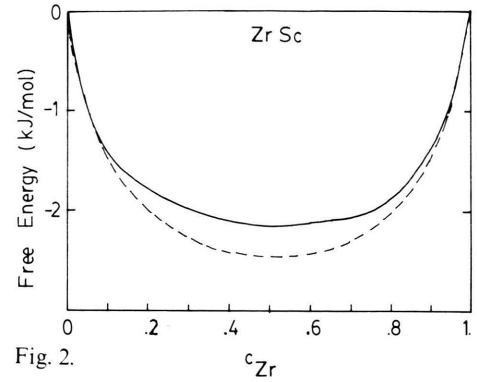

Fig. 2.

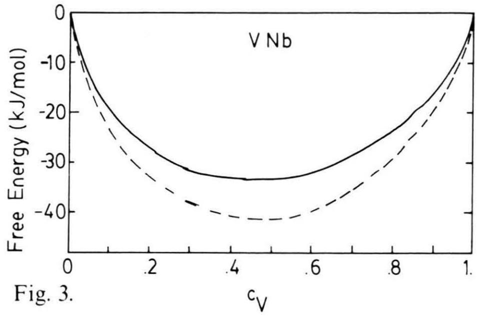

Fig. 3.

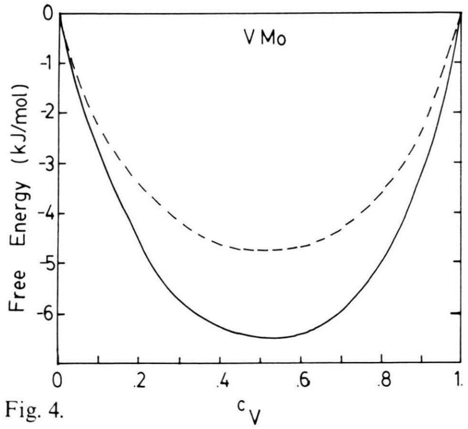

Fig. 4.

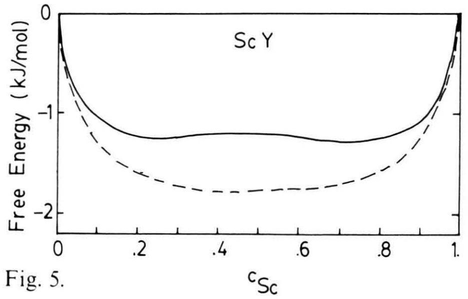

Fig. 5.

Figs. 2–5. Free energy of formation of disordered substitutional solid solutions versus concentration, at $T = 1000$ K. —— this work; - - - ref. [13].

ΔH_s at $T = (1376-1748)$ K is -456 ± 200 cal/mol. Our calculated value $\Delta H_s = -610$ cal/mol is consistent with the experiment and shows a clear improvement with respect to the value (-192 cal/mol) calculated in [13] for the same alloy.

4.2 Very Low Solid Solubility

The second group of alloys considered here consists in alloys formed by metals with very low mutual solid solubilities and without intermediate compounds. The results are very similar to those of [12]. Both sets of predicted solubilities are given in Table 1. The solubilities are predicted to be very small in these alloys, in agreement with the experiments.

4.3 Solid Solubility in Systems with Intermetallic Compounds

Finally we have studied the solid solubility in systems with stable intermetallic compounds. The extent of solid solubility is limited in these systems by the existence of a phase (the compound) with a more negative free energy of formation. Normally an intermetallic compound is stable only in a narrow composition range. This means that its free energy of formation increases very rapidly towards less negative values when the composition derivates from the stoichiometric one.

We have computed the free energy of formation of the intermetallic compound of nominal composition (taken from the phase diagram) using Miedema's theory [15]

$$\Delta G_c = \Delta h_s^c(\text{A in B})\, X_A [1 + 8 (X_A^s X_A^s)^2] . \qquad (20)$$

In writing this equation, the entropy of formation has been assumed to be very small with respect to

Table 1. Theoretical and experimental solid solubilities at the indicated temperatures (solubility in at%).

