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Influence of AlN precipitation on thermodynamic parameters in C-Al-V-N microalloyed steels

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Abstract

An estimation of the equilibrium compositions of the austenite and carbonitride phases, as well as the mole fraction of each phase in C-Al-V-N microalloyed steels at different austenitising temperatures was made by calculations based on experimental data. Further, a comparison of the mole fraction was made from two thermodynamic models due to Adrian and Rios, with and without considering aluminium in the steels. The results indicate that both models produce very similar results and can be used to calculate the equilibrium parameters and predict the solution temperature of carbonitrides and aluminium nitride in the range 800-1300 $^\circ C$ for an alloy system contained up to three microalloying elements and aluminium. Both models predict that most of the carbon remains in solution at the calculated temperature. When AlN precipitation is included in the calculation, it is seen that the mole fraction of the carbonitrides f_P and the atomic fraction of carbon in the interstitial lattice of the carbonitrides f_C decreases, while the atomic fraction of nitrogen in the interstitial lattice of carbonitride f_N, increases. The effect of aluminium on these equilibrium parameters depends on the chemical composition of the steel. Increasing the contents of Al, N, C, and V together in the experimental steels has a more significant influence on these equilibrium parameters than changing only the contents of Al; Al and V or Al and N.

KEY WORDS: carbonitride; aluminium nitride; microalloyed steel; precipitation; thermodynamic analysis; computer models.

1. Introduction

It is well known that small amounts of elements such as V, Nb and Ti can significantly improve the overall mechanical properties of high strength low alloy steels through retarding recrystallization and grain growth of austenite at high temperatures and through dispersion hardening both in austenite and in ferrite. A knowledge of the austenite composition, as well as of the amount and composition of the carbonitrides, is essential for determining the optimum composition for the steel, as well as the most favorable combination of heat treatment parameters. Thermodynamic analysis is found to be a very efficient method for studying the precipitation behavior of carbonitrides. Many experimental and theoretical studies on multicomponent carbonitride compositions have been carried out in the past.1–12) However, very few studies have considered the effect of AlN on the precipitation thermodynamic calculation, although in many microalloyed steels, aluminium is present and it is able to form AlN. We know quite a lot about the different precipitation kinetics of VCN and AlN, but little about solution kinetics. In addition, very little work has been done to examine and verify the limited models available. Owing to its different crystal structure (hcp), AlN does not show mutual solubility with the carbides or nitrides of V, Nb and Ti, all of which have NaCl cubic crystal structures. As a result, AlN precipitation competes for N with the NaCl-type carbonitride.13) Therefore, AlN precipitation is expected to change not only carbonitride composition and mole fraction but also the corresponding matrix composition.

In the present study, a comparison is made of two different methods of estimating the equilibrium compositions of the austenite and carbonitride phases, as well as the mole fraction of each phase including AlN in C-Al-V-N microalloyed steels, at different austenitising temperatures. One of the methods is called here the eleven parameter thermodynamic model[14)] and the other is called the two parameter thermodynamic model.[15)]

2. Derivation of the Thermodynamic Models

2.1 The eleven parameter thermodynamic model developed by Adrian for an $Fe - Al - M^{'} - M^{''} - M^{'''} - C - N$ *alloy system*

It was assumed that three microalloyed elements ($M^{'}, M^{''}, M^{'''}$) as well as the interstitial elements (C, N) form dilute solutions in austenite and that their activities are described by Henry's law. An ideal stoichiometry of the carbonitride was also assumed, which implies that the total number of metal atoms is equal to the number of carbon and nitrogen atoms in the carbonitride. In an alloy system neglecting Al, the molar free energy of the carbonitride G_m is obtained, for the chemical formula of the carbonitride $M^{'}_x M^{''}_v M^{'''}_z C_y N_{1-y}$, in which the value of z is equal to $\left(1 - x - v\right)$, as described previously by Hillert and Staffansson [16)]

$$
\begin{aligned}
G_m &= G_{M^{'}_x M^{''}_v M^{'''}_z C_y N_{1-y}} \\
&= xyG^{\circ}_{M^{'}C} + x(1-y)G^{\circ}_{M^{'}N} + vyG^{\circ}_{M^{''}C} + v(1-y)G^{\circ}_{M^{''}N} \\
&\quad zyG^{\circ}_{M^{'''}C} + z(1-y)G^{\circ}_{M^{'''}N} - TS^{1}_{m} + G^{E}_{m} \qquad (1)
\end{aligned}
$$

where $G^{\circ}_{M^{'}C}, G^{\circ}_{M^{'}N}, G^{\circ}_{M^{''}C}, G^{\circ}_{M^{''}N}, G^{\circ}_{M^{'''}C},$ and $G^{\circ}_{M^{'''}N}$ are the molar free energies of the respective pure binary compounds at a given austenitising temperature T, S^{1}_{m} is the integral molar entropy of mixing, and G^{E}_{m} is the integral excess molar free energy of mixing. Equation (1) can be rewritten in the following form

$$G_m = G_m^{ref} - TS_m^1 + G_m^E \tag{2}$$

where G_m^{ref} represents the molar free energy of the pure binary compounds forming the carbonitride. The ideal entropy of mixing S_m^1 is given by Temkin as[17)]

$$-S_m^1 / R = x \ln x + v \ln v + z \ln z + y \ln y + (1-y)\ln(1-y) \tag{3}$$

where $R = 8.3144\, J/K.mol$ is the gas constant. The integral excess molar free energy of mixing G_m^E is expressed by the regular solution parameters L

$$\begin{aligned} G_m^E &= xvyL^{C}_{M^{'}M^{''}} + xzyL^{C}_{M^{'}M^{'''}} + vzyL^{C}_{M^{''}M^{'''}} + xv(1-y)L^{N}_{M^{'}M^{''}} \\ &\quad + xz(1-y)L^{N}_{M^{'}M^{'''}} + vz(1-y)L^{N}_{M^{''}M^{'''}} + xy(1-y)L^{M^{'}}_{CN} \\ &\quad + vy(1-y)L^{M^{''}}_{CN} + zy(1-y)L^{M^{'''}}_{CN} \end{aligned} \tag{4}$$

It was assumed that $L^{C}_{M^{'}M^{''}} = L^{C}_{M^{'}M^{'''}} = L^{C}_{M^{''}M^{'''}} = L^{N}_{M^{'}M^{''}} = L^{N}_{M^{'}M^{'''}} = L^{N}_{M^{''}M^{'''}} = 0$, and $L^{M^{'}}_{CN} = L^{M^{''}}_{CN} = L^{M^{'''}}_{CN} = -4260 Jmol^{-1}$.[13)] At thermodynamic equilibrium, the free energies of the atoms of $M^{'}, M^{''}, M^{'''}, C,$ and N in the austenite and in the carbonitride are equal

$$\Delta G_{M^{'}C} = \bar{G}_{M^{'}C} - \bar{G}^{\gamma}_{M^{'}} - \bar{G}^{\gamma}_{C} = 0 \qquad (5)$$

$$\Delta G_{M^{'}N} = \bar{G}_{M^{'}N} - \bar{G}^{\gamma}_{M^{'}} - \bar{G}^{\gamma}_{N} = 0 \qquad (6)$$

$$\Delta G_{M^{''}C} = \bar{G}_{M^{''}C} - \bar{G}^{\gamma}_{M^{''}} - \bar{G}^{\gamma}_{C} = 0 \qquad (7)$$

$$\Delta G_{M^{''}N} = \bar{G}_{M^{''}N} - \bar{G}^{\gamma}_{M^{''}} - \bar{G}^{\gamma}_{N} = 0 \qquad (8)$$

$$\Delta G_{M^{'''}C} = \bar{G}_{M^{'''}C} - \bar{G}^{\gamma}_{M^{'''}} - \bar{G}^{\gamma}_{C} = 0 \qquad (9)$$

$$\Delta G_{M^{'''}N} = \bar{G}_{M^{'''}N} - \bar{G}^{\gamma}_{M^{'''}} - \bar{G}^{\gamma}_{N} = 0 \qquad (10)$$

