



# Kinetics of vanadium carbonitride precipitation in steel: A computer model

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## Abstract

We have constructed a computer model of the precipitation kinetics of vanadium carbonitride in steel that takes into account the composition evolution of the precipitates with time. The model takes advantage of the fast diffusion of nitrogen and carbon compared to niobium to derive the composition, size and rate of formation of the precipitates during their nucleation. A local equilibrium condition is used at the precipitate–matrix interface to derive the growth rate of each precipitate as a function of its size and the current matrix composition. Coarsening occurs naturally on account of the Gibbs–Thomson capillarity effect. For isothermal heat treatments, the calculations show that the precipitates nucleate as almost pure vanadium nitrides. They subsequently grow at the expense of solute nitrogen. When nitrogen is exhausted, the solute carbon precipitates and progressively transforms the nitrides into carbonitrides. The coarsening stage leads to a steady-state size distribution of niobium carbonitrides of the equilibrium composition. © 2005 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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## 1. Introduction

In order to monitor mechanical properties in relation to the microstructure, the knowledge of the precipitation state at the end of a thermo-mechanical treatment is of prime importance. For this purpose, various computer models are developed to allow for the prediction of the influence of the process parameters on the state of precipitation. The model that we have developed is one of them [1]. It predicts the precipitation kinetics of mono- and di-atomic phases in ferrite and austenite as a function of the time–temperature history. It is

based on the classical theories for diffusive phase transformation and treats simultaneously the nucleation, growth and coarsening phenomena. The state of precipitation that is predicted includes the particle size distribution, their number and volume fraction. From these values, the effects of the precipitates on the mechanical properties can be calculated.

The occurrence of nitrogen in solid solution in steels requires that the precipitation kinetics of the carbonitrides that form from the metallic elements in solid solution be understood and modelled. One of the main difficulties of this task is accounting for tri-atomic particles having a variable C/N ratio. This paper proposes a simple and fast computer model that treats the precipitation of the vanadium carbonitride V(C,N). This case is chosen here to exemplify the principles of a new version of the Multipreci model, which is designed to be valid for M(C,N)-type precipitates, M = V, Nb or Ti.

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## 2. The multipreci model

### 2.1. $V(C,N)$ versus $VC$

It is an experimental fact that the presence of nitrogen in austenite solid solution in addition to carbon during the precipitation of vanadium results in the formation of vanadium carbonitrides [2]. The ratio of C/N in the precipitates depends on the alloy composition and the thermal cycle. A comprehensive model of vanadium precipitation kinetics must take this fact into account and determine the following:

- Composition of the nuclei.
- Nucleation rate.
- Growth rate.
- Time evolution of the particle composition.
- Gibbs–Thomson effect and coarsening.

In Sections 2 and 3 of this paper, we provide analytical equations and a procedure to solve them to answer the above-mentioned questions.

### 2.2. Physical assumptions

The assumptions of the model are classical for this kind of problem:

- The precipitates are spherical particles.
- The thermodynamics of  $V(C,N)$  is an ideal solid solution of VC and VN.
- Nucleation occurs homogeneously according to the classical theory.
- Growth is limited by the diffusion of vanadium in the volume of the matrix.
- Coarsening is driven by the Gibbs–Thomson effect.

### 2.3. The class model

The kinetic equations of nucleation and growth are used to compute the time evolution of the size histogram of the particles. The size histogram is represented by the number per unit volume and the particle composition of each sized class. This approach has been chosen to render the size–composition correlation. We will see in the following that this approach also has the advantage of treating in a simple way non-trivial coarsening effects of particles of varying composition.

Each class of size is characterised by its radius  $R$  and its composition  $y$ . At each time step of the calculation, nucleation is modelled by the creation of a new class of radius  $R'$  and composition  $y_g$ . During the same time step, growth modifies the radius of each existing class of particles. The growth rate takes into account the Gibbs–Thomson effect. As a result, coarsening occurs by dissolution of the smallest particles to the advantage of the largest ones (see Fig. 1).