Alloy	T (K)	Theoret. ref. [12]	Theoret. this work	Exper. [19]
Sc in Nb	1500	0.07	0.015	< 0.1
Nb in Sc	1500	0.18	0.025	< 0.3
Sc in Cr	1350	< 0.001	0.14	< 0.1
Cr in Sc	1350	0.22	0.31	< 1
V in Sc	1570	0.45	0.07	< 0.5
Sc in V	1570	0.024	0.06	< 0.3
Ti in Y	1140	0.005	0.0003	0

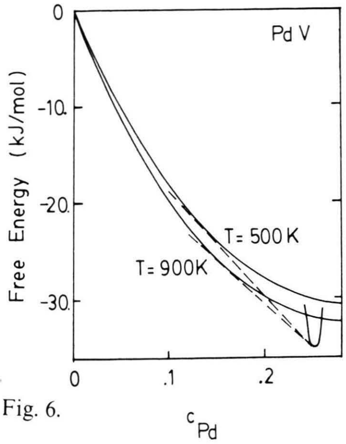

Fig. 6.

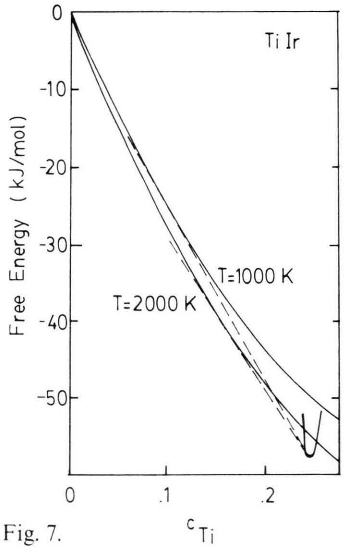

Fig. 7.

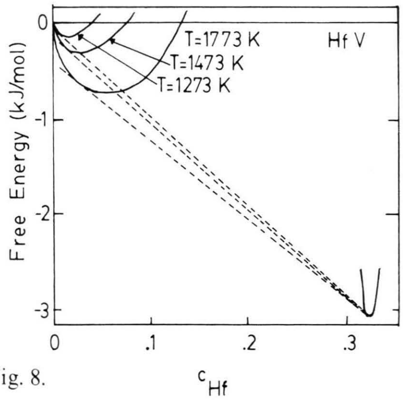

Fig. 8.

Figs. 6–8. Tangent construction to calculate the extent of solid solubility at a given temperature. Plotted are the free energy of formation of the solid solution and the free energy of formation of the compound of stoichiometric composition. The curve for the compound is schematic (only the minimum of this curve has been actually calculated).

Table 2. Theoretical and experimental solid solubilities, at the indicated temperatures, in alloys having intermetallic compounds (solubility in at%).

Alloy	Compound	T (K)	Solubility (theoret.)	Solubility (exper.) [20]
Pd in V	Pd V_3	900	17	15
Hf in V	Hf V_2	1273	0.5	0.6
		1475	1	1.2–1.5
		1773	2.8	2.1–2.4
Ti in Ir	Ti Ir_3	1500	14	13
		2000	16	14

the entropy of formation of a disordered solid solution [5, 8]. In comparison with a solid solution of the same composition, the factor $[1 + 8(X_A^s X_B^s)^2]$ accounts for the increased number of dissimilar neighbours in the ordered compound. The extent of solid solubility is obtained by comparing (20) with the free energy of formation of the solid solution using the tangent method. This is illustrated in Figs. 6–8 for the alloys Pd V, Ti Ir and Hf V, respectively, and for several temperatures indicated in each case. Only the minimum of the curve was calculated for the intermetallic compound although a schematic curve has been drawn to indicate that ΔG_{comp} changes rapidly around the nominal composition. The calculated solubilities are given in Table 2, showing an excellent agreement with experiment.

Conclusions

In this paper we have presented a semiempirical theory of solid solubility applicable to transition metal alloys. With respect to our previous works [12, 13] two new features are introduced in the present paper. One is the consideration of the structural contribution to the heat of formation of the solid solution. This contribution has been proposed by Miedema and Niessen [9, 10] and has been computed by these authors in the limit of dilute alloys (heat of solution). Here we have shown how the structural energy can be calculated in concentrated solid solutions too, which is a necessary requirement in estimating solid solubility limits. On the other hand, changes in the atomic volumes of the components in the alloy, induced by charge transfer, have also been taken into account.

Three clases of alloys have been studied: alloys showing complete solubility, alloys with very low solubility and without compounds, and alloys having intermediate compounds. The agreement with experiment is very satisfactory in all cases.

Acknowledgements

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