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ON THE THEORY OF CARBONITRIDE NUCLEATION KINETICS IN MICROALLOYED AUSTENITE

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On the base of the critical analysis of existing models of strain induced precipitation of carbonitrides in austenite of microalloyed steels, a new kinetic model is developed. The driving chemical force for nucleation of carbonitrides can be calculated within the framework of Hillert and Staffansson's regular solution theory, which treats carbonitrides as a binary mixture of carbides and nitrides, allowing further analysis of the nucleation kinetics using the formalism of Reiss' binary nucleation theory. The nucleation rate calculated using this approach can differ significantly from the predictions of earlier models that used classical nucleation theory for single-component (unary) systems.

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1. INTRODUCTION

The microalloying elements, such as Nb, Ti, and V, precipitate in austenite as carbides, nitrides, or carbonitrides during thermomechanical processing, and contribute to the mechanical properties of the microalloyed steels via grain refinement, solid solution hardening, and precipitation hardening [1]. It was revealed that carbonitride precipitation in microalloyed austenite takes place through diffusion-controlled nucleation and growth. For this reason, the growth and coarsening mechanisms of carbonitride precipitation have been extensively investigated [2, 3]. By contrast, nucleation, the initial stage of the process, has received much less attention to date, both theoretically and experimentally.

The kinetics of carbonitride precipitation in deformed and undeformed austenite has been studied experimentally by a number of authors (e. g., [4–6]), who have shown that deformation greatly accelerates precipitation. Dutta and Sellars [7, 8] proposed a kinetic model for $\mathrm{Nb(C,N)}$ precipitation based on nucleation theory and empirical analysis of available experimental data, in order to predict the characteristics of strain induced precipitation as a function of the steel composition and thermomechanical processing variables. For this reason, the focus of the nucleation model was on strain effects, taken into account by adjusting the modifying factor of the chemical driving force for homogeneous nucleation in undeformed austenite. However, the calculation of the chemical driving force itself, which is determined by supersaturation of the solid solution, has been simplified basing on classical nucleation theory for single-component systems. In particular, it was assumed that the nitrogen concentration c_N at typical levels in commercial steels simply changes the effective carbon concentration c_C to $(c_\mathrm{C} + 12c_\mathrm{N}/14)$.

This model deficiency was partially overcome by Liu and Jonas [9], who more adequately considered the influence of the $\mathrm{Ti(C,N)}$ nucleus composition on the chemical driving force. However, their analysis was based on the additional simplifying assumption that the composition of nuclei is close to equilibrium values at the temperature of their formation. In turn, this equilibrium composition was determined from a simplified thermodynamic model based on the ideal solution approximation, considering carbonitrides as an ideal mixture of carbides and nitrides.

The first simplification of the model [9] was overcome by Maugis and Gouné [10], who calculated the composition of $\mathrm{V(C,N)}$ nuclei in the critical point of the phase transformation and correspondingly modified the chemical driving force for homogeneous nucleation. However, similar to [9], this was done in the

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ideal solution approximation for carbonitrides. Besides, the pre-exponential kinetic factor of the nucleation rate was taken from classical nucleation theory for single-component systems (also similar to previous models), whereas the number of nucleation sites was chosen equal to the number of substitutional sites per volume in austenite matrix, which can lead to overestimation of homogeneous nucleation rate by many orders of magnitude (as discussed below in Section 3).

A more comprehensive analysis of the equilibrium composition for complex carbonitrides $(\mathrm{Ti},\mathrm{Nb})(\mathrm{C},\mathrm{N})$ in undeformed austenite was presented by Zou and Kirkaldy [11], who used Hillert and Staffansson's regular solution theory [12] (instead of the ideal solution models discussed above) for evaluation of the chemical driving force for nucleation. However, the nucleation kinetics (as well as the critical nucleus composition) was not considered, assuming that all nuclei are formed immediately after quenching and are uniformly distributed.

In order to calculate the homogeneous nucleation rate of simple carbonitrides $\mathrm{M}(\mathrm{C},\mathrm{N})$ with $\mathrm{M} \equiv \mathrm{V}$, Ti or Nb in undeformed austenite (as was observed, e. g., during the isothermal precipitation of Nb(C,N) in experiments [5]), this work proposes a new kinetic model based on the Reiss theory for homogeneous nucleation in two-component (binary) systems [13]. The driving chemical force for nucleation of simple carbonitrides can be calculated within the framework of Hillert and Staffansson's regular solution theory (as shown in Section 2), which treats carbonitrides as a binary mixture of carbides and nitrides, allowing further analysis of the nucleation kinetics (presented in Section 4) using the formalism of Reiss' binary nucleation theory (outlined in Section 3). In order to take into account strain effects in the case of deformed austenite, this driving force can be modified, following [7], by the adjusting factor (as discussed above), or, alternatively, by adjusting the modifying factor for supersaturation (as discussed in Section 2).

The developed approach of the binary nucleation theory can be extended to mixed carbides, $(\mathrm{M},\mathrm{M}')\mathrm{C}$, or nitrides, $(\mathrm{M},\mathrm{M}')\mathrm{N}$, in microalloyed steels (e. g., $(\mathrm{V},\mathrm{Ti})\mathrm{C}$ observed in [14]), whereas the most general case of complex carbonitrides, (M,M')(C,N), can be analysed within the framework of Langer's nucleation theory [15], generalizing Reiss' binary theory to multicomponent systems. These future developments of the present model will be briefly discussed in the final part of this work (Section 4.1).

2. MODEL FORMULATION

As explained, e. g., in [2, 3], the carbides and nitrides of microalloying elements M (niobium, titanium, or vanadium) have fcc crystal structures and similar lattice parameters; for this reason, they show complete mutual solid solubility, and thus can be considered as a mixture of MC and MN molecules (or 'monomers' of the pure carbide and nitride phases) with perfect stoichiometry (usually assumed for simplicity). Correspondingly, the Gibbs free energy of $\mathrm{M}(\mathrm{C},\mathrm{N})$ nucleus formation takes the form

$$\Delta G_0(n_a, n_b) = \\ = n_a(\mu_a^{(p)} - \mu_a^{(\gamma)}) + n_b(\mu_b^{(p)} - \mu_b^{(\gamma)}) + 4\pi R^2\sigma, \quad (1)$$

where n_i, $i = a, b$, are the numbers of MN and MC monomers, respectively, in the spherical nucleus of radius

$$R = (3/4\pi)^{1/3}\,(n_a v_a + n_b v_b)^{1/3}$$

with molecular volumes of the components v_i; $\mu_i^{(p)}$ and $\mu_i^{(\gamma)}$ are the chemical potentials of monomers in the carbonitride particle and in the fcc (γ) steel matrix, respectively; σ is the surface tension of the particle (nucleus). Taking into account close values of molar volumes of MC and MN molecules (which in the case of the vanadium carbonitride, $\mathrm{M} \equiv \mathrm{V}$, are $10.8\,\mathrm{cm}^3/\mathrm{mol}$ and $10.5\,\mathrm{cm}^3/\mathrm{mol}$, respectively), it will further be assumed for simplicity

$$v_a \approx v_b \equiv v \approx 1.8 \cdot 10^{-29}\,\mathrm{m}^3,$$

and thus

$$R \approx (3v/4\pi)^{1/3}(n_a + n_b)^{1/3}.$$

In accordance with Hillert and Staffansson's regular solution theory [12], the Gibbs free energy of mixing of carbides and nitrides in the carbonitride phase takes the form

$$G_{mix}\,(n_a, n_b) = n_a\mu_a^{(0)} + n_b\mu_b^{(0)} + kTS_{ab} + G_{ab}, \quad (2)$$

where $\mu_i^{(0)}$ is the chemical potentials of pure nitride and carbide phases, respectively; S_{ab} is the entropy of mixing given by the equation proposed by Temkin [16],

$$S_{ab} = n_a \ln\frac{n_a}{n_a + n_b} + n_b \ln\frac{n_b}{n_a + n_b}, \quad (3)$$

and G_{ab} is the excess molar free energy of mixing, which in an ordinary multicomponent system is often represented by a power series, and in the regular solution model is given by the second power term

$$G_{ab} = L_{ab}\frac{n_a n_b}{n_a + n_b} \quad (4)$$

with the regular solution parameter L_{ab}. This approximation, Eq. (4), becomes well-grounded in the case when the concentration of one of the components (say, b) in the particle is small,

$$x_b \equiv n_b/(n_a+n_b) \ll 1,$$

which is well satisfied, e. g., in the case of V(C, N) and Ti(C, N) nuclei (see below), and, in fact, corresponds to the weak solution model (with a linear dependence $G_{ab} \approx L_{ab}n_b$). Therefore,

$$\mu_a^{(p)} = \frac{\partial G_{mix}(n_a,n_b)}{\partial n_a} = \\ = \mu_a^{(0)} + kT\ln\frac{n_a}{n_a+n_b} + L_{ab}\left(\frac{n_b}{n_a+n_b}\right)^2, \quad (5)$$

$$\mu_b^{(p)} = \frac{\partial G_{mix}(n_a,n_b)}{\partial n_b} = \\ = \mu_b^{(0)} + kT\ln\frac{n_b}{n_a+n_b} + L_{ab}\left(\frac{n_a}{n_a+n_b}\right)^2. \quad (6)$$