## 3. Equations of the model

### 3.1. The model Fe–V–C–N steel

The generic case of vanadium carbonitride precipitation in a model Fe–V–C–N steel is used here to exemplify the approach used in the Multipreci model. The composition of the steel is shown in Table 1.

The steel is composed of a metallic alloying element, V, and two interstitial elements C and N, the balance being a majority of Fe atoms. The ratio of the interstitial atoms is  $C/N \approx 15$ . The ratio of substitutional over interstitial atoms is  $V/(C + N) \approx 0.25$ . This ratio being less than 1, the maximum quantity of precipitated vana-

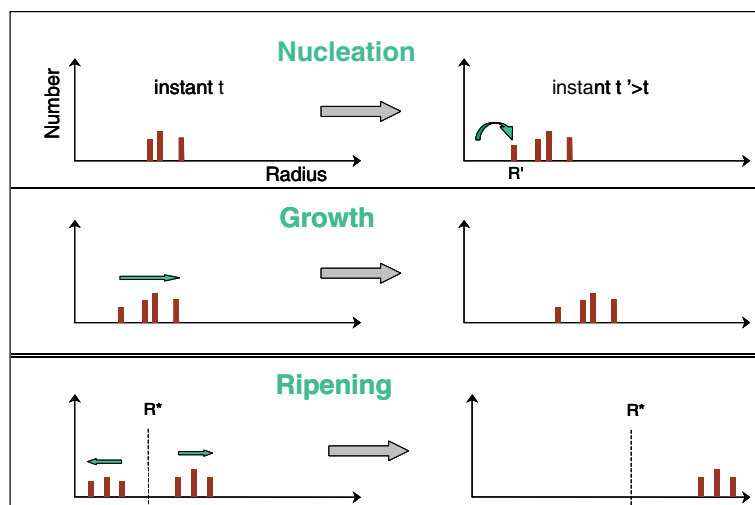


Fig. 1. Schematics of the treatment of the classes of size, rendering nucleation, growth and coarsening.

Table 1  
Composition of the steel, in weight ppm and atomic fraction

	Weight (ppm)	Atomic fraction
V	2150	$2.36 \times 10^{-3}$
C	1900	$8.87 \times 10^{-3}$
N	150	$6.0 \times 10^{-4}$

dium is not limited by the amount of interstitial elements in the steel, but by the total amount of vanadium.

### 3.2. Thermodynamics

The thermodynamic model used in this paper is based on the approach of [3] for predicting the austenite/carbonitride equilibrium in the Fe–Nb–V–C–N system. The equilibrium at a given temperature in austenite is the state towards which the system evolves from its initial, out of equilibrium state. It is useful to compute this state as a reference for the precipitation kinetics.

The equilibrium between the austenite matrix and the carbonitride  $VC_yN_{1-y}$  is described by the mass action law

$$RT[\ln a_V^e + y \ln a_C^e + (1 - y) \ln a_N^e] = \Delta G_{VC_yN_{1-y}}^\circ \quad (1)$$

In this equation,  $a_i^e$  is the activity of the element  $i$  ( $i = V, C, N$ ) at equilibrium. In the case of infinite dilution, the activity is proportional to the atomic fraction at equilibrium  $X_i^e$  (Henry state of reference).  $\Delta G_{VC_yN_{1-y}}^\circ$  is the Gibbs energy of formation of the carbonitride and is a function of its composition  $y$ . VC and VN are both of the face-centered cubic NaCl type crystal structure of very similar molar volume (see Table 2). We thus consider the carbonitride as an ideal mix of VC and VN, and following Hillert and Staffansson [4], we can write

$$\Delta G_{VC_yN_{1-y}}^\circ = y\Delta G_{VC}^\circ + (1 - y)\Delta G_{VN}^\circ + RT[y \ln y + (1 - y) \ln(1 - y)], \quad (2)$$

where  $\Delta G_{VC}^\circ$  and  $\Delta G_{VN}^\circ$  are the Gibbs energy of formation of VC and VN, respectively. According to our assumptions, Eq. (2) does not include the regular solution parameters that would otherwise account for interactions between VC and VN. In other words, we have neglected the excess molar free energy of mixing of VC and VN. Let us further assume that the austenite solid solution is dilute enough such that the activity coefficients of V, C and N do not depend on concentrations.