Where $\bar{G}_{MX}, \bar{G}^{\gamma}_{M}$ and $\bar{G}^{\gamma}_{X}$ are the partial molar free energies of MX, M and X, respectively in the austenite. The final form of the system of equations describing the thermodynamic equilibrium in the alloy system $Fe - M^{'} - M^{''} - M^{'''} - C - N$ was obtained as 14)

$$y \ln \frac{xyK_{M^{'}C}}{M^{'}_{S} C_{S}} + (1-y) \ln \frac{x(1-y)K_{M^{'}N}}{M^{'}_{S} N_{S}} + y(1-y) \frac{L_{CN}}{RT} = 0 \qquad (11)$$

$$y \ln \frac{vyK_{M^{''}C}}{M^{''}_{S} C_{S}} + (1-y) \ln \frac{v(1-y)K_{M^{''}N}}{M^{''}_{S} N_{S}} + y(1-y) \frac{L_{CN}}{RT} = 0 \qquad (12)$$

$$y \ln \frac{zyK_{M^{'''}C}}{M^{'''}_{S} C_{S}} + (1-y) \ln \frac{z(1-y)K_{M^{'''}N}}{M^{'''}_{S} N_{S}} + y(1-y) \frac{L_{CN}}{RT} = 0 \qquad (13)$$

$$vy \ln \frac{xM_S^{''} K_{M^{'}C}}{vM_S^{'} K_{M^{''}C}} + z(1-y) \ln \frac{zM_S^{'} K_{M^{'''}N}}{xM_S^{'''} K_{M^{'}N}}$$

$$+(1-y) \ln \frac{x(1-y) K_{M^{'}N}}{M_S^{'} N_S} + y^2 (1-y) \frac{L_{CN}}{RT} = 0 \qquad (14)$$

$$M_0^{'} = \left(\frac{x}{2}\right) f_P + \left(1 - f_P\right) M_S^{'} \qquad (15)$$

$$M_0^{''} = \left(\frac{v}{2}\right) f_P + \left(1 - f_P\right) M_S^{''} \qquad (16)$$

$$M_0^{'''} = \left(\frac{1-x-v}{2}\right) f_P + \left(1 - f_P\right) M_S^{'''} \qquad (17)$$

$$C_0 = \left(\frac{y}{2}\right) f_P + \left(1 - f_P\right) C_S \qquad (18)$$

$$N_0 = \left(\frac{1-y}{2}\right) f_P + \left(1 - f_P\right) N_S \qquad (19)$$

Therefore, the thermodynamic equilibrium is described by a system of nine non-linear equations with nine unknown variables describing the compositions of the austenite ($M_S^{'}, M_S^{''}, M_S^{'''}, C_S$, and N_S), the carbonitrides ($x, v,$ and y) and the molar faction of the carbonitride $\left(f_P\right)$. The entry data for the solution of the system of equations are the alloy composition ($M_0^{'}, M_0^{''}, M_0^{'''}, C_0$ and N_0), the austenitising temperature T, and the solubility products K_{MX} for the binary compounds MX. All composition data are expressed in atomic fractions and solubility products are related to atomic fractions of the dissolved compounds.

Considering AlN, which has a hexagonal lattice and therefore precipitates independently, the new modified system consists of equations (11)-(14) and the following additional equations for the calculation of the thermodynamic equilibrium in the alloy system $Fe - Al - M^{'} - M^{''} - M^{'''} - C - N$

$$Al_S N_S = K_{AlN} \tag{20}$$

$$M_0^{'} = \left(\frac{x}{2}\right) f_P + \left(1 - f_P - f_{AlN}\right) M_S^{'} \tag{21}$$

$$M_0^{''} = \left(\frac{x}{2}\right) f_P + \left(1 - f_P - f_{AlN}\right) M_S^{''} \tag{22}$$

$$M_0^{'''} = \left(\frac{1 - x - v}{2}\right) f_P + \left(1 - f_P - f_{AlN}\right) M_S^{'''} \tag{23}$$

$$Al_0 = \frac{f_{AlN}}{2} + \left(1 - f_P - f_{AlN}\right) Al_S \tag{24}$$

$$C_0 = \left(\frac{y}{2}\right) f_P + \left(1 - f_P - f_{AlN}\right) C_S \tag{25}$$

$$N_0 = \left(\frac{1 - y}{2}\right) f_P + \frac{f_{AlN}}{2} + \left(1 - f_P - f_{AlN}\right) N_S \tag{26}$$

where f_{AlN} is the molar fraction of AlN, Al_0 and Al_S are the total and dissolved contents of aluminium, respectively, expressed as atomic fractions. Including f_{AlN} and Al_S, the thermodynamic equilibrium consists of a system of eleven non-linear equations with eleven unknown variables.

2.2 The two parameter thermodynamic model developed by Rios for an alloy system with a multicomponent NaCl-type carbonitride and AlN

On basis of the theory of molar free energy and also assuming that Henry's law is followed by the solutes, a mole of the complex carbonitride, neglecting any Al addition to the system, constituted by n metal elements M_i , is derived as

$$\begin{aligned}&\text{mole}\left(M_{f_1},\ldots,M_{f_n}\right)\left(C_{f_C},N_{f_N}\right)\\&\quad=\sum f_i + f_C + f_N\end{aligned} \tag{27}$$

where $\sum$ denotes the sum over all i . f_i is the atomic fraction of the microalloyed element M in the substitutional lattice $\left(\sum f_i = 1\right)$, while f_C and f_N are the atomic fractions of carbon and nitrogen respectively in the interstitial lattice of the complex carbonitride $\left(f_C + f_N = 1\right)$. This definition yields a molar fraction which is half given by Adrian [14)] and consequently the present mole fractions must be multiplied by two to be consistent with their definition.

If the composition of the steel in atomic fractions is given by M_{0i}, C_0 and N_0, the mass balance requires that

$$M_{Pi} = M_{0i} - \left(1-2f_P\right)M_{Si} \tag{28}$$

$$C_P = C_0 - \left(1-2f_P\right)C_S \tag{29}$$

$$N_P = N_0 - \left(1-2f_P\right)N_S \tag{30}$$

where M_{Pi}, C_P and N_P are the atomic fractions of microalloyed and interstitial elements that form the carbonitride, f_P is the mole fraction of the carbonitride and M_{Si} is the atomic fraction of the i^{th} microalloyed element in solution in austenite.

When perfect stoichiometry is assumed, then

$$\sum \frac{M_{0i} - \left(1 - 2 f_P\right) M_{Si}}{C_0 + N_0 - \left(1 - 2 f_P\right)(C_S + N_S)} = 1 \tag{31}$$

Therefore, the system of equations describing the thermodynamic equilibrium in the alloy system with multicomponent NaCl-type carbonitride is given as follows [15)]

$$f_P = \frac{C_0 + N_0 - C_S - N_S}{1 - 2\left(C_S + N_S\right)} \tag{32}$$

$$f_C = \frac{C_P}{f_P} = \frac{C_0 - \left(1 - 2 f_P\right) C_S}{f_P} \tag{33}$$

$$f_N = \frac{N_P}{f_P} = \frac{N_0 - \left(1 - 2 f_P\right) N_S}{f_P} \tag{34}$$

$$f_i = \frac{M_{Pi}}{f_P} = \frac{M_{0i} - \left(1 - 2 f_P\right) M_{Si}}{f_P} \tag{35}$$

$$M_{Si} = \frac{M_{0i}}{1 - 2 f_P + f_P\left(C_S / K_{M_iC} + N_S / K_{M_iN}\right)} \tag{36}$$

$$C_S = \frac{f_C}{\sum \left(M_{0i} / K_{M_iC}\right) \Big/ \left[1 - 2 f_P + f_P\left(C_S / K_{M_iC} + N_S / K_{M_iN}\right)\right]} \tag{37}$$

$$N_S = \frac{f_N}{\sum \left(M_{0i} / K_{M_iN}\right) \Big/ \left[1 - 2 f_P + f_P\left(C_S / K_{M_iC} + N_S / K_{M_iN}\right)\right]} \tag{38}$$

where K_{M_iC} and K_{M_iN} are the solubility products of the NaCl-type of carbide and nitride respectively of element M_i. These solubility products must refer to concentrations in atomic fractions and to the NaCl-type of carbide or nitride. 3)