The atomic concentrations c_j of alloying elements, j = M, C, N, in the γ phase (austenite) are so small that the chemical potential of these elements can be written in the ideal solution approximation,

$$\mu_j^{(\gamma)} = \mu_j^{(0)} + kT\ln c_j \quad (7)$$

and therefore, the chemical potentials of nitride and carbide molecules in the matrix, subject to the equilibrium conditions MN $\leftrightarrow$ M+N and MC $\leftrightarrow$ M+C, are equal to

$$\mu_a^{(\gamma)} \equiv \mu_{\rm MN}^{(\gamma)} = \mu_{\rm M}^{(\gamma)} + \mu_{\rm N}^{(\gamma)} = \\ = \mu_{\rm M}^{(0)} + \mu_{\rm N}^{(0)} + kT\ln(c_{\rm M}c_{\rm N}), \quad (8)$$

$$\mu_b^{(\gamma)} \equiv \mu_{\rm MC}^{(\gamma)} = \mu_{\rm M}^{(\gamma)} + \mu_{\rm C}^{(\gamma)} = \\ = \mu_{\rm M}^{(0)} + \mu_{\rm C}^{(0)} + kT\ln(c_{\rm M}c_{\rm C}), \quad (9)$$

whereas chemical potentials of pure nitride and carbide phases are calculated, respectively, as

$$\mu_a^0 = \mu_{\rm M}^{(0)} + \mu_{\rm N}^{(0)} + kT\ln(c_{\rm M}^*c_{\rm N}^*) = \\ = \mu_{\rm M}^{(0)} + \mu_{\rm N}^{(0)} + kT\ln K_a, \quad (10)$$

where $c_{\rm M}^*$ and $c_{\rm N}^*$ are saturation concentrations of M and N in austenite in equilibrium with pure nitride, $K_a = c_{\rm M}^*c_{\rm N}^*$ is the solubility product of nitride, and

$$\mu_b^0 = \mu_{\rm M}^{(0)} + \mu_{\rm C}^{(0)} + kT\ln(c_{\rm M}^{**}c_{\rm C}^{**}) = \\ = \mu_{\rm M}^{(0)} + \mu_{\rm C}^{(0)} + kT\ln K_b, \quad (11)$$

where $c_{\rm M}^{**}$ and $c_{\rm C}^{**}$ are saturation concentrations of M and N in austenite in equilibrium with pure carbide, $K_a = c_{\rm M}^{**}c_{\rm C}^{**}$ is the solubility product of carbide.

Therefore,

$$\mu_a^{(p)} - \mu_a^{(\gamma)} = kT\ln K_a + kT\ln\frac{n_a}{n_a+n_b} + \\ + L_{ab}\left(\frac{n_b}{n_a+n_b}\right)^2 - kT\ln\left(c_{\rm M}c_{\rm N}\right), \quad (12)$$

$$\mu_b^{(p)} - \mu_b^{(\gamma)} = kT\ln K_b + kT\ln\frac{n_b}{n_a+n_b} + \\ + L_{ab}\left(\frac{n_a}{n_a+n_b}\right)^2 - kT\ln\left(c_{\rm M}c_{\rm C}\right), \quad (13)$$

which, after substituting into Eq. (1), gives

$$\Delta G_0\left(n_a,n_b\right) = n_a\left[-kT\ln S_a + \right. \\ \left. + kT\ln\frac{n_a}{n_a+n_b} + L_{ab}\left(\frac{n_b}{n_a+n_b}\right)^2\right] + \\ + n_b\left[-kT\ln S_b + kT\ln\frac{n_b}{n_a+n_b} + L_{ab}\left(\frac{n_a}{n_a+n_b}\right)^2\right] + \\ + 4\pi\sigma\left(\frac{3v}{4\pi}\right)^{2/3}\left(n_a+n_b\right)^{2/3}, \quad (14)$$

where

$$S_a \equiv c_{\rm M}c_{\rm N}/K_a = c_{\rm M}c_{\rm N}/{}^*_{\rm M}c^*_{\rm N}$$

and

$$S_b \equiv c_{\rm M}c_{\rm C}/K_b = c_{\rm M}c_{\rm C}/c_{\rm M}^{**}c_{\rm C}^{**}$$

are supersaturations.

The morphology and crystallography of carbide precipitates in austenite steel were studied by transmission electron microscope (TEM) observation [17, 18], where it was shown that VC particles, precipitated preferentially on dislocations in the austenite matrix during aging at 1173 K, display a cube-on-cube orientation with austenite. The interface between the matrix and nucleated particles is initially coherent, but becomes partly coherent during growth. Previously, TEM images of coherence strain field associated with vanadium carbide disc and spherical particles were observed by Baker [19], who noted that the limited number of observations of coherent precipitates in austenite was due to the very small size at which they lose coherence [20].

TEM observations in the tests on precipitation of NbC in austenite [21] also showed that fine particles (of the mean size ~ 5 nm) formed during the initial time of post-deformation holding of 10 s at 1200 K were coherent with the austenite matrix. The coherency was lost after holding time of 30 s, when the mean size increased to ~ 8 nm, displaying an increasing number of misfit dislocations, in accordance with the general understanding of nucleation in solids (cf. [22]). Since carbides, nitrides and carbonitrides of microalloying elements Ti, Nb or V have similar to NbC fcc crystal structures and lattice parameters, the same conclusion can be generalized to the nucleation of all these phases (as also confirmed in [1]).

For a slightly oversized coherent spherical inclusion with volume $V_p = (n_a + n_b)\, v$, which is inserted in the spherical cavity with volume V_m in the (unstrained) matrix with the atomic volume $v_m \approx 1.23 \cdot 10^{-29}$ m^3, the misfit strain δ is determined by the relation

$$(V_p - V_m)/V_p = (v - v_m)/v \approx 3\delta,$$

which for vanadium carbonitrides with $v \approx 1.8 \cdot 10^{-29}$ m^3 (see above) is $\delta \approx 0.1 \ll 1$.

If the matrix and the precipitate are elastically identical (which is not the case for carbonitrides in steel), the elastic strain energy associated with such inclusion is determined by the misfit strain as

$$\Delta G_{el} = 2\mu \left(\frac{1+\nu}{1-\nu}\right) \delta^2 V_p = 2\mu \left(\frac{1+\nu}{1-\nu}\right) \delta^2 v\, (n_a + n_b),$$

where μ is the shear modulus, and ν is Poisson's ratio, whereas for carbonitrides, which are stiffer than the matrix, the elastic strain energy will somewhat increase (cf. [23]). This energy contributes to the formation free energy, Eq. (14), and, being proportional to $(n_a + n_b)$, effectively modify supersaturations,

$$S_{a,b} \to \widetilde{S}_{a,b} = S_{a,b} \exp\left[-2\mu \left(\frac{1+\nu}{1-\nu}\right) \delta^2 v / kT\right].$$

Consequently, elastic strains can significantly reduce or even completely suppress carbonitride nucleation, in agreement with experimental observations that nucleation in undeformed austenite becomes extremely difficult [1–3].

However, in deformed austenite, the elastic strain contribution can be reduced, if an oversized precipitate nucleates on the dilatation side of an edge dislocation, as follows from the Dollins – Barnett theory [24, 25]. Therefore, in the simplest approach, strain effects can be taken into account by adjusting the modifying factor $\lambda < 1$ for supersaturations, $S_{a,b} \to \widetilde{S}_{a,b} = \lambda S_{a,b}$ (along with changing the density of nucleation sites, see Section 3.1 below), and for this reason, only homogeneous nucleation (without strain effects) will be analysed further (with comments and corrections for the more realistic case where necessary). In fact, this approach is an alternative to the approach used in [7] (which, however, assumed incoherent nucleation), where strain effects (from dislocations) were taken into account by adjusting the modifying factor of the chemical driving force for homogeneous nucleation.