Table 2  
Logarithm of the solubility products of VC and VN in austenite ( $T$  in K, compositions in wt.%)

	Solubility product	Molar volume
VC	$\log(\%V \cdot \%C) = 6.72 - 9500/T$	10.81
VN	$\log(\%V \cdot \%N) = 3.02 - 7840/T$	10.52

Molar volumes of VC and VN in  $\text{cm}^3 \text{mol}^{-1}$ .

Then, the thermodynamic functions  $\Delta G_{VC}^\circ$  and  $\Delta G_{VN}^\circ$  are related to the solubility products for the individual VC or VN compounds in equilibrium with the matrix by the relations

$$\begin{aligned} \ln(X_V^e \cdot X_C^e) &= \Delta G_{VC}^\circ/RT, \\ \ln(X_V^e \cdot X_N^e) &= \Delta G_{VN}^\circ/RT. \end{aligned} \quad (3)$$

By substituting Eq. (2) into Eq. (1), it is easily shown that the equilibrium equations are [5,6]

$$\begin{aligned} yK_{VC} &= X_V^e \cdot X_C^e, \\ (1 - y)K_{VN} &= X_V^e \cdot X_N^e, \end{aligned} \quad (4)$$

where  $K_{VC}$  and  $K_{VN}$  are the solubility products of VC and VN, respectively. This set of equations will be used later in this chapter for the derivation of the nucleation and growth rates. Relations (4) in association with the conservation equations of the alloying elements allow for the calculation of the equilibrium concentration of V, C and N in solid solution, as well as the composition  $y$  of the carbonitride. The values of the solubility products can be found in the literature, and we have chosen the data selected by Gladman [7] (Table 2 and Fig. 2):

From Fig. 2, it can be seen that the solubility product of VN is more than 100 times smaller than that of VC. In other words, vanadium nitride is much more thermodynamically stable than vanadium carbide in austenite. This will have important consequences on the kinetics of nucleation and growth, as will be demonstrated later.

The results of the calculation of the equilibrium state as a function of temperature are summarised in Fig. 3. The temperature for complete dissolution is 1150 °C. Below this temperature, when the temperature decreases:

- Nitrogen precipitation increases.
- The proportion of carbon in the precipitates increases.
- Under 900 °C, the full precipitation of nitrogen is achieved.

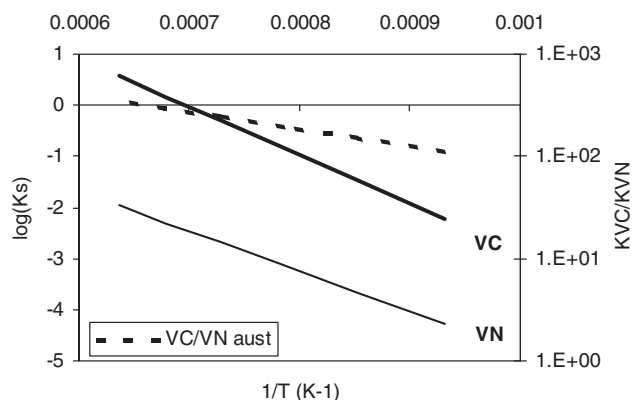


Fig. 2. Arrhenius plot of the solubility product of VC and VN in austenite from Table 2 ( $T$  in K, compositions in wt.%). The ratio  $K_{VC}/K_{VN}$  is plotted by dashed line.