Equations (32) to (38) can be modified to account for the presence of AlN by essentially rewriting the mass balance and allowing for the formation of a separate aluminium nitride phase. Hence

$$f_{AlN} = Al_0 - Al_S\left[1 - \frac{2(C_0 + N_0 - C_S - N_S)}{1 - 2\left(C_S + N_S\right)}\right] \tag{39}$$

$$f_P = \frac{C_0 + N_0 - C_S - N_S}{1 - 2\left(C_S + N_S\right)} - f_{AlN} \tag{40}$$

$$f_C = \frac{C_0 - \left(1 - 2f_P - 2f_{AlN}\right)C_S}{f_P} \tag{41}$$

$$f_N = \frac{N_0 - \left(1 - 2f_P - 2f_{AlN}\right)N_S - 2f_{AlN}}{f_P} \tag{42}$$

$$f_i = \frac{M_{0i} - \left(1 - 2f_P - 2f_{AlN}\right)M_{Si}}{f_P} \tag{43}$$

$$M_{Si} = \frac{M_{0i}}{1 - 2f_P - 2f_{AlN} + f_P\left(C_S/K_{M_iC} + N_S/K_{M_iN}\right)} \tag{44}$$

$$C_S = \frac{f_C}{\sum\left(M_{0i}/K_{M_iC}\right)\Big/\left[1 - 2f_P - 2f_{AlN} + f_P\left(C_S/K_{M_iC} + N_S/K_{M_iN}\right)\right]} \qquad (45))$$

$$N_S = \frac{f_N}{\sum \left(M_{0i} \big/ K_{M_i N} \right) \Big/ \left[1 - 2 f_P - 2 f_{AlN} + f_P \left(C_S \big/ K_{M_i C} + N_S \big/ K_{M_i N} \right) \right]} \qquad (46)$$

where $Al_S = K_{AlN} / N_S$. Although there are eight equations above, only two unknown parameters, i.e. C_S and N_S need to be solved initially. From the values of C_S and N_S, all the other parameters f_{AlN}, f_P, f_C, f_N, f_i and M_{Si} can be obtained from equations (39)-(44).

3. Results and Discussion

3.1 *Thermodynamic analysis programs*

Because the above thermodynamic equilibrium equations contain non-linear terms, they can only be solved by using numerical methods with the aid of a computer. Based upon the MINPACK routine HYBRD1,18) two similar FORTRAN programs 19) have been written for the two models which choose the correction at each step as a convex combination of the Newton and scaled gradient directions. This guarantees global convergence for starting points far from the solution and a fast rate of convergence. The Jacobian is updated by the rank-1 method of Broyden given by More *et al.*.18) At the starting point, the Jacobian is approximated by forward differences, but these are not used again until the rank-1 method fails to produce a satisfactory process. Since the methods are iterative, an initial guess at the solution has to be made. It should be emphasized that the functions of these parameters and their derivatives are, in fact, discontinuous, and successive approximations often occur as singularities. In such cases, the calculation was carried out starting from a new point selected by the approximate solution given by the previous results. Once a new point is input, the programs automatically run several dozen and sometimes over one hundred times, before an approximate solution is produced. The final solution is ensured to have a calculated relative error of less than 10^{-8}.

Relatively speaking, the program for the two parameter thermodynamic model developed by Rios is more easy to run than the eleven parameter thermodynamic model developed by Adrian because it only involves two unknown parameters and requires two initial data parameters instead of eleven for the eleven parameter thermodynamic model. Even so, it cannot be solved without using numerical methods. In fact, all the equations (39)-(46) in the two parameter thermodynamic model have to be solved simultaneously, because both unknown parameters are involved in the eight equations.

3.2 Thermodynamic analysis for experimental steels neglecting AlN

The effects of the austenitising temperature on the austenite composition, as well as on the amount and composition of the carbonitrides, have been analyzed for experimental microalloyed steels whose compositions are listed in **Table 1**. In order to compare the influence of Al on the precipitation process, firstly, the thermodynamic analysis was carried out by both models without considering the presence Al in the steels, i.e. $Al = f_{AlN} = 0$. With only one alloying element, vanadium, being added to the current steels, taking $v = z = 0$ and $M'' = M''' = 0$, the equations (11)-(19) in the eleven parameter thermodynamic model are simplified for carbonitride VC_yN_{1-y} as follows.

$$\ln\frac{yK_{VC}}{V_S C_S} + (1-y)^2\frac{L_{CN}}{RT} = 0 \tag{47}$$

$$\ln\frac{(1-y)K_{VN}}{V_S N_S} + y^2\frac{L_{CN}}{RT} = 0 \tag{48}$$

$$V_0 = \left(\frac{x}{2}\right) f_P + \left(1 - f_P\right)V_S \tag{49}$$

$$C_0 = \left(\frac{y}{2}\right) f_P + \left(1 - f_P\right)C_S \tag{50}$$

$$N_0 = \left(\frac{1-y}{2}\right) f_P + \left(1 - f_P\right)N_S \tag{51}$$

Similarly, from the equations (32)-(38) in the two parameter thermodynamic model, this gives

$$f_P = \frac{C_0 + N_0 - C_S - N_S}{1 - 2\left(C_S + N_S\right)} \tag{52}$$

$$f_C = \frac{C_0 - \left(1 - 2f_P\right)C_S}{f_P} \tag{53}$$

$$f_N = \frac{N_0 - \left(1 - 2f_P\right)N_S}{f_P} \tag{54}$$

$$f_i = \frac{V_0 - \left(1 - 2f_P\right)V_S}{f_P} \tag{55}$$

$$V_S = \frac{V_0}{1 - 2f_P + f_P\left(C_S/K_{VC} + N_S/K_{VN}\right)} \tag{56}$$

$$C_S = \frac{f_C}{\sum \left(V_0 / K_{VC} \right) / \left[1 - 2 f_P + f_P \left(C_S / K_{VC} + N_S / K_{VN} \right) \right]} \tag{57}$$

$$N_S = \frac{f_N}{\sum \left(V_0 / K_{VN} \right) / \left[1 - 2 f_P + f_P \left(C_S / K_{VC} + N_S / K_{VN} \right) \right]} \tag{58}$$

where $x = f_i = 1$, $y = f_C$, $1 - y = f_N$, i.e. $VC_y N_{1-y} = VC_{f_C} N_{f_N}$, and V_0 and V_S are the total and dissolved contents of vanadium, respectively. Various experimental and theoretically determined solubility products for vanadium carbide and nitride are available,[20] and the following data have been adopted here [21–22]

$$Log_{10} K_{VC} = -9500/T + 6.72 \tag{59}$$

$$Log_{10} K_{VN} = -7840/T + 3.02 \tag{60}$$

The calculated results of mole fractions of the carbonitrides, the carbonitride composition and the matrix composition as a function of temperature are shown in **Figs. 1-3**. As expected, the mole fraction of the carbonitrides decreases as the temperature increases (Fig. 1). The precipitation of the carbonitrides could extend up to $1050^\circ C$ for Steel 2, which contains a higher nitrogen content, before they totally dissolve into austenite. By contrast, all the carbonitrides go into solution before $950^\circ C$ for the other steels, which contain a lower nitrogen content, due to insufficient nitrogen to form a more stable carbonitride. The temperature at which the calculated mole fraction of precipitates goes to zero, i.e. the temperature where all vanadium goes into solution in austenite, is considered to be equal to the carbonitride solution temperature. The atomic fraction of carbon in the interstitial lattice, f_C, decreases while the atomic fraction of nitrogen f_N, increases with temperature for all four experimental steels (Fig. 2). Fig. 3 shows that the quantity of a particular element remaining in solution in austenite, from which it can be seen that most of the carbon tends to remain in solution, and as expected, the proportion of vanadium and nitrogen in solution increases as the temperature increases.