The critical nucleus (n_a^*, n_b^*) is determined by minimization of Eq. (14) with respect to the two variables,

$$\frac{\partial \Delta G_0 (n_a^*, n_b^*)}{\partial n_a} = \frac{\partial \Delta G_0 (n_a^*, n_b^*)}{\partial n_b} = 0,$$

which leads to the expressions

$$-kT \ln S_a + kT \ln \frac{n_a^*}{n_a^* + n_b^*} + \\ + L_{ab} \left(\frac{n_b^*}{n_a^* + n_b^*}\right)^2 + \frac{2\sigma v}{R^*} = 0, \quad (15)$$

and

$$-kT \ln S_b + kT \ln \frac{n_b^*}{n_a^* + n_b^*} + \\ + L_{ab} \left(\frac{n_a^*}{n_a^* + n_b^*}\right)^2 + \frac{2\sigma v}{R^*} = 0. \quad (16)$$

Superposition of Eqs (15) and (16) gives

$$kT \ln \left(\frac{S_b}{S_a}\right) + kT \ln \frac{n_a^*}{n_b^*} - L_{ab} \left(\frac{n_a^* - n_b^*}{n_a^* + n_b^*}\right) = 0, \quad (17)$$

which under the condition $n_b^* \ll n_a^*$, justifying Eq. (4), takes the form

$$\ln \frac{n_b^*}{n_a^*} \approx -\frac{L_{ab}}{kT} - \ln \left(\frac{S_a}{S_b}\right), \quad (18)$$

or

$$\alpha \equiv \frac{n_b^*}{n_a^*} \approx \frac{S_b}{S_a} \exp\left(-\frac{L_{ab}}{kT}\right) = \frac{K_a c_{\mathrm{C}}}{K_b c_{\mathrm{N}}} \exp\left(-\frac{L_{ab}}{kT}\right). \quad (19)$$

Substituting Eq. (19) into Eq. (15), we obtain for the critical nucleus size to the first approximation in $\alpha \ll 1$,

$$n_a^* + n_b^* \approx \frac{\sigma^3 v^2}{(kT)^3} \frac{32\pi}{3 (\ln S_a + \alpha)}, \quad (20)$$

or

$$R^* \approx \frac{2\sigma v}{kT (\ln S_a + \alpha)}. \quad (21)$$

After substituting Eqs (19) and (20) into Eq. (14), the chemical free energy of the critical nucleus formation can be calculated as

$$\frac{1}{kT} \Delta G_0 (n_a^*, n_b^*) \approx \frac{16\pi}{3} \frac{\sigma^3 v^2}{(kT)^3 (\ln S_a + \alpha)^2}. \quad (22)$$

In Eqs. (20)–(22), it was additionally assumed that supersaturation S_a does not approach too close to its critical value (determined by the pole of Eq. (20)), i. e.,

$$|\ln S_a + \alpha| \gg \alpha^2 L_{ab}/kT,$$

and for this reason, the term proportional to α^2, arising in the next order approximation in Eq. (17), can be neglected in the denominator.

In this case, the critical supersaturation S_a^* is characterized by a small negative value of $\ln S_a^* \approx -\alpha$. Correspondingly, the nucleation occurs at

$$S_a \geq S_a^* \approx \exp(-\alpha) < 1,$$

i. e., the onset of nucleation is shifted to the undersaturated solution of nitride monomers.

The regular solution parameter $L_{ab} = -4260$ J/mol was determined for C–N mixing in Ti carbonitrides [26, 27]. Commonly (e. g., in [11, 28]) the assumption is used that the C–N mixing should be approximately the same in different carbonitrides, due to the general similarity of the systems.

The solubility products for pure VC and VN precipitation are taken also from [27], where ‘best fit’ relationships were obtained using the data of several investigators,

$$\lg K_a = 3.02 - 7840/T[\mathrm{K}], \quad \lg K_b = 6.72 - 9500/T[\mathrm{\ K}]$$

(where concentrations C_i in the solubility products are in wt%). For typical V microalloyed steel composition,

$$C_{\mathrm{V}} = 0.215\,\mathrm{wt}\,\%,\ C_{\mathrm{C}} = 0.19\,\mathrm{wt}\,\%,\ C_{\mathrm{N}} = 0.015\,\mathrm{wt}\,\%$$

(e. g., used in calculations [10]) at $T = 1200$ K one obtains

$$L_{ab}/kT \approx 0.43,\ K_a \approx 3.2 \cdot 10^{-4},\ K_b \approx 6.3 \cdot 10^{-2},$$

$$S_a \approx 10, \quad S_b \approx 0.65,$$

giving

$$S_b/S_a \approx 0.065,$$

which does not depend on the modifying factor λ for $S_{a,b}$ (and thus is the same for nuclei in deformed and undeformed matrix).

Substitution of these values into Eq. (19) leads to $\alpha \approx 0.041$ (regardless of the deformation state of austenite), which self-consistently confirms the above assumption $n_b^*/n_a^* \approx \alpha \ll 1$, and thus gives for the composition z of the critical nucleus, $\mathrm{V}\,(\mathrm{C}_z\mathrm{N}_{1-z})$, small value,

$$z = x_b^* = n_b^*/\big(n_a^* + n_b^*\big) = \alpha/(1+\alpha) \approx 0.04.$$

This value is notably smaller than the value ≈ 0.1 calculated in [10] for the same system, but considered in the ideal solution approximation, assuming $L_{ab} = 0$.

For $\mathrm{Ti(C,N)}$ in austenite with

$$C_{\mathrm{Ti}} = 0.215\,\mathrm{wt}\,\%,\ C_{\mathrm{C}} = 0.1\,\mathrm{wt}\,\%,\ C_{\mathrm{N}} = 0.01\,\mathrm{wt}\,\%$$

and

$$\lg K_a = 3.82 - 15020/T, \quad \lg K_b = 5.3 - 10475/T$$

(from [2,3]) at $T = 1200$ K one obtains

$$K_a \approx 1.2 \cdot 10^{-9}, \quad K_b \approx 3.7 \cdot 10^{-4},$$

$$S_a \approx 1.8 \cdot 10^{6}, \quad S_b \approx 58,$$

giving

$$S_b/S_a \approx 3 \cdot 10^{-5},$$

and the parameter α turns to be extremely small, $\alpha \approx 1.3 \cdot 10^{-5}$ (and thus $x_b^* \approx 1.3 \cdot 10^{-5}$), which means that the composition of nucleated carbonitrides practically coincides with that of pure nitrides. Correspondingly, it might be expected that the nucleation kinetic of $\mathrm{Ti(C,N)}$ precipitates is close to that of pure nitrides (as will be confirmed below in Section 4).

For $\mathrm{Nb(C,N)}$ in austenite with

$$C_{\mathrm{C}}/C_{\mathrm{N}} \approx 10,$$

$$\lg K_a = 2.8 - 8500/T, \quad \lg K_b = 3.42 - 7900/T$$

(from [2,3]), the parameter α is not very small, $\alpha \approx 0.73$ (and thus $x_b^* \approx 0.42$), which makes the above results, Eqs. (19)–(22), obtained assuming $\alpha \ll 1$, only qualitatively correct. For this reason, the nucleation of $\mathrm{Nb(C,N)}$ will not be considered further.

It should be noted that the composition of the critical $\mathrm{V(C,N)}$ nucleus markedly differs from the equilibrium composition calculated in [29] (with the same values of the model parameters K_a, K_b and L_{ab}). For instance, for 900° C, used in calculations [29], the equilibrium composition of vanadium carbonitrides in austenite with $C_{\mathrm{V}} = 0.2$ wt%, $C_{\mathrm{C}} = 0.1$ wt%, $C_{\mathrm{N}} = 0.01$ wt% was calculated as $x_b^{(eq)} = 0.39$, whereas the composition of the critical nucleus can be evaluated from Eq. (19) as $x_b^* = 0.06$. This means that the particle composition substantially changes during the growth and coarsening stages of the precipitation process, which, in particular, contradicts the assumption of the models [9, 11] that the composition of nuclei is close to equilibrium values at the temperature of their formation.

3. BINARY NUCLEATION THEORY

The problem of nucleation of carbonitrides, which can be considered as a mixture of MC and MN monomers, is an example of homogeneous nucleation in binary systems. However, the classical nucleation theory [30–32] was developed in relation to single-component (unary) systems, and for this reason, is valid only for pure carbides MC or nitrides MN.

The classical nucleation theory was generalized to binary systems by Reiss [13]. In his theory, the parent phase is thought of as a mixture of molecules (monomers) of two components X and Y with number densities N_x and N_y, respectively, together with clusters of all sizes and compositions. A particular molecular cluster is characterized by the numbers of single molecules (or monomers) x and y of species X and Y, respectively, that it contains. Reiss showed that the critical point of unstable equilibrium (associated with the phase transition) corresponds in this case to a saddle point (x^*, y^*) on the free energy surface $\Delta G_0(x, y)$. He characterized the transition by a two-dimensional steady state flow $\mathbf{J}(x, y)$ of clusters in the phase space of cluster sizes x, y, which is pronounced in one direction (the axis of the pass x') that, in comparison with it, any lateral flow (in the perpendicular direction y') may be neglected, i. e., $J_{y'} \approx 0$. Due to the steady state condition,

$$\operatorname{div} \mathbf{J} = \partial J_{x'}/\partial x' + \partial J_{y'}/\partial y' \approx \partial J_{x'}/\partial x' = 0,$$

this leads to

$$J_{x'} \approx J(y'),$$

which was calculated by Reiss as

$$J\left(y' - y^*\right) = f_0\left(x^*, y^*\right) \frac{\beta_x^* \beta_y^* \left(1 + \tan^2\theta\right)}{\beta_y^* + \beta_x^* \tan^2\theta} \times \\ \times \left(\frac{|D'_{11}|}{\pi k T}\right)^{1/2} \exp\left[-\frac{|\det \mathbf{D}| \left(y' - y^*\right)^2}{kT\,|D'_{11}|}\right], \quad (23)$$

where $f_0(x, y)$ is the equilibrium size distribution function

$$f_0(x, y) = F \exp\left[-\frac{\Delta G_0(x, y)}{kT}\right], \quad (24)$$

F is the so called number density of potential nucleation sites discussed below in Section 3.1; θ is the angle between the original axis x and the axis of the pass x'; $\beta_i^* = \beta_i\left(x^*, y^*\right)$, $i = x, y$, are the arrival rates of monomers X and Y to the critical cluster (x^*, y^*) of radius R^*;

$$D_{ij} = (1/2)\,\partial^2 \Delta G_0\left(x^*, y^*\right)/\partial x_i \partial x_j$$

are elements of the matrix $\mathbf{D} = (D_{ij})$, which determinant is negative (in accordance with the properties of the saddle point),

$$\det \mathbf{D} = D_{11} D_{22} - D_{12}^2 < 0;$$

$$D'_{11} = \frac{1}{2} \left.\frac{\partial^2 \Delta G_0\left(x', y'\right)}{\partial x'^2}\right|_{x^*, y^*} = \\ = D_{11}\cos^2\theta + D_{22}\sin^2\theta + 2D_{12}\sin\theta\cos\theta, \quad (25)$$

is the second derivative of ΔG_0 at the critical point in the direction x' of the orthogonal coordinate system (x', y') obtained by rotating the original coordinate system (x, y) through the angle θ; this derivative should be negative, $D'_{11} < 0$, to provide a maximum of the free energy at the critical point in the direction of the x'-axis.