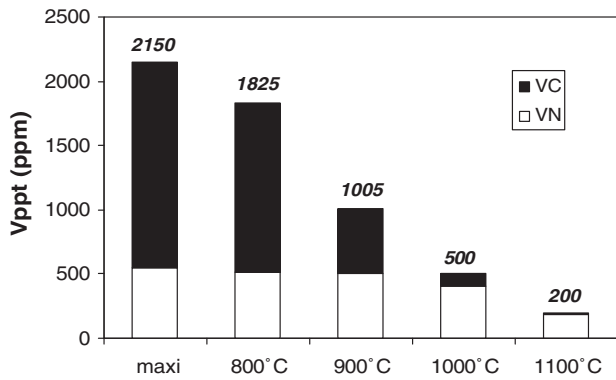


Fig. 3. Equilibrium state of precipitation as a function of temperature calculated for the steel in Table 1 with data of Table 2. The bars represent the vanadium content under the form of VC (black bar) and VN (white bar) in the precipitates. Above each bar is the total vanadium precipitated, in ppm.

We note that the total precipitation of vanadium cannot be achieved in austenite ( $T > 800$  °C).

### 3.3. Nucleation

Neglecting the strain energy term, the Gibbs energy for the formation of a spherical embryo of vanadium carbonitride from the elements in solid solution is classically expressed as the sum of a volume and an interface term

$$\Delta G = \Delta g \frac{4}{3} \pi R^3 + \gamma 4\pi R^2. \quad (5)$$

In this equation,  $\Delta g$  is the driving energy for nucleation per unit volume and  $R$  is the radius of the embryo.  $\gamma$  is its interface energy with the matrix and is supposed to be isotropic. The expression for the driving energy  $\Delta g$  is needed for the derivation of the size and composition of the critical nucleus. To find this expression we proceed as follows.

#### 3.3.1. Driving energy for nucleation

In the simple case of a binary compound of formula  $A_yB_{1-y}$ , the driving energy for nucleation is

$$V_m \Delta g = \mu_{A_yB_{1-y}}(y) - (y\mu_A + (1-y)\mu_B). \quad (6)$$

Table 3

Values of the entry data of the calculations

	Symbol	Value
Vanadium nominal atomic fraction	$X_V$	$2.36 \times 10^{-3}$
Carbon nominal atomic fraction	$X_C$	$8.87 \times 10^{-3}$
Nitrogen nominal atomic fraction	$X_N$	$6.0 \times 10^{-4}$
Carbon diffusion coefficient (cm <sup>2</sup> /s)	$D_C$	$0.1 \exp(-137,500/RT)$
Nitrogen diffusion coefficient (cm <sup>2</sup> /s)	$D_N$	$0.91 \exp(-168,600/RT)$
Vanadium diffusion coefficient (cm <sup>2</sup> /s)	$D_V$	$0.25 \exp(-264,200/RT)$
Interface energy	$\gamma$	$0.5 \text{ J m}^{-2}$
Molar volume of VCN	$V_{VCN}$	$10.65 \text{ cm}^3 \text{ mol}^{-1}$
Molar volume of austenite	$V_{Fe}$	$7.11 \text{ cm}^3 \text{ mol}^{-1}$
Solubility product of VN	$\log(K_{VN})$	$3.02 - 7840/T$
Solubility product of VC	$\log(K_{VC})$	$6.72 - 9500/T$

Except for the interface energy, the physical constants are from Gladman [7].

In the case of the  $VC_yN_{1-y}$  compound, Eq. (6) can be generalised. The chemical potentials  $\mu_i$  are developed as a function of the molar fractions in solid solution  $X_i^{ss}$  according to the regular matrix solid solution assumption, and the equilibrium fractions  $X_i^e$  are introduced. This leads to the following expression [8,9]:

$$\Delta g = -\frac{RT}{V_{VCN}} \left[ \ln \left( \frac{X_V^{ss}}{X_V^e} \right) + y \ln \left( \frac{X_C^{ss}}{X_C^e} \right) + (1-y) \ln \left( \frac{X_N^{ss}}{X_N^e} \right) \right], \quad (7)$$

where  $V_{VCN}$  is the molar volume of the vanadium carbonitride. Taking into account that the molar volume of VC and VN are almost identical,  $V_{VCN}$  is considered here to be independent of the composition  $y$  (see Table 3).