Table 1. Compositions of Experimental Steels, wt%

No.	C_0	Si_0	Mn_0	P_0	S_0	Al_0	N_0	V_0
1	0.13	0.30	1.43	0.010	0.003	0.032	0.002	0.10
2	0.12	0.31	1.43	0.011	0.002	0.037	0.015	0.10
3	0.12	0.31	1.45	0.011	0.003	0.026	0.0049	0.10
4	0.13	0.30	1.45	0.012	0.003	0.029	0.0043	0.049

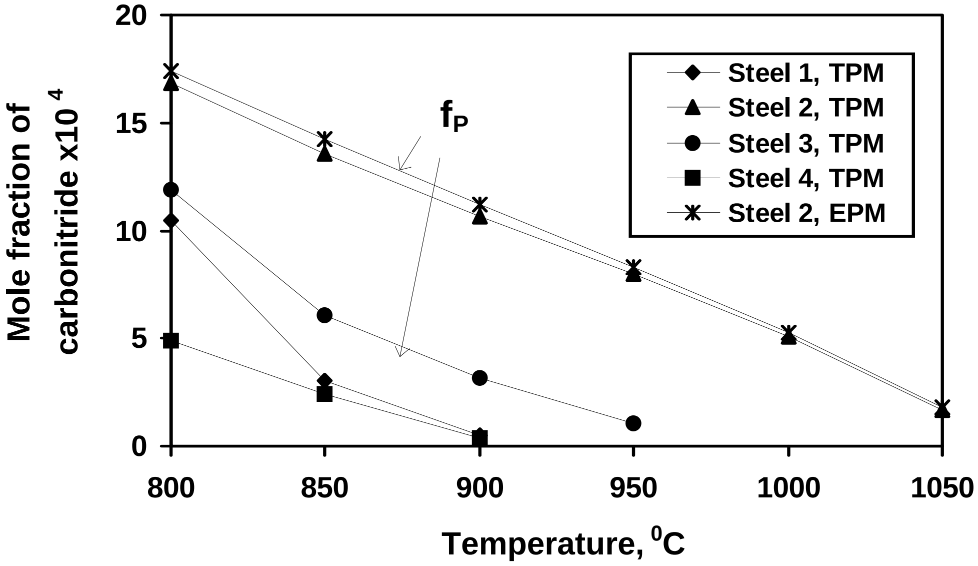


Fig. 1 Mole fraction of carbonitride as a function of temperature for C-Al-V-N steels neglecting AlN, calculated by the two parameter model (TPM) and the eleven parameter model (EPM).

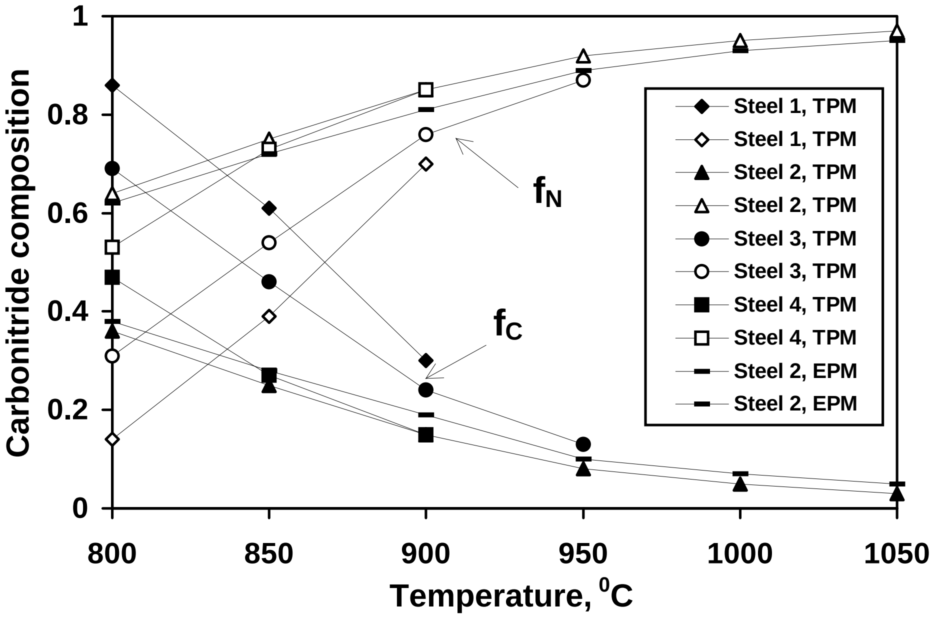


Fig. 2 The atomic fractions of carbon and nitrogen required to form VCN as a function of temperature for C-Al-V-N steels neglecting AlN, calculated by the two parameter model (TPM) and the eleven parameter model (EPM).

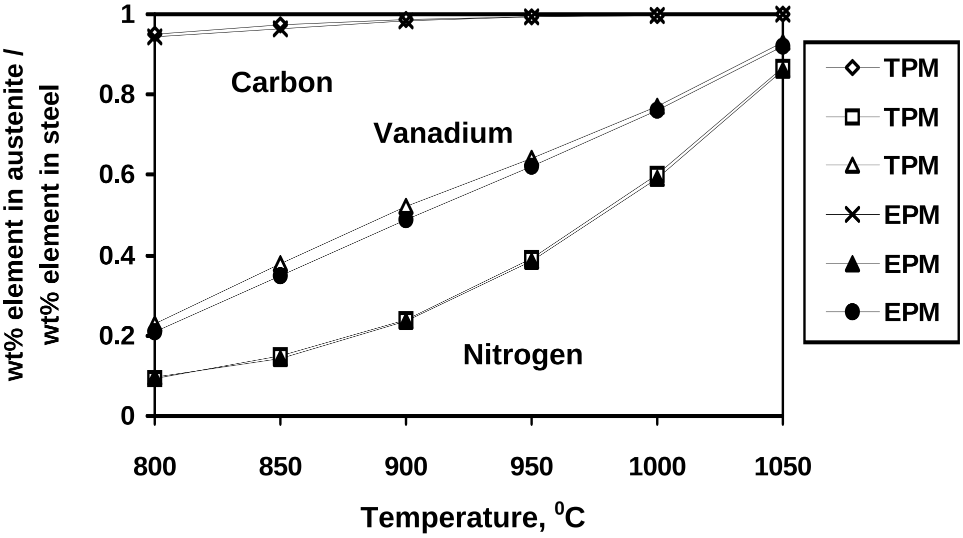


Fig. 3 The quantity of C, N and V in austenite as a function of temperature in Steel 2 neglecting AlN, calculated by the two parameter model (TPM) and eleven parameter model (EPM).

Both models produce very similar results (see Figs. 1-3), especially for the compositions of the austenite C_S, N_S and V_S. Although the mole fraction of carbonitrides f_P, and the atomic fractions of carbon in the interstitial lattice of the carbonitrides f_C calculated by the eleven parameter thermodynamic model (EPM) are slightly higher than those calculated by the two parameter thermodynamic model (TPM), the atomic fractions of nitrogen in the interstitial lattice of carbonitrides f_N calculated by the eleven parameter thermodynamic model are slightly lower than those calculated by the two parameter thermodynamic model, but the differences are small.

3.3 Thermodynamic analysis for experimental steels including the effects of AlN

When AlN precipitation in steels also is considered, the effects of austenitising temperature on the parameters of precipitation and the austenite matrix can be evaluated by equations (47)-(48), plus equations (20)-(21) and (24)-(26) in the eleven parameter thermodynamic model. These parameters also can be calculated by equations (39)-(46) using the two parameter thermodynamic model. The same solubility product data [21)] employed by other researchers [14–15)] for AlN are used here,

$$Log_{10} K_{AlN} = -7184/T + 1.79 \tag{61}$$

Fig. 4 demonstrates the calculated austenite/carbonitride equilibrium parameters for Steel 2 by considering AlN in both models, which produce almost identical results. The results are similar to those shown in Figs. 1-3 without considering AlN. The mole fraction of carbonitride f_P, and the atomic fraction of carbon in the interstitial lattice of carbonitride f_C are slightly higher, while the atomic fraction of nitrogen in the interstitial lattice of carbonitride f_N and the dissolved vanadium in the austenite are slightly lower, when calculated by the eleven parameter thermodynamic model rather than by the two parameter thermodynamic model. The mole fraction of AlN, f_{AlN}, increases slightly to about $1000^\circ C$ and then decreases, until finally the AlN particles go into solution with increasing temperature (Fig. 4(a)). As a result, the dissolved aluminium in the austenite at first also slightly decreases and then increases (Fig. 4(c)).