Therefore, the nucleation rate, defined as the total flux of clusters through the critical zone,

$$\dot{N} = \int_{-\infty}^{\infty} J\left(y' - y^*\right) dy', \quad (26)$$

was calculated by Reiss by substituting Eq. (23) into Eq. (26) as

$$\dot{N} \approx -f_0\left(x^*, y^*\right) \frac{\beta_x^* \beta_y^* \left(1 + \tan^2\theta\right)}{\beta_y^* + \beta_x^* \tan^2\theta} \times \\ \times D'_{11} \left(\frac{1}{D_{12}^2 - D_{11} D_{22}}\right)^{1/2}. \quad (27)$$

In the Reiss theory, the axis of the pass x' runs in the direction of the steepest descent of the free energy surface $\Delta G_0(x, y)$, which for this reason was determined in the thermodynamic approach (i. e., solely from the properties of the free energy). This assumption was modified by Langer [15] (with subsequent reiteration by Stauffer [33]), who corrected the orientation of the flux vector in the direction parallel to the direction of the unstable mode at the saddle point (the new axis of the pass x'). The modified value of θ was explicitly calculated in [33] and later refined in [34] as

$$\tan\theta = s + \left(r + s^2\right)^{1/2}, \text{ if } D_{21} < 0, \quad (28)$$

and

$$\tan\theta = s - \left(r + s^2\right)^{1/2}, \text{ if } D_{21} > 0, \quad (29)$$

where

$$r = \beta_y^*/\beta_x^*, \quad s = (d_x - r d_y)/2,$$

$$d_x = -D_{11}/D_{12}, \quad d_y = -D_{22}/D_{12}.$$

As explained in [2, 3], measurements of diffusion coefficients in austenite show that in the temperature range of interest, diffusion of carbon and nitrogen is 5–7 orders of magnitude faster than diffusion of microallying elements M. Thus, the arrival rates in Eq. (23) are controlled by the transport of elements M,

$$\beta^*_{a,b} = 4\pi D_{\mathrm{M}} c_{\mathrm{M}} R^* \Omega^{-1}, \qquad (30)$$

where Ω, c_{M} and D_{M} are atomic volume, atomic concentration and diffusivity, respectively, of element M in austenite, and for this reason,

$$r = \frac{\beta^*_y}{\beta^*_x} = 1. \qquad (31)$$

3.1. Number density of potential nucleation sites F

In the Reiss theory, given the total number density N_{xy} of spherical clusters $\mathrm{X}_x\mathrm{Y}_y$ consisting of (x, y) monomers is small compared to the number densities N_x, N_y of single molecules (monomers) X and Y in the parent phase (consisting of molecules X and Y), $N_{xy} \ll N_x, N_y$, the pre-exponential factor F of the equilibrium size distribution function in Eq. (24) takes the form

$$F = N_x + N_y. \qquad (32)$$

This approach was a generalization of the Frenkel model [35], which characterizes the size distribution of clusters X_x in a single-component solid solution of molecules X in the matrix Y with the number density of nucleation sites $F = N_x$.

The extension of Eq. (32) to the lattice gas with $N_x, N_y \ll N_0$, where $N_0 = \Omega^{-1}$ is the number density of lattice sites for monomers in the parent phase (i. e., in the presence of high concentration of vacant sites, $N_v \equiv N_0 - N_x - N_y \approx N_0$), gives

$$F = N_0 \left(c_x + c_y\right) = \Omega^{-1} \left(c_x + c_y\right), \qquad (33)$$

where $c_x = N_x/N_0 \ll 1$ and $c_y = N_y/N_0 \ll 1$ are concentrations of monomers in the matrix.

This expression, Eq. (33), was widely criticized in the literature. In particular, Lothe and Pound [36] suggested that degrees of freedom corresponding to the translation of clusters have been neglected in this expression. As a result, they predicted that the number density of potential nucleation centres F is equal to the number density of lattice sites N_0, rather than the total number density of solute monomers, Eq. (32), leading to a large discrepancy with the previous approach. A similar conclusion was made in a large number of subsequent works, reviewed and supported in [37].

This disagreement (‘translation paradox’) was discussed by Reiss and Katz [38], who evaluated the partition function of the system taking into account permutations of monomers among clusters and showed that Lothe and Pound’s correction to the nucleation theory does not arise (for unary systems). However, later Katz disregarded his previous results [38] and modified the Frenkel model similarly to Lothe and Pound in his subsequent works (e. g., in [39, 40]).

Therefore, the contradiction between different approaches has not been completely resolved and required further analysis. Such an analysis for unary systems (consisting of N_x monomers and N_n clusters X_n, with $N_n \ll N_x \ll N_0$) was carried out in the recent work of the author [41] within the framework of the general thermodynamic approach, taking into account the interaction of monomers with clusters, $\mathrm{X}_n \pm \mathrm{X} = \mathrm{X}_{n\pm1}$ (considered in the statistical mechanics approach [38] as permutations, and disregarded in Lothe and Pound’s model [36]). The excess (or mixing) entropy calculated thermodynamically in [41] was consistent with the value calculated in the statistical approach by Reiss, Kegel and Katz [42], which confirmed the original conclusion of [38].

In particular, it was shown in [41] (for unary systems) that erroneous prediction, $F = N_0$, of the Lothe and Pound model is associated with considering a mixture of monomers and clusters in the ideal gas approximation, neglecting their interactions; whereas their interactions can be taken into account in the weak solution approximation, which leads to $F = N_x$. A generalization of this consideration to binary gas systems (where N_x, N_y and N_0 correspond to two vapours and carrier gas densities, respectively), leading to Eq. (32), was given in the author’s paper [43], and is extended to binary solid solutions in the Appendix A.

In the case of heterogeneous nucleation on extended defects (such as (sub)grain boundaries or dislocations) in the deformed matrix, N_0 in Eq. (33) corresponds to the number density of lattice sites on these defects (e. g., for dislocations, $N_0 \approx \rho_d/a$, where ρ_d is the total dislocation line density and $a \approx \Omega^{1/3}$ is the lattice parameter), whereas c_x and c_y are relative concentrations of monomers on these defects (which should be further assessed by taking into account the effects of segregation).

4. RESULTS AND DISCUSSION

When applying the Reiss theory to the nucleation of V(C, N) carbonitrides, the index x will be assigned to nitrides (i. e., $x = a$, in designations of Section 2) and the index y to carbides (i. e., $y = b$).

Results of calculations of the elements of the matrix $\mathbf{D} = (D_{ij})$ and other related parameters of Eq. (23) for the Gibbs energy of nucleus formation, Eq. (14), are presented in the Appendix B. In particular, it is confirmed that $\det \mathbf{D} < 0$ (i. e., the critical point is a saddle), and thus

$$(-\det \mathbf{D})^{1/2} \approx \frac{(kT)^4}{64\pi\sigma^3 v^2}(\ln S_a + \alpha)^3 \times \times \left[3\left(1 + \frac{\ln S_a}{\alpha}\right)\right]^{1/2}, \quad (34)$$

and that

$$D_{12} \approx -3(kT)^4 (\ln S_a + \alpha)^3/(64\pi\sigma^3 v^2)$$

is negative above the critical supersaturation,

$$S_a > S_a^* \approx \exp(-\alpha),$$

and thus Eq. (28) is valid.