#### 3.3.2. Composition of the critical nucleus

Using Eq. (4), the unknown equilibrium compositions in the solid solution in Eq. (7) are replaced by the solubility products  $K_{VC}$  and  $K_{VN}$

$$\Delta g(y) = -\frac{RT}{V_{VCN}} \ln \left[ \frac{(X_V^{ss})(X_C^{ss})^y (X_N^{ss})^{1-y}}{(yK_{VC})^y [(1-y)K_{VN}]^{1-y}} \right]. \quad (8)$$

Here,  $\Delta g$  is a function of  $y$ . We state that the nuclei that appear in the matrix are those that produce the maximum variation of Gibbs energy during their formation. The composition of the critical nucleus is then the value of  $y$  that minimises the driving energy (8) for nucleation. The expression is found to be

$$y_g = \left[ 1 + \frac{X_N^{ss} K_{VC}}{X_C^{ss} K_{VN}} \right]^{-1}. \quad (9)$$

This equation shows that the composition  $y_g$  of the critical nucleus does not depend on the vanadium concentration in solid solution, and depends exclusively on

- the temperature, via the ratio  $K_{VC}/K_{VN}$ ,
- the composition in C and N of the solid solution, via the ratio  $X_C^{ss}/X_N^{ss}$ .

Notice that Eq. (9) relates in a linear way the ratio C/N in the critical nucleus to the ratio C/N in solid solution

$$(X_C/X_N)_{\text{nucleus}} = (K_{VN}/K_{VC})(X_C/X_N)_{\text{matrix}}. \quad (10)$$

It appears from Eq. (10) and Table 2 that for a given  $X_C^{\text{ss}}/X_N^{\text{ss}}$  ratio, a decrease in temperature leads to an enrichment in carbon of the carbonitride. On the other hand, if carbon and nitrogen in solid solution are of equal order of magnitude, the nucleus will be very rich in nitrogen, similar to a pure vanadium nitride. In particular, for the ratio C/N  $\cong$  15, characteristic of our reference steel, the composition of the carbonitride is VC<sub>0.1</sub>N<sub>0.9</sub>. The explanation for this is as follows: as we have seen previously, the nitride VN is much more stable thermodynamically than the carbide VC. Then, it is the nucleation of VN that reduces most of the total Gibbs energy. This is rendered by the ratio  $K_{VC}/K_{VN} \gg 1$  present in Eq. (9). The counterbalance of this effect of relative stability is possible if the carbon concentration in solid solution is increased relative to the nitrogen concentration. Hence at 800 °C, nuclei of equimolar composition will appear if the carbon concentration in solid solution is approximately 110 times that of nitrogen.

### 3.3.3. Radius of the critical nucleus

Given the composition of the critical nucleus, its radius can be calculated. The Gibbs energy for the formation of an embryo,  $\Delta G$  (Eq. (5)), reaches a maximum value  $\Delta G^*$  for a particular value of  $R$ , the critical radius  $R^* = -2\gamma/\Delta g(y_g)$ .  $R^*$  corresponds to a nucleus that is in equilibrium with the matrix, taking into account the radius-dependent Gibbs–Thomson effect. For a precipitate to be able to grow effectively, it has to have a radius  $R'$  slightly higher than  $R^*$  such that  $\Delta G(R') = \Delta G^* - k_B T$ , where  $k_B$  is the Boltzmann constant.  $R'$  is the solution of the following equation:

$$R^3 + \frac{3\gamma}{\Delta g} R^2 = \left[ \frac{4}{3} \frac{\gamma^3}{\Delta g^3} - \frac{3k_B T}{4\pi\Delta g} \right]. \quad (11)$$

The approximate solution

$$R' = R^* + \frac{1}{2} \sqrt{\frac{k_B T}{\pi\gamma}}, \quad (12)$$

proves to be precise enough in practice.