It should be pointed out that for a particular composition of steel, when the austenitising temperature reaches a particular temperature, a negative value of f_P or f_{AlN} will be obtained in the calculation, which means that in an equilibrium condition all the particles have gone to solution in austenite at this temperature. In the case of $f_P < 0$ and $f_{AlN} > 0$, at higher temperatures, the calculation has to be repeated, with

$f_P = f_C = f_N = 0$ but only calculating f_{AlN} in the simplified equations. This additional calculation can be carried out by the eleven parameter thermodynamic model but is mathematically impossible by the two parameter thermodynamic model due to the way this model was defined and derived. Therefore, the data available from the two parameter thermodynamic model in Fig. 4 is only given up to $950^\circ C$, the temperature at which the carbonitrides almost totally dissolve into austenite in Steel 2. However, the advantage of the two parameter thermodynamic model is that it can be easily generalized to account for the presence of any number of separate nitrides and carbides coexisting with NaCl-type carbonitride.[15)]

The comparison of the mole fraction of carbonitrides and equilibrium composition of carbonitrides and austenite with and without considering AlN clearly show the influence of Al on these parameters in the steels (**Fig. 5**). When considering AlN precipitation, which competes for nitrogen with the vanadium carbonitride, the mole fraction of carbonitride f_P decreases (Fig. 5(a)), due to the impoverishment in nitrogen. Naturally, the atomic fraction of nitrogen in the interstitial lattice of carbonitride f_N also decreases, dropping from 0.64 to 0.42 at $800^\circ C$ for Steel 2 (Fig. 5(b)). Subsequently, within the low temperature austenite range, more vanadium and less nitrogen go into solution in austenite, compared with the situation without AlN (Fig. 5(c)).

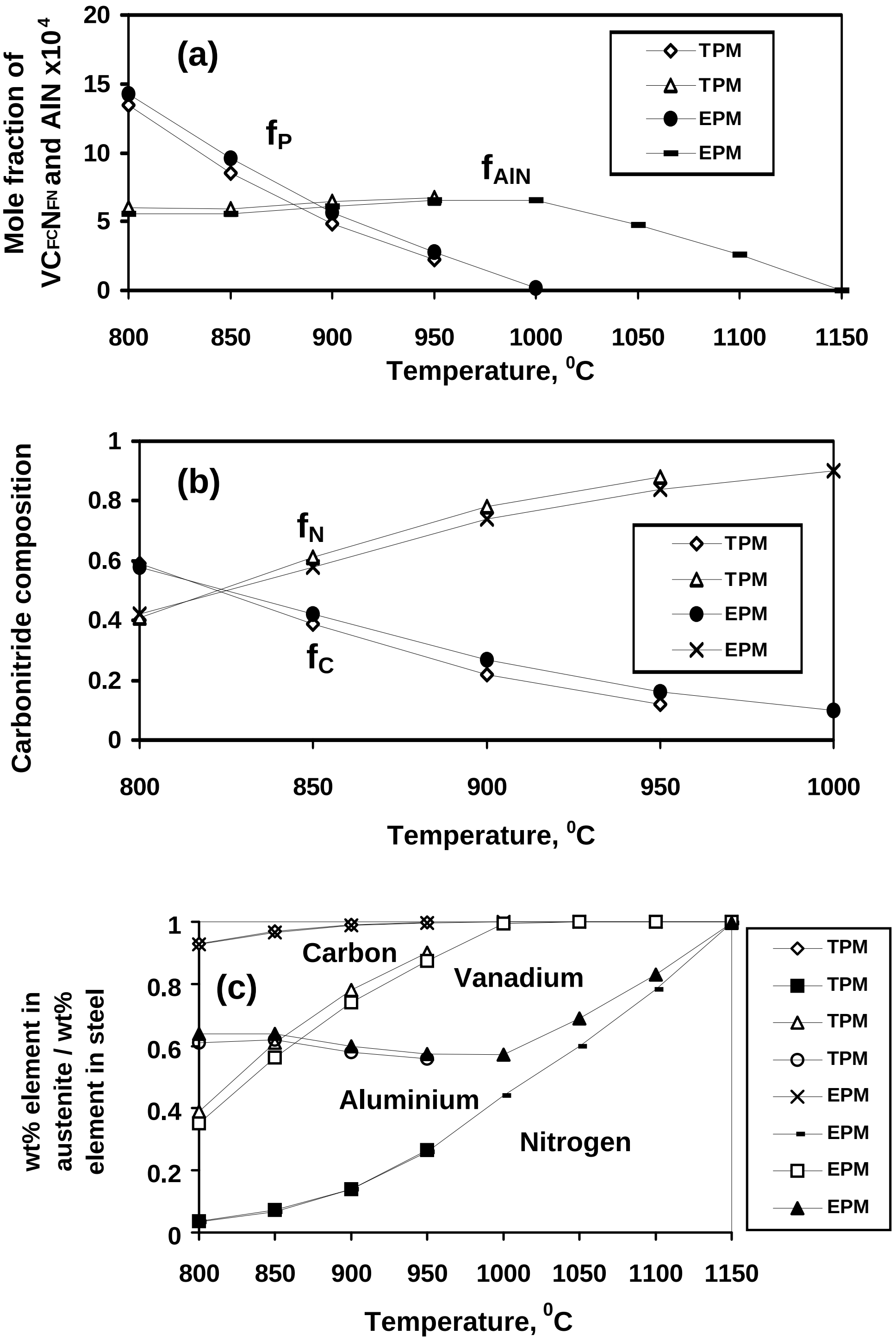


Fig. 4 Comparison of the mole fractions of carbonitride and equilibrium composition of carbonitride and austenite for Steel 2 considering AlN, calculated by the two parameter model (TPM) and the eleven parameter model (EPM).