For typical composition of V microalloyed steels, calculations can be simplified (as shown in the Appendix B), leading to $\tan\theta \ll 1$. In this case, Eq. (25) takes the form

$$D'_{11} \approx \frac{(kT)^4}{64\pi\sigma^3 v^2}(\ln S_a + \alpha)^3 \times \times \left[(2\alpha - \ln S_a) - \frac{\alpha}{3}\left[(3 + \ln S_a)\right]^2\right], \quad (35)$$

which is always negative and thus provides a maximum for the free energy at the critical point in the direction of the n'_a-axis (as assumed in the Reiss theory), and the kinetic factor Eq. (27) takes the form

$$\frac{\beta_x^* \beta_y^* \left(1 + \tan^2\theta\right)}{\beta_y^* + \beta_x^* \tan^2\theta} \approx \beta_a^* = = 4\pi D_{\mathrm{M}} c_{\mathrm{M}} R^* \Omega^{-1} \approx 4\pi D_{\mathrm{M}} c_{\mathrm{M}} \frac{2\sigma}{kT \ln S_a}\frac{v}{\Omega}. \quad (36)$$

In application to carbonitrides consisting of ‘monomers’ of two types, MN and MC, Eq. (33) takes the form

$$F = (c_{\mathrm{MN}} + c_{\mathrm{MC}})\,\Omega^{-1}, \quad (37)$$

where c_{MN} and c_{MC} are molecular concentrations of MN and MC in austenite, respectively, which are in equilibrium with alloying components M, N and C in austenite, Eqs (8) and (9), and thus obey the relationships

$$c_{\mathrm{M}} c_{\mathrm{N}} = K_a^{(d)} c_{\mathrm{MN}}, \quad (38)$$

and

$$c_{\mathrm{M}} c_{\mathrm{C}} = K_b^{(d)} c_{\mathrm{MC}}, \quad (39)$$

where $K_{a,b}^{(d)}$ is the dissociation constants, which are normally not small, and thus the concentrations of MN and MC molecules are very small, $c_{\mathrm{MN}}, c_{\mathrm{MC}} \ll c_{\mathrm{M}}, c_{\mathrm{N}}, c_{\mathrm{C}}$ (and can be generally neglected in the total balance of concentrations in the austenite matrix).

Dissociation constants, regularly measured in aqueous solutions (see, e. g., [44]), are little known for solid solutions. For this reason, they can be roughly evaluated by extrapolating the thermodynamic model of nitride (or carbide) particles to dimers MN (or MC) in the approach, commonly used in the cluster dynamics modelling (see the Appendix C).

As opposed to the kinetic factor, Eq. (36), which is completely determined by diffusion transfer of M species through the matrix, Eq. (37) has a purely thermodynamic nature (as shown in the Appendix A) and thus does not depend on the kinetic mechanism of mass transfer at the interface between two phases (carried out either through the transfer of MN (or MC) molecules, or through the congruent (1:1) transfer of M and N (or C) species).

Substituting Eqs (22), (24), (33)-(38) in Eq. (27) one obtains for the nucleation rate

$$\dot{N} \approx 8\pi D_{\mathrm{M}} c_{\mathrm{M}}^2 \left(\frac{c_{\mathrm{N}}}{K_a^{(d)}} + \frac{c_{\mathrm{C}}}{K_b^{(d)}}\right) \frac{\sigma v}{kT\Omega^2}\left(\frac{\alpha}{3\ln S_a}\right)^{1/2} \times \times \left[\ln S_a - 2\alpha + \frac{\alpha}{3}\left[(3 + \ln S_a)\right]^2\right] \times \times \exp\left[-\frac{16\pi}{3}\frac{\sigma^3 v^2}{(kT)^3 (\ln S_a + \alpha)^2}\right]. \quad (40)$$

This expression significantly differs from the expression for homogeneous nucleation in a one-component (unary) system (used, e. g., in [7–10]). The reason for such a contradiction was discussed in the author’s paper [43], where it was shown that Reiss’ expression for the binary nucleation rate, Eq. (27), is valid if

$$\frac{|\det \mathbf{D}|}{|D'_{11}|} \ll \pi kT,$$

which corresponds to

$$\ln^3 S_a \ll 64\pi^2\sigma^3 v^2 \alpha/(3(kT)^3).$$

For V(C, N) with $\ln^3 S_a \approx 12$ (as estimated above in Section 2 for the unstressed case) this inequality takes the form $\ln^3 S_a \ll 10^2$ and thus is satisfied.

Strain effects, which effectively reduce supersaturation, only exacerbate this inequality, and thus Eq. (40) with the effective supersaturation $\widetilde{S}_a = \lambda S_a$ (defined in Section 2) can also be justified for deformed austenite with heterogeneous nucleation of carbonitrides on dislocations, leading to

$$\dot{N} \approx 8\pi D_{\mathrm{M}} c_{\mathrm{M}} \left(\widetilde{c}_{\mathrm{MN}} + \widetilde{c}_{\mathrm{MC}}\right) \rho_d \frac{\sigma v}{kT\Omega^{4/3}} \left(\frac{\alpha}{3\ln S_a}\right)^{1/2} \times$$
$$\times \left[\ln \widetilde{S}_a - 2\alpha + \frac{\alpha}{3}\left[\left(3 + \ln \widetilde{S}_a\right)\right]^2\right] \times$$
$$\times \exp\left[-\frac{16\pi}{3}\frac{\sigma^3 v^2}{(kT)^3\left(\ln \widetilde{S}_a + \alpha\right)^2}\right], \quad (41)$$

where ρ_d is the dislocation line density, and $\widetilde{c}_{\mathrm{MN}}, \widetilde{c}_{\mathrm{MC}}$ are relative concentrations of MN and MC molecules on these defects (as discussed in Section 3.1), assessed by taking into account the effects of segregation.

In the opposite limit,

$$|\det \mathbf{D}|/|D'_{11}| \gg \pi kT,$$

or

$$\ln^3 S_a \gg 64\pi^2\sigma^3 v^2 \alpha/(3(kT)^3),$$

corresponding to the condition of a narrow saddle point passage width (so-called 'quasi-classical approximation'), when only one ('classical') trajectory (passing through the critical point (x^*, y^*)) gives contribution to the integral in Eq. (26), the nucleation rate reduces to

$$\dot{N}_0 \approx J(0) = F\frac{\beta_x^*\beta_y^*\left(1+\tan^2\theta\right)}{\beta_y^* + \beta_x^*\tan^2\theta}\left(\frac{|D'_{11}|}{\pi kT}\right)^{1/2} \times$$
$$\times \exp\left(-\frac{\Delta G_0^*}{kT}\right) \approx F\beta_x^* Z \exp\left(-\frac{\Delta G_0^*}{kT}\right), \quad (42)$$

where

$$Z = \left(\frac{|D'_{11}|}{\pi kT}\right)^{1/2} \approx \left(\frac{|D_{11}|}{\pi kT}\right)^{1/2} =$$
$$= \left(-\frac{1}{2\pi kT}\frac{\partial^2 \Delta G_0\left(x^*, y^*\right)}{\partial x^2}\right)^{1/2} \approx \frac{(kT)^{3/2}\ln^2 S_a}{8\pi\sigma^{3/2}v} \quad (43)$$

converges to the Zeldovich factor in the unary system [32] (considering that according to Eq. (9), $\alpha \propto S_a^{-1}$ decreases with increasing S_a at a fixed S_b), and consequently, Eq. (42) consistently converges to the nucleation rate in the classical nucleation theory.

As a result, Eq. (41) converges to the expression for unary nucleation,

$$\dot{N}_0 = \left(c_{\mathrm{MN}} + c_{\mathrm{MC}}\right)\Omega^{-1}\beta_a^* Z \exp\left(-\frac{\Delta G_0^*}{kT}\right) \approx$$
$$\approx D_{\mathrm{M}} c_{\mathrm{M}}^2 \left(\frac{c_{\mathrm{N}}}{K_a^{(d)}} + \frac{c_{\mathrm{C}}}{K_b^{(d)}}\right)\frac{(kT)^{1/2}\ln S_a}{\sigma^{1/2}\Omega^2} \times$$
$$\times \exp\left[-\frac{16\pi}{3}\frac{\sigma^3 v^2}{(kT)^3\left(\ln S_a + \alpha\right)^2}\right], \quad (44)$$

which differs from the binary nucleation rate calculated from Eq. (40) by the factor

$$\frac{\dot{N}}{\dot{N}_0} \approx \frac{8\pi\sigma^{3/2}v}{(kT)^{3/2}\ln^{3/2} S_a}\left(\frac{\alpha}{3}\right)^{1/2} \times$$
$$\times \left[\ln S_a + \frac{\alpha}{3}\left(3 + \ln S_a\right)^2\right] \approx 10 \gg 1, \quad (45)$$

where $\sigma \approx 0.5$ J/m^2, $\ln S_a \approx 2.3$ and $\alpha \approx 0.04$ for V(C, N) is assumed.

On the other hand, for $\mathrm{Ti}\left(\mathrm{C}_z\mathrm{N}_{1-z}\right)$ with $\alpha \approx 1.3 \cdot 10^{-5}$ and $\ln S_a \approx 14.4$ (estimated in Section 2), the condition of applicability of the unary limit takes the form $\ln^3 S_a \gg 0.1$, which thus is valid. This conclusion is consistent with the above result for the composition of nucleated Ti carbonitrides, which is very close to pure nitrides, $z \approx 1.3 \cdot 10^{-5}$ (see Section 2).