In the Multipreci model, we treat the nucleation stage at each time step as follows: a new class is introduced in the histogram of size of radius  $R'$  and composition  $y_g$  according to Eqs. (9) and (12). The number of precipitates per volume  $N$  of size  $R'$  is given by the classical non-stationary nucleation rate equation [10]

$$\frac{dN}{dt} = N_0 \exp\left(-\frac{\Delta G^*}{kT}\right) \Gamma Z \left[1 - \exp\left(-\frac{t}{\tau}\right)\right], \quad (13)$$

where  $N_0$  is the number of substitutional sites per volume in austenite,  $\Gamma$  the absorption frequency of a

vanadium atom by the critical nucleus,  $Z$  is the Zeldovitch constant and  $\tau$  is the incubation time. Note that the incorporation of the Zeldovitch constant in this equation is consistent with the choice of  $R'$  as the radius of the precipitates introduced by nucleation.

### 3.4. Growth

For each individual class of particle of radius  $R$ , the growth rate has to be established as a function of the composition of the solid solution. Carbon and nitrogen, being interstitial elements, are very fast diffusing species compared to vanadium. As a result, the growth of a precipitate is limited by the diffusion of vanadium from the matrix towards the precipitate. A gradient in vanadium concentration builds around the precipitate while the concentration profiles of carbon and nitrogen are almost flat.

To a very good approximation, the quasi-stationary approximation for the diffusion profiles can be applied. From the mass balance at the precipitate/matrix interface the classical Zener equation for the growth rate is derived [11]. For vanadium, the equation is

$$\frac{dR}{dt} = \frac{D_V}{R} \frac{X_V^{\text{ss}} - X_V^i}{\frac{V_{\text{Fe}}}{V_{\text{VCN}}} - X_V^i}. \quad (14)$$

During an isothermal precipitation treatment, the composition of vanadium in solid solution  $X_V^{\text{ss}}$  decreases, and consequently the growth rate decreases. In the meantime, the composition of vanadium at the interface  $X_V^i$  evolves. Note that Eq. (14) is also valid for dissolution, a feature that is used for the modelling of the coarsening phenomenon (see Section 3.5).

Growth occurs by accretion of successive shells of carbonitrides. Each shell has its specific composition  $y_c$ . The calculation of the shell composition is done together with the calculation of the matrix composition in the vicinity of the interface by the simultaneous resolution of the local equilibrium and a flux-compatibility condition:

- The local equilibrium of the shell with the surrounding matrix is given by Eq. (4)

$$yK_{VC} = X_V^i \cdot X_C^i, \quad (15)$$

$$(1 - y)K_{VN} = X_V^i \cdot X_N^i.$$

- The composition of the precipitating shell has to be compatible with the flux of precipitating species. This can be written in a simplified way as  $J_C = yJ_V$  and  $J_N = (1 - y)J_V$ . According to the quasi-stationary assumption, this leads to

$$D_C(X_C^i - X_C^{\text{ss}}) = yD_V(X_V^i - X_V^{\text{ss}}), \quad (16)$$

$$D_N(X_N^i - X_N^{\text{ss}}) = (1 - y)D_V(X_V^i - X_V^{\text{ss}}).$$



At each time interval, the solution of the set of equations (15) and (16) gives the composition  $y_c$  of the shell and the concentrations  $X_V^i$ ,  $X_N^i$  and  $X_C^i$  at the interface. From the condition  $D_C \gg D_V$  and  $D_N \gg D_V$ , a very good approximation of the shell composition can be achieved, that is

$$y_c = \left[ 1 + \frac{X_N^{ss}}{X_C^{ss}} \frac{K_{VC}}{K_{VN}} \right]^{-1}. \quad (17)$$

It appears that, at each time interval, the composition of the shell is the same as that of the critical nucleus ( $y_c = y_g$ ), and is only driven by the composition in carbon and nitrogen of the solid solution. This can be understood by the following reasoning. Notice first that the composition of the shell is independent of the diffusion coefficients of carbon and nitrogen (Eq. (17)). This non-trivial result is due to the fact that C and N, being interstitial elements, are very fast diffusing species compared to V. As a result, the characteristic time for C and N diffusion towards the precipitate is much smaller than for V. In other words, C and N have enough time to equilibrate with one another around the particle during the precipitation of vanadium. They do so such that the Gibbs energy of the interfacial region is minimum. This minimisation criterion is exactly the one that led to the expression of the critical nucleus, implying that  $y_c = y_g$ .