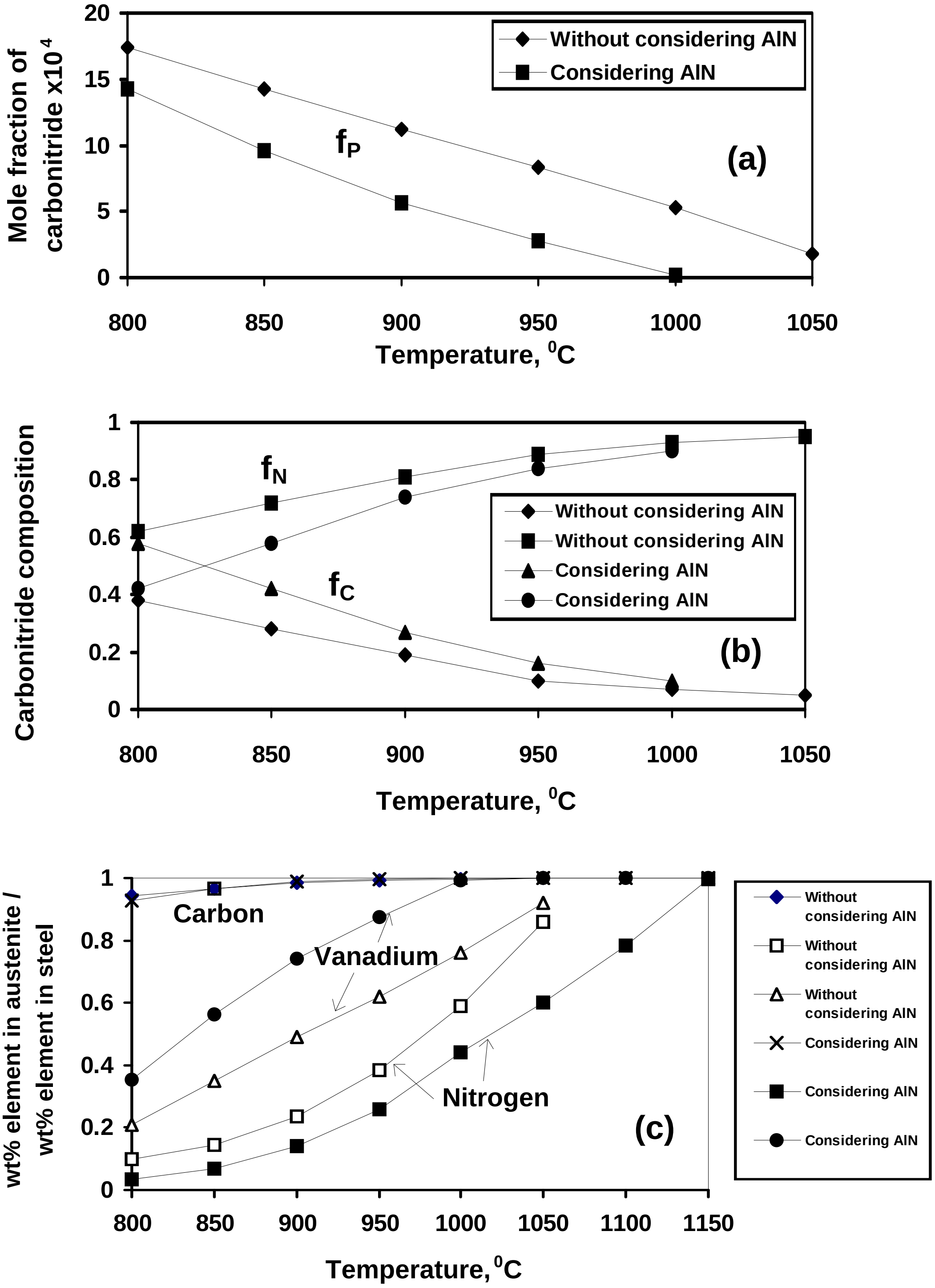
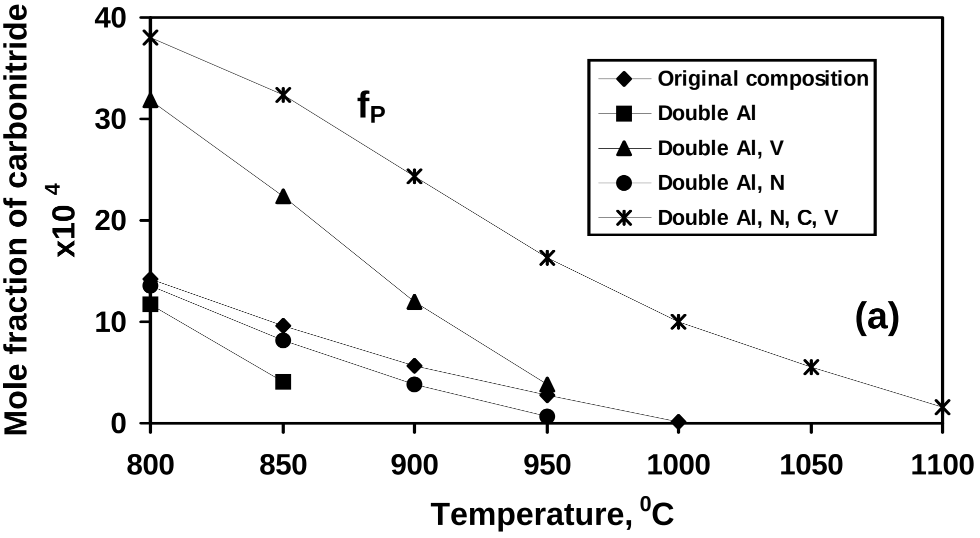


Fig. 5 Comparison of the mole fractions of carbonitride and equilibrium composition of carbonitride and austenite for Steel 2 with and without considering AlN calculated by the eleven parameter model.

It has been noticed that the effect of Al on these equilibrium parameters depends strongly on the chemical composition of the steel.[10,14)] In order to examine this effect, the composition of experimental steels has been deliberately changed to double their contents in Al; Al+V; Al+N and Al+N+C+V; respectively (see **Figs. 6-8**). It is interesting to note that simultaneously increasing Al, N, C, and V has a more significant influence on these equilibrium parameters than changes only in the content of Al; Al and V or Al and N, which extends the temperature range of precipitation (Fig. 6), increases f_P and f_C (Fig. 6(a) and Fig. 7(a)), and decreases f_N and the dissolved nitrogen and vanadium in the austenite (Fig. 7(b) and Fig. 8(b-c)). As expected, the mole fraction of AlN depends more on the amount of Al and N (Fig. 6(b)).

The limitation of the both models is that no kinetic considerations have been taken into account. In general, a primary binding of nitrogen to aluminium is assumed in thermodynamic calculations, the residual nitrogen being available for carbonitride formation. However, depending upon the temperature and the steel composition, aluminium nitride precipitation may be expected to take place concurrently with the carbonitrides.[23)] The two reactions compete for the available nitrogen, and the progress of one reaction is therefore dependent on the progress of the other. According to Kern and Reif [24)] and Emnicke and Billington,[25)] in certain circumstances aluminium nitride begins to form only after vanadium, niobium and titanium



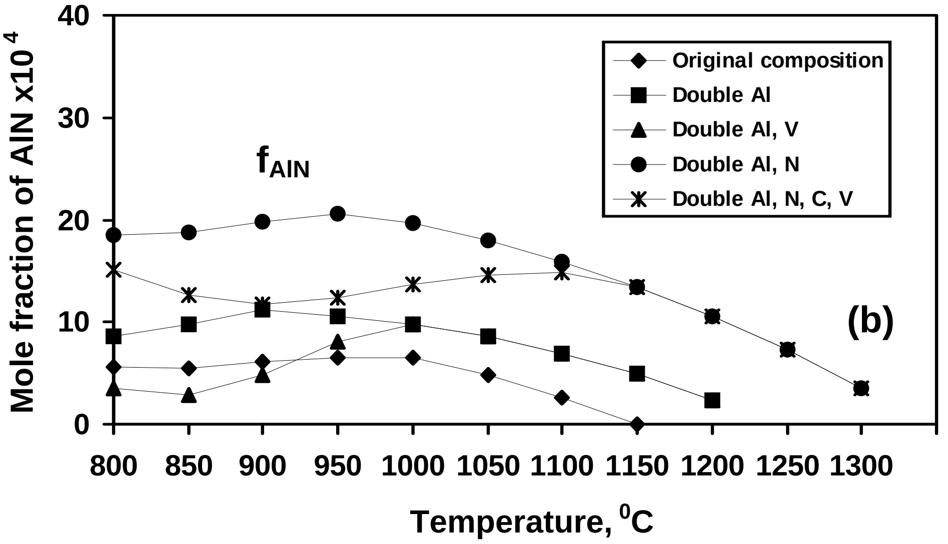


Fig. 6 The influence of composition change in Steel 2 on the mole fractions of carbonitride and AlN when considering AlN calculated by the eleven parameter model.

carbonitrides. The experimental results by Konig *et al.*[26)] indicated that vanadium nitride precipitates much faster from austenite than aluminium nitride. By holding at the precipitation temperature for a longer time, the vanadium nitride which is precipitated first, against the conditions of the equilibrium, decomposes in favour of the formation of aluminium nitride. Speer *et al.*[13)] found good agreement between