In application to typical V microalloyed steels at $T \approx 1200$ K with $c_{\mathrm{M}} \equiv c_{\mathrm{V}} = 2.36 \cdot 10^{-3}$ (corresponding to $C_{\mathrm{V}} = 0.215$ wt%), $c_{\mathrm{C}} = 8.87 \cdot 10^{-3}$ (corresponding to $C_{\mathrm{C}} = 0.19$ wt%), $c_{\mathrm{N}} = 6 \cdot 10^{-4}$ (corresponding to $C_{\mathrm{N}} = 0.015$ wt%), $D_{\mathrm{V}} = 0.25 \cdot 10^{-4}\exp\left(-264200/RT\right) = 8 \cdot 10^{-17}$ m^2/s (from [2]), $\sigma \approx 0.5$ J/m^2 (used in [7, 10]), and dissociation constants estimated in the Appendix C as $K_a^{(d)} \approx 1$, $K_b^{(d)} \approx 0.5 \cdot 10^2$, Eq. (40) gives $\dot{N} \approx 10^{13}$ m^{-3}·s^{-1} (which will be less, if strain effects and reduced density of nucleation sites are taken into account, as presented in Eq. (41)).

In the lack of direct measurements of the nucleation rate of V(C, N) precipitates, this value can be compared (qualitatively) with available data for NbC precipitates in deformed Nb microalloyed austenite from [21]. In these tests, the concentration of small coherent precipitates (of ∼ 2-5 nm size), observed after $\tau \approx 30$ s holding at 1200 K, was $\sim 10^{21}$ m^{-3}, which gives a much higher value of $\dot{N} \sim 3 \cdot 10^{19}$ m^{-3}·s^{-1}. However, Eq. (40) is very sensitive to the value of surface tension, and for $\sigma \approx 0.3$ J/m^2 (used in [11]) the nucleation rate becomes overestimated, $\dot{N} \approx 10^{22}$ m^{-3}·s^{-1}. Therefore, a more reasonable value can be obtained from Eq. (41), which takes into account strain effects (and the reduction of the number of nucleation sites) that reduce the nucleation rate.

A more direct comparison with typical experiments, in which precipitation-to-temperature (PTT) diagrams have been measured, requires coupling the developed nucleation model with the growth-coarsening and recovery-recrystallization models, as was done, e. g., in [8,45], which can help to improve numerical algorithms from the literature by applying the advanced nucleation model.

4.1. Nucleation of complex carbonitrides

The above developed model can be equally applied to the nucleation of complex carbides (or nitrides), (M,M')C (or (M,M')N), if MC and M'C (MN and M'N) show complete mutual solid solubility, and thus can be considered as a mixture of MC and M'C (MN and M'N) molecules (or 'monomers' of two carbide (nitride) phases). In these cases, the index a should be assigned in the above theory to MC (or MN), and the index b to M'C (or M'N).

In the case of complex carbonitrides (M,M')(C,N), which form homogeneous solutions (i. e., without phase separation) and thus can be considered as a (regular) mixture of monomers of four types, MC, MN, M'C and M'N, the above theory should be generalized to four-component systems following Langer's multicomponent approach [15]. In this approach, the nucleation rate is calculated as

$$\dot{N} = \frac{|\chi|}{|\det \mathbf{D}|^{1/2}} F \exp\left(-\frac{\Delta G_0^*}{kT}\right), \qquad (46)$$

where the Gibbs free energy is a function of $X = (x_1, x_2, x_3, x_4)$ with indices $1, 2, 3, 4$, numerating monomers MC, MN, M'C and M'N, respectively, which generalizes Eq. (14) similarly to [29]; $\mathbf{D} = (D_{ij})$ is the matrix with elements

$$D_{ij} = (1/2)\, \partial^2 \Delta G_0\, (X^*)/\partial x_i \partial x_j$$

calculated in the critical point $X^* = (x_1^*, x_2^*, x_3^*, x_4^*)$; χ is the negative eigenvalue of the matrix $\boldsymbol{\beta}\mathbf{D}$, and $\boldsymbol{\beta} = (\beta_1, \beta_2, \beta_3, \beta_4)$ is the matrix of the arrival rates of monomers.

Generalization of the calculations presented in Section 4 to this case is straightforward, but involves a wide range of simplifications (related to the weak solution approximation for all four components) and unknown parameters, and, in the absence of experimental data on nucleation rates, was not attempted in this work.

5. CONCLUSIONS

On the base of the critical analysis of existing models of strain induced precipitation of simple carbonitrides in microalloyed austenite, a new kinetic model is developed. In this model, the driving chemical force for nucleation in undeformed austeinte is calculated within the framework of Hillert and Staffansson's regular solution theory [12], with additional consideration of elastic strain energy of coherent precipitates, which effectively modifies supersaturation of the solid solution by a strain-dependent factor. In deformed austenite, the elastic strain contribution to the free energy of nucleus formation can be reduced, if precipitates nucleate heterogeneously on dislocations (as observed in numerous tests), which can be taken into account by adjusting the modifying factor for supersaturation. This approach is an alternative to the approach used in the literature (e. g., [7]), where strain effects (from dislocations) were taken into account by adjusting the modifying factor of the chemical driving force for homogeneous nucleation (however, with the additional assumption that nuclei are incoherent with the matrix).

It is shown that the main simplification of the theory of regular solutions of Hillert and Staffansson, in which the excess molar free energy of mixing of carbides and nitrides in the carbonitride phase is given by a second-order term, can be justified in relation to V and Ti carbonitrides, for which the excess molar free energy of mixing can be described with good accuracy in the weak solution approximation. This allows further analysis of the kinetics of carbonitride nucleation using the formalism of Reiss' binary nucleation theory [13] as applied to weak solution, avoiding simplifications of the earlier models based on classical nucleation theory for single-component (unary) systems.

In particular, it is shown that the composition of $\mathrm{V(C, N)}$ nuclei differs significantly from equilibrium values at the temperature of their formation (in contrast to the assumption of the earlier models [9,11]), as well as from the composition calculated in [10] within the ideal mixture model. Besides, the pre-exponential kinetic factor of the $\mathrm{V(C, N)}$ nucleation rate is underestimated in unary models, whereas the number of nucleation sites (pre-exponential thermodynamic factor) can be significantly (by several orders of magnitude) overestimated in the existing models.

The developed approach of the binary nucleation theory can be extended to mixed carbides, (M,M')C, whereas the most general case of complex carbonitrides, (M,M')(C,N), can be analysed within the framework of Langer's nucleation theory [15], which generalizes

Reiss' binary theory to multicomponent systems; these future developments of the model are briefly discussed.

APPENDIX A. CALCULATION OF THE NUMBER DENSITY OF NUCLEATION SITES IN THE SOLID SOLUTION

Although the Lothe and Pound approach [36] correctly identified the limitations of the earlier approach, in which the presence of vacancy sites in the lattice gas was ignored, it inherited the main drawback of this approach, considering the system of monomers and clusters as an ideal mixture.

Indeed, such consideration is valid only in the case of Boltzmann statistics (to which the ideal gas obeys), when all particles are distributed over different thermodynamic states completely independently of each other [46]. For clusters of finite sizes, their interaction with monomers (described in the statistical mechanics approach [38] by permutations of monomers among clusters), cannot be neglected, since clusters, in contrast to monomers, cannot be considered as point particles.

In accordance with general thermodynamics, the additivity of thermodynamic quantities, such as free energy or entropy, is preserved only as long as the interaction between different parts of the system is negligible, as in the case of ideal gas mixtures, for which, for example, the entropy of the mixture is equal to the sum of the entropies of each of gases [46]. Therefore, for a non-ideal mixture of several substances (for example, monomers and clusters), the entropy is no longer equal to the sum of the entropies of each of the substances.

To find the excess entropy of a mixture of monomers and clusters, let $\Phi_0\left(P,T,N_x,N_y\right)$ be the Gibbs free energy of an ideal solid solution (the metastable phase) in the crystal matrix (with the number density of lattice sites N_0) of monomers X and Y (with the number densities N_x and N_y, respectively), whose chemical potentials are $\mu_i\left(P,T,c_i\right) = \psi_i(P,T) + kT\ln c_i$, where $i = x,y$, and $c_i = N_i/N_0 \ll 1$. Let α_{xy} denote the small change which would occur in the free energy if one spherical cluster $\mathrm{X}_x\mathrm{Y}_y$ (a nucleus of the new phase), consisting of x monomers X and y monomers Y, was added to the system. In the thermodynamic approach, clusters are considered as 'macroscopic' subsystems (or 'bodies') with $n_x, n_y \gg 1$, homogeneously distributed in the 'external medium' (the metastable phase).