### 3.5. Coarsening

Coarsening is the process by which the smallest precipitates dissolve to the profit of the bigger ones, leading to the coarsening of the size distribution. This phenomenon is particularly important when the system reaches the equilibrium precipitate fraction. It is to be noted that coarsening can occur at every stage of the precipitation process, even when the matrix is still supersaturated, as will be demonstrated by the numerical results later. The coarsening will automatically be dealt with by the class treatment as soon as the growth rate is written in a proper way as a function of the precipitate size. We proceed as follows.

The incorporation of the interface energy in the total energy of formation of a precipitation of radius  $R$  introduces an additional curvature-dependent term to the chemical potential of the precipitate, equal to  $2\gamma V_{VCN}/R$ . We introduce this term in the right-hand side of Eq. (1) and perform the calculation of the equations of local equilibrium of the shell with the surrounding matrix as in Section 3.2. This leads to a similar set of equilibrium equations as Eq. (4), where the solubility products of VC and VN have to be replaced by the radius-dependent functions  $K_{VC}(R)$  and  $K_{VN}(R)$

$$\begin{aligned} K_{VC}(R) &= K_{VC} \exp\left(\frac{2\gamma V_{VCN}}{RR_g T}\right), \\ K_{VN}(R) &= K_{VN} \exp\left(\frac{2\gamma V_{VCN}}{RR_g T}\right). \end{aligned} \quad (18)$$

In Eq. (18), the usual solubility products are just multiplied by a factor of  $\exp(2\gamma V_{VCN}/RR_g T)$ , where  $R_g$  is the gas constant. To treat the coarsening phenomenon, the radius-dependant solubility products are simply substituted for  $K_{VN}$  and  $K_{VC}$  in Eqs. (15) and (16). The solution of this modified system of equation allows for the incorporation of the Gibbs–Thomson effect on the concentrations  $X_V^i$ ,  $X_N^i$  and  $X_C^i$  at the interface. The interface compositions are affected in such a way that for supercritical precipitates ( $R > R^*$ ) the condition  $X_V^{ss} - X_V^i > 0$  applies. According to Eq. (14), those precipitates grow. On the contrary, the undercritical precipitates dissolve since for them  $X_V^{ss} - X_V^i$  is negative. This treatment renders in a natural way the coarsening phenomenon without any additional hypothesis.

In addition, it can be easily shown that the composition of the shell at a given time does not depend on the size of the precipitate, and is still given by Eq. (17).

## 4. Results of the model

### 4.1. Calculation procedure

The model is programmed in FORTRAN language. In addition to the physical constants, an initial state of precipitation can be introduced. The model computes the histogram of size at each time along any thermal cycle, including stages of reheating and cooling. The calculation proceeds iteratively: at each time step, nucleation introduces a new class of size in the histogram and the new radius of every existing class is computed. The mass balance in the system gives the new composition of the solid solution, before the next calculation loop. The calculations presented in this section run in less than 1 min on a PC computer.

### 4.2. Entry data

The Multipreci model is applied here to isothermal treatments of the model alloy presented above. The entry data of the model are summarised in Table 3.

### 4.3. Isotherms of 800 and 900 °C

The isotherm at 800 °C illustrates the various steps of precipitate formation through the stages of nucleation, growth and coarsening. Those stages are in fact non-fully differentiated as discussed in detail in the following sections. The isotherm at 900 °C is used to illustrate the

non-trivial coarsening stage that occurs with composition-varying particles.

4.3.1. Isotherm of 800 °C

As can be seen in Fig. 4(a), the nucleation rate of the particles increases rapidly during the first 5 s of transitory nucleation stage. The precipitates that form are

nitrogen rich VC<sub>0.1</sub>N<sub>0.9</sub> (Fig. 4(g)). It can be shown that the presence of nitrogen increases considerably the nucleation rate of the precipitates, since the driving energy for the nucleation of VC<sub>0.1</sub>N<sub>0.9</sub> is much higher than that of VC (see Section 3.2). During the nucleation stage, nitrogen and vanadium are consumed from the matrix, which decreases the driving energy and tends