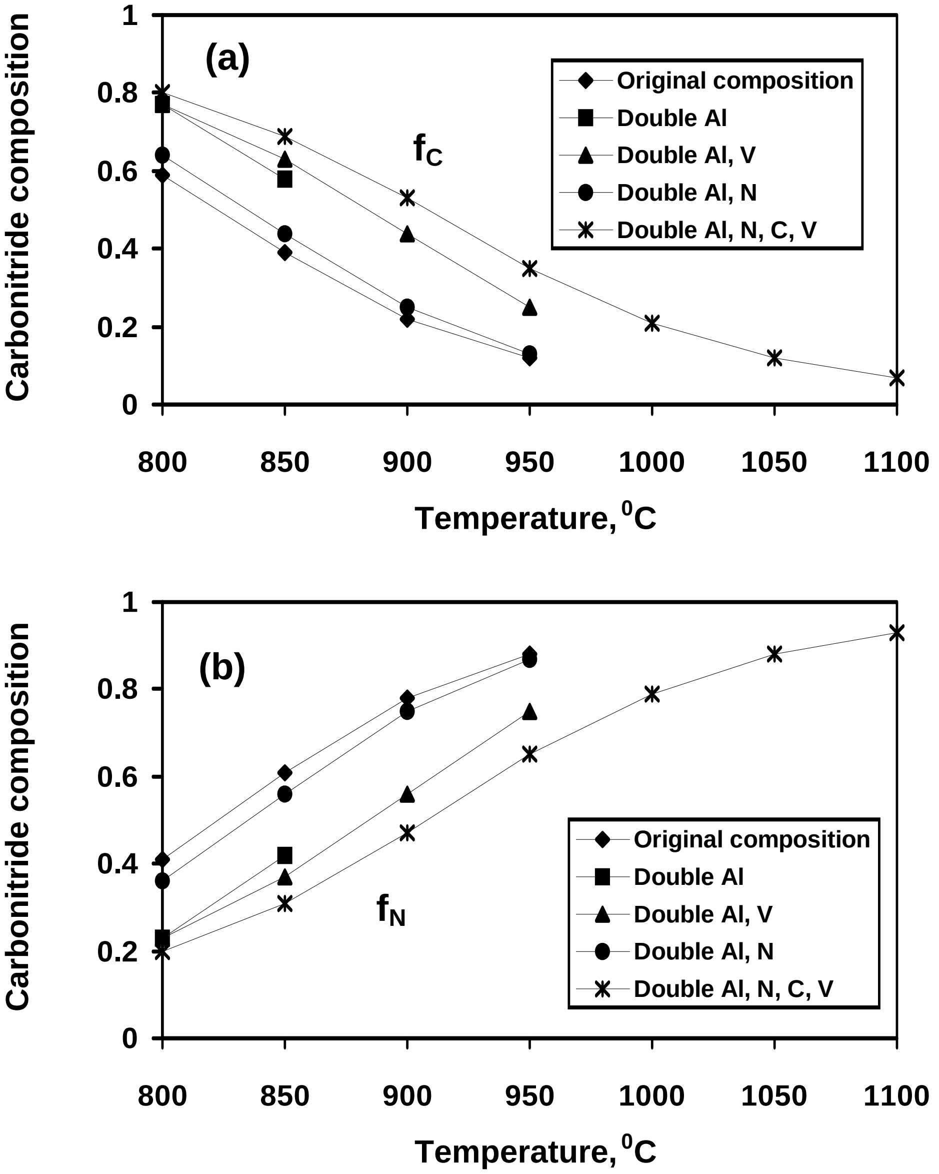


Fig. 7 The influence of composition change in Steel 2 on carbonitride composition when considering AlN calculated by the two parameter model.

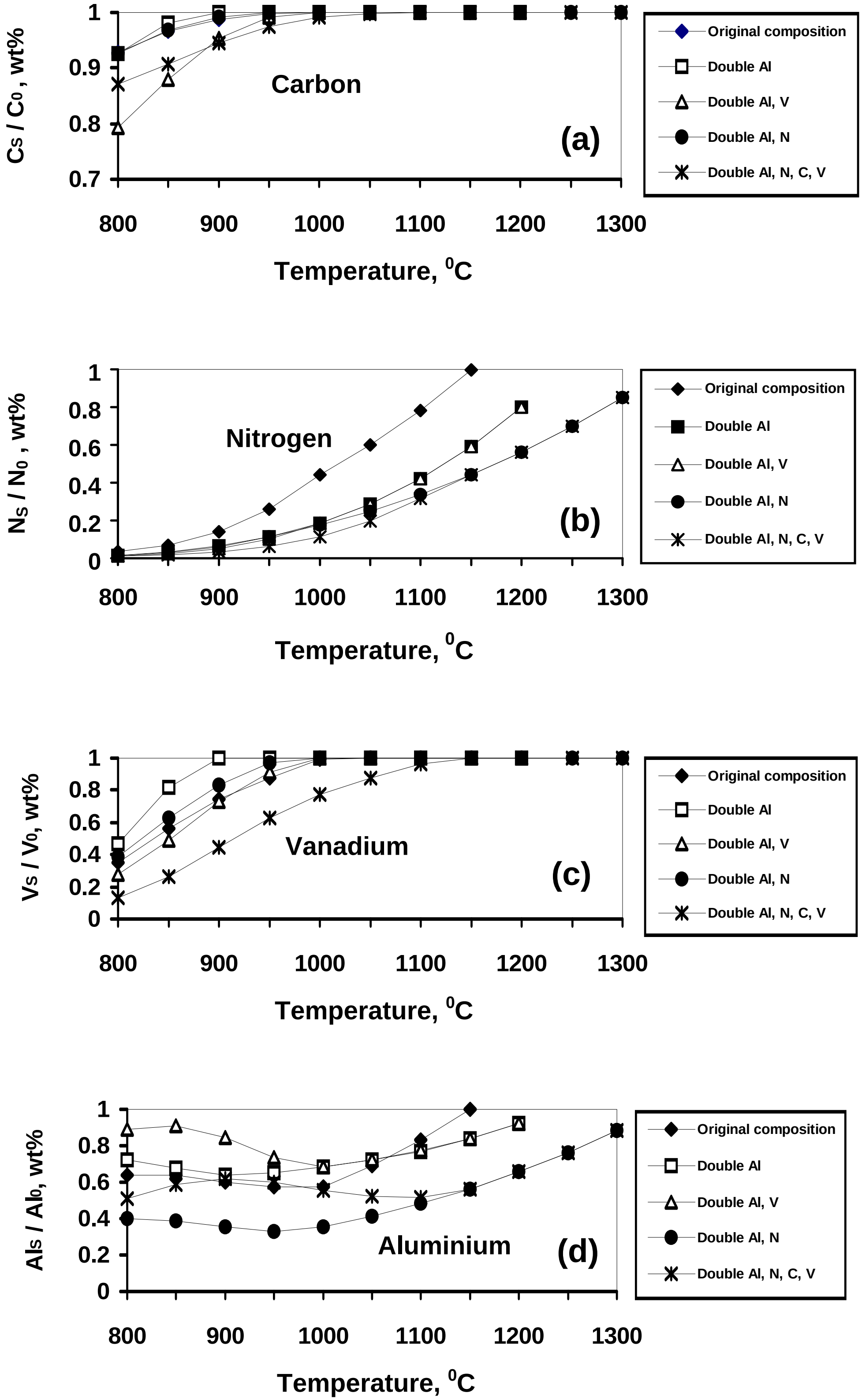


Fig. 8 The influence of composition change in Steel 2 on the austenite composition when considering AlN calculated by the eleven parameter model.

experimental and calculated compositions of the large carbonitrides which formed at the austenite grain boundaries but not with the fine carbonitrides which formed in the matrix. They attributed the different precipitation to kinetics. The above calculations may be expected to hold for the case of reheating prior to rolling, or normalizing.

4. Conclusions

An estimation of the equilibrium compositions of the austenite and carbonitride phases, as well as the mole fraction of each phase in C-Al-V-N microalloyed steels at different austenitising temperatures was made by two thermodynamic models due to Adrian and Rios, with and without considering aluminium in the steels. The following results were obtained.

(1) Both models produce very similar results and can be used to calculate the equilibrium parameters and predict solution temperature of carbonitrides and aluminium nitride for an alloy system contained up to three microalloying elements and aluminium. Compared with the eleven parameter thermodynamic model of Adrian, the advantage of the two parameter thermodynamic model is that it can be easily generalized to account for the presence of any number of separate nitrides and carbides coexisting with NaCl-type carbonitride. However, a further calculation faces difficulty from the two parameter thermodynamic model when a negative value of f_P occurs.