Due to the interactions of clusters with monomers, $\mathrm{X}_x\mathrm{Y}_y \pm \mathrm{X} = \mathrm{X}_{x\pm1}\mathrm{Y}_y$, and $\mathrm{X}_x\mathrm{Y}_y \pm \mathrm{Y} = \mathrm{X}_x\mathrm{Y}_{y\pm1}$, α_{xy} should be sought in the weak solution approximation as a function of N_x and N_y, i. e., $\alpha_{xy} = \alpha_{xy}\left(P,T,N_x,N_y\right)$. Due to $N_{xy} \ll N_x, N_y$, where N_{xy} is the (macroscopic) number density of clusters of size (x,y), interactions between clusters can be neglected, and thus the free energy takes the form

$$\Phi = N_x\mu_x + N_y\mu_y + N_{xy}\alpha_{xy}\left(P,T,N_x,N_y\right) + \\ + kT\ln\left(N_{xy}!\right), \quad (\text{A.1})$$

where the translational entropy term,

$$kT\ln\left(N_{xy}!\right) \approx kTN_{xy}\ln\left(N_{xy}/e\right),$$

takes into account that all (spherical) clusters of one size (x,y) are identical and, being 'macroscopic bodies', are homogeneously distributed in the 'external medium'. Accordingly, Eq. (A.1) can be represented in the form

$$\Phi = N_x\mu_x + N_y\mu_y + \\ + kTN_{xy}\ln\left[\frac{N_{xy}}{e}\exp\left(\frac{\alpha_{xy}}{kT}\right)\right]. \quad (\text{A.2})$$

This consideration is principally different from the Lothe and Pound approach [36], where clusters were considered as a new ideal lattice gas Z with density $N_z = N_{xy} \ll N_0$ added to the existing lattice gas mixture of monomers X and Y, and, therefore, become a constituent part of the 'external medium'. With this approach the configurational entropy (which enters Φ through the chemical potential terms) is transformed from

$$kT\ln\left(\frac{N_0!}{N_v!N_x!N_y!}\right) \approx -kT\left[N_v\ln\left(\frac{N_v}{N_0}\right) + \right. \\ \left. + N_x\ln\left(\frac{N_x}{N_0}\right) + N_y\ln\left(\frac{N_y}{N_0}\right)\right] \approx \\ \approx -kT\left[N_x\ln\left(\frac{N_x}{N_0}\right) + N_y\ln\left(\frac{N_y}{N_0}\right)\right],$$

where

$$N_v = N_0 - N_x - N_y \approx N_0$$

is the number density of vacant sites in the lattice, to

$$kT\ln\left(N_0!/(N_v'!N_x!N_y!N_z!)\right),$$

where

$$N_v' = N_0 - N_x - N_y - N_z \approx N_0,$$

and hence the additional entropy term in Eq. (A.1) will be

$$kTN_z\ln\left(N_z/N_0!\right),$$

instead of

$$kTN_z \ln(N_z/e) \equiv kTN_{xy} \ln(N_{xy}/e),$$

while the interaction term

$$N_{xy}\alpha_{xy} \equiv N_z\alpha_z$$

does not appear in Eq. (A.1) (since the lattice gas Z is ideal).

Since Φ in Eq. (A.2) must be a homogeneous function of the first order in N_x, N_y and N_{xy} [46], the term $\exp[\alpha_{xy}(P,T,N_x,N_y)/kT]$ in the argument of the logarithm should be sought in the most general form $f_{xy}(P,T)/(N_x+\beta N_y)$. Given that after redefining $x \leftrightarrow y$, the free energy should not change, we can conclude that $\beta = 1$. Accordingly,

$$\Phi = N_x\mu_x + N_y\mu_y + \\ + kTN_{xy} \ln\left[\frac{N_{xy}}{e(N_x+N_y)} f_{xy}(P,T)\right], \quad \text{(A.3)}$$

or, introducing a new function

$$\psi_{xy}(P,T) = kT \ln f_{xy}(P,T),$$

$$\Phi = N_x\mu_x + N_y\mu_y + N_{xy}\ \psi_{xy}(P,T) + \\ + kTN_{xy} \ln\left[\frac{N_{xy}}{e(N_x+N_y)}\right]. \quad \text{(A.4)}$$

The comparison of Eq. (A.4) with Eq. (A.1) shows that

$$N_{xy}\alpha_{xy}(P,T,N_x,N_y) = \\ = N_{xy}\psi_{xy}(P,T) - kTN_{xy} \ln(N_x+N_y). \quad \text{(A.5)}$$

Therefore, since the first term in Eq. (A.5), $N_{xy}\psi_{xy}(P,T)$, does not depend on the number of monomers, the value $\psi_{xy}(P,T)$ is the standard free energy of a cluster, while the second term of Eq. (A.5), $kTN_{xy}\ln(N_x+N_y)$, is the excess entropy of the mixture.

This leads to the following expressions for the chemical potentials of the 'solvents'

$$\mu'_x = \frac{\partial\Phi}{\partial N_x} = \mu_x - kTc_{xy} \approx \mu_x, \quad \text{(A.6)}$$

$$\mu'_y = \frac{\partial\Phi}{\partial N_y} = \mu_y - kTc_{xy} \approx \mu_y, \quad \text{(A.7)}$$

where

$$c_{xy} \approx N_{xy}/(N_x+N_y) \ll 1,$$

and of the 'solute'

$$\mu_{xy} = \frac{\partial\Phi}{\partial N_{xy}} = kT \ln c_{xy} + \psi_{xy}. \quad \text{(A.8)}$$

Therefore, from the equilibrium condition of the chemical reaction $x\mathrm{X} + y\mathrm{Y} = \mathrm{X}_x\mathrm{Y}_y$,

$$x\mu_x + y\mu_y = \mu_{xy}, \quad \text{(A.9)}$$

the mass action law can be derived as

$$c_{xy} \approx \frac{N_{xy}}{(N_x+N_y)} = K_{xy}(T), \quad \text{(A.10)}$$

with the equilibrium constant

$$K_{xy}(T) = \exp\left(-\frac{\Delta G_0(x,y)}{kT}\right), \quad \text{(A.11)}$$

where

$$\Delta G_0(x,y) = \psi_{xy} - x\mu_x - y\mu_y$$

is the Gibbs free energy of formation of a cluster.

If concentrations of clusters of other sizes are also small, their contributions to the total free energy of the system are linear; therefore, the equilibrium size distribution function has the form

$$f_0(x,y) = (N_x+N_y)\exp\left(-\frac{\Delta G_0(x,y)}{kT}\right), \quad \text{(A.12)}$$

which is derived, as mentioned above, in the thermodynamic approach for 'macroscopic' clusters with $x, y \gg 1$. For this reason, the assertion in Ref. [40] that this expression for a cluster size of 1 does not return the number of monomers is irrelevant.

It is straightforward to see that, considering (following Lothe and Pound [36]) clusters as an ideal lattice gas Z with the chemical potential

$$\mu_z = \psi_z(P,T) + kTN_z \ln(N_z/N_0)$$

(as discussed above), the solution to Eq. (A.9) will have the form

$$c_z = N_z/N_0 = \exp(-\Delta G_0(x,y)/kT),$$

where

$$\Delta G_0(x,y) = \psi_z - x\mu_x - y\mu_y,$$

and thus the pre-exponential factor in Eq. (A.12) will be equal to the number density of lattice sites N_0, derived (erroneously) in [36].

APPENDIX B. CALCULATION OF THE NUCLEATION RATE PARAMETERS

The elements

$$D_{ij} = (1/2)\,\partial^2 \Delta G_0\,(n_a^*, n_b^*)/\partial n_i \partial n_j$$

of the matrix $\mathbf{D}$ calculated in the first approximation in the small parameter $\alpha \ll 1$ using Eq. (14) take the form

$$D_{11} \approx \frac{(kT)^4}{64\pi\sigma^3 v^2}\,(\ln S_a + \alpha)^3\,(2\alpha - \ln S_a)\,, \tag{B.1}$$

$$D_{22} \approx \frac{3(kT)^4}{64\pi\sigma^3 v^2}\frac{(\ln S_a + \alpha)^3}{\alpha}, \tag{B.2}$$

$$D_{12} \approx -\frac{(kT)^4}{64\pi\sigma^3 v^2}\,(\ln S_a + \alpha)^3\,(3 + \ln S_a)\,, \tag{B.3}$$

leading to

$$\det \mathbf{D} = D_{11}D_{22} - D_{12}^2 \approx \approx -\left[\frac{(kT)^4}{64\pi\sigma^3 v^2}\,(\ln S_a + \alpha)^3\right]^2 3\left(1 + \frac{\ln S_a}{\alpha}\right), \tag{B.4}$$

which is negative above the critical supersaturation, $\ln S_a > -\alpha$, and thus

$$(-\det \mathbf{D})^{1/2} \approx \frac{(kT)^4}{64\pi\sigma^3 v^2}\,(\ln S_a + \alpha)^3\left[3\left(1 + \frac{\ln S_a}{\alpha}\right)\right]^{1/2}. \tag{B.5}$$

On the other hand, D_{11} changes its sign at $\ln S_a = 2\alpha$, and thus for $\ln S_a > 2\alpha$ becomes negative, $D_{11} < 0$. In this case,

$$d_a = -\frac{D_{11}}{D_{12}} \approx \frac{(2\alpha - \ln S_a)}{(3 + \ln S_a)} < 0 \quad |d_a| < 1, \tag{B.6}$$

and

$$d_b = -\frac{D_{22}}{D_{12}} \approx \frac{3}{\alpha\,(3 + \ln S_a)} \gg 1, \tag{B.7}$$

which is valid for the typical composition of V microalloyed steels with $\ln S_a \approx 2.3$ and $\alpha \approx 0.04$ (see Section 2).