(2) The mole fraction of the carbonitrides f_P and the atomic fraction of carbon in the interstitial lattice of carbonitride f_C decrease, while the atomic fraction of nitrogen in

the carbonitride f_N increases with temperature for all four experimental steels. Most of the carbon remains in solution for the calculated temperature and the proportion of vanadium and nitrogen in solution increases as the temperature increases. The mole fraction of AlN, f_{AlN}, slightly increases up to a certain temperature and then decreases until the precipitates finally go into solution with increasing temperature.

(3) When AlN precipitation is included in the calculations, it is seen that f_P and f_N decrease while f_C increases, and at low temperatures $\left(\sim 1050^\circ C\right)$ in the austenite range, more vanadium and less nitrogen go into solution in austenite, compared the situation when AlN precipitation is neglected.

(4) The effect of aluminium on these equilibrium parameters depends on the chemical composition of the steel. Increasing the contents of Al, N, C, and V simultaneously in the experimental steels has a more significant influence than changing only the contents of Al; Al and V or Al and N separately.

References

1. R. C. Hudd, A. Jones, and M. N. Kale, J. Iron Steel Inst., **209**(1971), 121.
2. D. C. Houghton, G. C. Weatherly, and J. D. Embury, in *'Thermomechanical processing of microalloyed austenite'*, Metall. Soc. AIME, (1981), 267.
3. P. R. Rios, *Mater. Sci. Technol.*, **4**(1988), 324.
4. W. J. Liu and J. J. Jonas, *Metall. Trans. A.*, **20**(1989), 1361.
5. P. R. Rios, *Mater. Sci. Eng.*, **A142**(1991), 87.
6. H. Adrian and F. B. Pickering, *Mater. Sci. Technol.*, **4**(1988), 176.
7. H. Zhou and J. S. Kirkaldy, *Metall. Trans. A.*, **22**(1991), 1511.
8. H. Zhou and J. S. Kirkaldy, *Metall. Trans. A.*, **23**(1992), 651.
9. G. J. Wang and J. Chen, in *'HSLA steels: Processing , Properties and Applications'*, (eds. G. Tither and S. H. Zhang), The Minerals, Metals & Materials Society, Beijing, (1992), 197.
10. H. J. Eckstein, M. Fennert, and J. Ohser, *Steel Research*, **64**(1993), 143.
11. X. Liu, J. K. Solberg, R. Gjengedal, and A. Kluken, *Mater. Sci. Eng.*, **A188**(1994), 247.
12. M. Prikryl, A. Kroupa, G. C. Weatherly, and S. V. Subramanian, *Metall. Trans. A.*, **27**(1996), 1147.
13. J. G. Speer, J. R. Michael, and S. S. Hansen, *Metall. Trans. A.*, **18**(1987), 211.
14. H. Adrian, *Mater. Sci. Technol.*, **8**(1992), 406.
15. P. R. Rios, *Mater. Sci. Eng.*, **A156**(1992), L5.
16. M. Hillert and L. I. Staffansson, *Acta Chem. Scand.*, **24**(1970), 3618.
17. M. Temkin, *Acta Phys. Chim. USSR*, **20**(1945), 411.

18. J. J. More, B. S. Garbow, and K. E. Hillstrom, *User Guide for MINPACK-1*, Argonne National Laboratory, ANL-80-74.
19. N. Gao and T. N. Baker, *Computer Programs for Thermodynamic Analysis*, Research Report, (1996). unpublished work.
20. N. Gao and T. N. Baker, *Characteristics of Microstructures and Precipitation for Microalloyed C-Mn-Al-V-N Steels*, presented in the HSLA Seminar, British Steel, Rotherham, (1995). unpublished work
21. K. Narita, *Transactions, Iron and Steel Institute of Japan*, **15** (1975), 145.
22. W. Roberts and A. Sandberg, *The Compositions of V(CN) as precipitated in HSLA Steels Microalloyed with V*, Swedish Institute for Metals, Research Report Series, IM-1489, (1980).
23. W. C. Leslie, R. L. Rickett, C. L. Dotson, and C. S. Walton, Trans. ASM, **46**(1954), 1470.
24. R. Kern and W. Reif, *Steel Research*, **57**(1986), 331.
25. C. O. I. Emnicke and J. C. Billington, *Mater. Sci. Technol.*, **5**(1989), 450.
26. P. Konig, W. Scholz, and H. Ulmer, *Archs Eisenhutt*, **32**(1961), 541.
27. M. J. D. Powell, in '*Numerical Methods for Nonlinear Algebraic Equations'*, (ed. P. Rabinowitz), Gordon and Breach, (1970).
28. C. E. Froberg, *Numerical Mathematics* - *Theory and Computer Applications*, The Benjamin/Cummings Publishing Company, Inc. (1985).

Appendix

Numerical solution of system of equations (11)-(14) and (20)-(26)

By modification of the Powell hybrid method,$^{27-28)}$ the system of equations in the eleven parameter thermodynamic model is defined as

$$\begin{cases} F_1\left(M_S^{'}, M_S^{''}, M_S^{'''}, C_S, N_S, Al_S, x, v, y, f_P, f_{AlN}\right) = 0 \\ F_2\left(M_S^{'}, M_S^{''}, M_S^{'''}, C_S, N_S, Al_S, x, v, y, f_P, f_{AlN}\right) = 0 \\ \qquad\qquad\qquad\qquad \vdots \\ F_{11}\left(M_S^{'}, M_S^{''}, M_S^{'''}, C_S, N_S, Al_S, x, v, y, f_P, f_{AlN}\right) = 0 \end{cases} \qquad \text{(A1)}$$

It is assumed that the functions are continuous and differentiable, so that there is a matrix of first partial derivatives of the functions, the Jacobian matrix $J_{ij}(X) = \left(\partial F_i / \partial X_j\right)$ evaluated at the point X. Hence

$$J_{ij}(X) = \begin{pmatrix} \frac{\partial F_1}{\partial M_S^{'}}, \frac{\partial F_1}{\partial M_S^{''}}, \frac{\partial F_1}{\partial M_S^{'''}}, \frac{\partial F_1}{\partial C_S}, \frac{\partial F_1}{\partial N_S}, \frac{\partial F_1}{\partial Al_S}, \frac{\partial F_1}{\partial x}, \frac{\partial F_1}{\partial v}, \frac{\partial F_1}{\partial y}, \frac{\partial F_1}{\partial f_P}, \frac{\partial F_1}{\partial f_{AlN}} \\ \frac{\partial F_2}{\partial M_S^{'}}, \frac{\partial F_2}{\partial M_S^{''}}, \frac{\partial F_2}{\partial M_S^{'''}}, \frac{\partial F_2}{\partial C_S}, \frac{\partial F_2}{\partial N_S}, \frac{\partial F_2}{\partial Al_S}, \frac{\partial F_2}{\partial x}, \frac{\partial F_2}{\partial v}, \frac{\partial F_2}{\partial y}, \frac{\partial F_2}{\partial f_P}, \frac{\partial F_2}{\partial f_{AlN}} \\ \vdots \\ \frac{\partial F_{11}}{\partial M_S^{'}}, \frac{\partial F_{11}}{\partial M_S^{''}}, \frac{\partial F_{11}}{\partial M_S^{'''}}, \frac{\partial F_{11}}{\partial C_S}, \frac{\partial F_{11}}{\partial N_S}, \frac{\partial F_{11}}{\partial Al_S}, \frac{\partial F_{11}}{\partial x}, \frac{\partial F_{11}}{\partial v}, \frac{\partial F_{11}}{\partial y}, \frac{\partial F_{11}}{\partial f_P}, \frac{\partial F_{11}}{\partial f_{AlN}} \end{pmatrix}$$

(A2)

where the values of function F_i and its derivatives $\left(\partial F_i / \partial X_j\right)$ are calculated for the point having co-ordinates $M_S^{'}, M_S^{''}, M_S^{'''}, C_S, N_S, Al_S, x, v, y, f_P, f_{AlN}$.