Taking into account Eq. (31) (i. e., $r \approx 1$), this leads to

$$s = \frac{1}{2}\,(d_a - r d_b) \approx -\frac{1}{2} d_b \approx \approx -\frac{3}{2\alpha\,(3 + \ln S_a)} < 0, \tag{B.8}$$

and

$$\frac{s^2}{r} \approx s^2 \gg 1. \tag{B.9}$$

Strain effects that reduce the effective supersaturation but maintain the same value of α (as explained in Section 2) only exacerbate this inequality.

Under this condition, Eq. (28) can be simplified to the form

$$\tan\theta = -|s| + \left(r + s^2\right)^{\frac{1}{2}} \approx \frac{1}{2|s|} \ll 1, \tag{B.10}$$

and hence

$$\cos^2\theta = \frac{1}{1 + \tan^2\theta} \approx \frac{4s^2}{4s^2 + 1} \approx 1. \tag{B.11}$$

A similar result can be obtained for typical Ti microalloyed steels with $\alpha \approx 2 \cdot 10^{-5}$and $\ln S_a \approx 14.4$ (see Section 2), which gives $|s| \approx 4.3 \cdot 10^3 \gg 1$.

Since the effective supersaturation in deformed steels is reduced due to strain effects (with the unchanged value of α), D_{11} can become positive at $-\alpha < \ln S_a < 2\alpha$. In this case,

$$d_a = -\frac{D_{11}}{D_{12}} \approx \frac{(2\alpha - \ln S_a)}{(3 + \ln S_a)} \approx \approx \frac{1}{3}\,(2\alpha - \ln S_a) < \alpha \ll 1, \tag{B.12}$$

$$d_b = -\frac{D_{22}}{D_{12}} \approx \frac{3}{(3 + \ln S_a)\,\alpha} \approx \alpha^{-1} \gg 1, \tag{B.13}$$

and thus

$$s = \frac{1}{2}\,(d_a - r d_b) \approx -\frac{1}{2} d_b \approx -\frac{1}{2\alpha} < 0, \tag{B.14}$$

$$\frac{s^2}{r} \approx \frac{1}{4\alpha^2} \gg 1, \tag{B.15}$$

leading to Eqs (B.11) and (B.12) also in this case.

Substituting these values into Eq. (25) leads to

$$D_{11}' \approx \frac{(kT)^4}{64\pi\sigma^3 v^2}\,(\ln S_a + \alpha)^3\left[(2\alpha - \ln S_a) - - \frac{\alpha}{3}\,[(3 + \ln S_a)]^2\right], \tag{B.16}$$

which is negative in both cases, $-\alpha < \ln S_a < 2\alpha$ and $\ln S_a > 2\alpha$, and thus provides a maximum of the free energy at the critical point in the direction of the n_a'-axis (as assumed in the Reiss theory).

APPENDIX C. ESTIMATION OF THE DISSOCIATION CONSTANTS

For a one-component solid solution (with concentration c), the growth kinetics of a cluster containing n monomers is described as

$$\dot{n} = \beta_n(c) - \alpha_n,$$

where $\beta_n = 4\pi D c R_n \Omega^{-1}$ is the arrival rate of monomers (with diffusivity D) into the cluster of radius $R_n = (3vn/4\pi)^{1/3}$, calculated in Eq. (30), and α_n is the emission rate of monomers from the cluster, calculated from the detailed balance at concentration $c_n^{(0)}$ in equilibrium with the cluster (i. e., when $\dot{n} = 0$),

$$\beta_n \left(c_n^{(0)}\right) - \alpha_n = 0. \tag{C.1}$$

Representing the Gibbs free energy of the cluster formation in the form

$$\Delta G_0(n) = -nkT \ln S + 4\pi R_n^2 \sigma,$$

where $S = c/c_e$ is supersaturation of the solid solution, σ is surface tension of the cluster, and calculating $c_n^{(0)}$ using the Gibbs-Kelvin equilibrium condition,

$$d\Delta G_0(n)/dn = 0,$$

one obtains

$$kT \ln\left(\frac{c_n^{(0)}}{c_e}\right) = \sigma \frac{d\left(4\pi R_n^2\right)}{dn}, \tag{C.2}$$

which, by using Eq. (C.1), leads to the relation

$$\frac{\alpha_n}{\beta_n} = \frac{\beta_n\left(c_n^{(0)}\right)}{\beta_n(c)} = \frac{c_n^{(0)}}{c} = S^{-1}\frac{c_n^{(0)}}{c_e} = S^{-1}\exp\left[\frac{\sigma}{kT}\frac{d\left(4\pi R_n^2\right)}{dn}\right] = \exp\left(\frac{1}{kT}\frac{d\Delta G_0(n)}{dn}\right). \tag{C.3}$$

In cluster dynamics (see, e. g., [47, 48]), the master equations describe the change with time of the number density of precipitates containing n monomers, where the relation between the arrival rate β_n and emission rate α_n are calculated using Eq. (C.3) represented in the discrete form

$$\alpha_n = \beta_{n-1} S^{-1} \times \exp\left\{\frac{2\sigma\left(36\pi v^2\right)^{1/3}}{3kT}\left[n^{2/3} - (n-1)^{2/3}\right]\right\}. \tag{C.4}$$

Although the Gibbs free energy $\Delta G_0(n)$, as well as surface tension σ, are the thermodynamic functions, defined only for $n \gg 1$, in cluster dynamics Eq. (C.3) is extrapolated to small clusters, including $n = 2$, for which the thermodynamic Gibbs-Kelvin equation is not applicable. Nevertheless, such an approach leads to reasonable predictions of the nucleation kinetics, and thus will be used in the present work for evaluation of the dissociation constants.

In this approach, the equilibrium concentration of nitride (or carbide) molecules in the matrix can be estimated by extrapolating the Gibbs free energy of cluster formation $\Delta G_0^{(a)}(x,y) \equiv \Delta G_0^{(\mathrm{MN})}(x,y)$ (or $\Delta G_0^{(b)}(x,y) \equiv \Delta G_0^{(\mathrm{MC})}(x,y)$) to the corresponding dimers MN (or MC) in the system of monomers $\mathrm{X} \equiv \mathrm{M}$ and $\mathrm{Y} \equiv \mathrm{N}$ (or C) (in notations of the Appendix A),

$$\frac{1}{kT}\Delta G_0^{(a)}(1,1) \approx -\ln S_a + \frac{4\pi\left(\frac{3v}{4\pi}\right)^{\frac{2}{3}}\sigma_a}{kT}, \tag{C.5}$$

$$\frac{1}{kT}\Delta G_0^{(b)}(1,1) \approx -\ln S_b + \frac{4\pi\left(\frac{3v}{4\pi}\right)^{\frac{2}{3}}\sigma_b}{kT}, \tag{C.6}$$

which, after substituting into Eq. (A.12), also extrapolated to dimers, gives

$$c_{MN} \approx f_0^{(a)}(1,1) = (c_\mathrm{M} + c_\mathrm{N})\exp\left(-\frac{\Delta G_0^{(a)}(1,1)}{kT}\right), \tag{C.7}$$

$$c_{MC} \approx f_0^{(b)}(1,1) = (c_\mathrm{M} + c_\mathrm{C})\exp\left(-\frac{\Delta G_0^{(b)}(1,1)}{kT}\right), \tag{C.8}$$

and thus,

$$K_a^{(d)} = \frac{c_\mathrm{M} c_\mathrm{N}}{c_\mathrm{MN}} \approx \frac{c_\mathrm{M} c_\mathrm{N}}{(c_\mathrm{M} + c_\mathrm{N})} S_a^{-1} \exp\left[\frac{(4\pi)^{1/3}(3v)^{2/3}\sigma_a}{kT}\right], \tag{C.9}$$

$$K_b^{(d)} = \frac{c_\mathrm{M} c_\mathrm{C}}{c_\mathrm{MC}} \approx \frac{c_\mathrm{M} c_\mathrm{C}}{(c_\mathrm{M} + c_\mathrm{C})} S_b^{-1} \exp\left[\frac{(4\pi)^{1/3}(3v)^{2/3}\sigma_b}{kT}\right]. \tag{C.10}$$

For the typical composition of V microalloyed steels (considered in Section 2) with $c_\mathrm{M} \equiv c_\mathrm{V} = 2.36 \cdot 10^{-3}$ (corresponding to 0.215 wt%), $c_\mathrm{C} = 8.87 \cdot 10^{-3}$ (corresponding to 0.19 wt%), $c_\mathrm{N} = 6 \cdot 10^{-4}$ (corresponding to 0.015 wt%), and $\sigma_a \approx \sigma_b \approx \sigma \approx 0.5$ J/m^2 (used in [7, 10]), the dissociation constants at 1200 K can be evaluated as $K_a^{(d)} \approx 1$, $K_b^{(d)} \approx 0.5 \cdot 10^2$. Being substituted in Eqs (38) and (39), these dissociation constants provide very small concentrations of nitrides and carbides, $c_\mathrm{MV}, c_\mathrm{MC} \ll c_\mathrm{M}, c_\mathrm{N}, c_\mathrm{C}$, as was assumed in calculations.

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