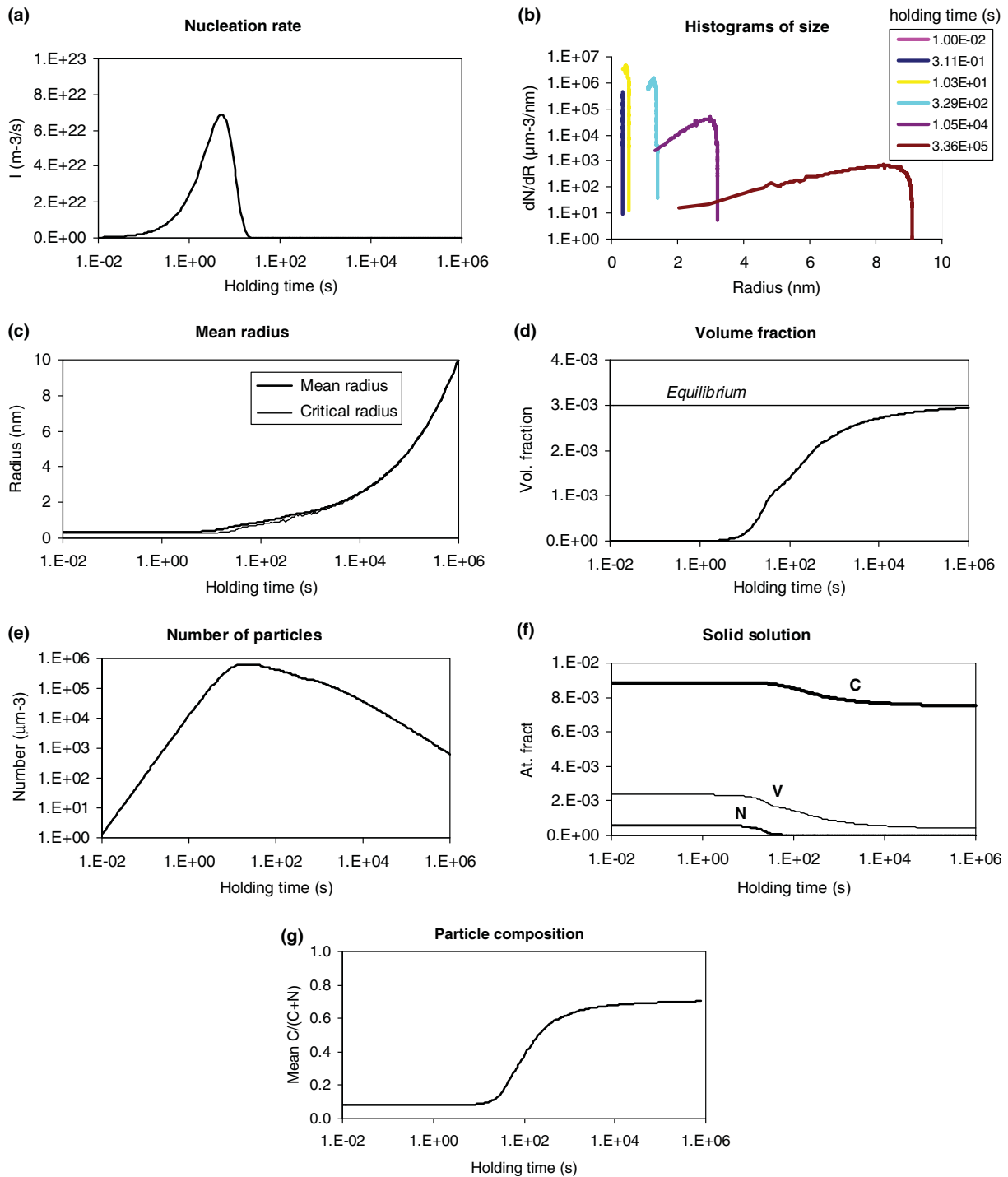


Fig. 4. Results of the calculations for the holding temperature of 800 °C. The entry data are in Table 3: (a) nucleation rate, (b) histograms of size, (c) mean radius, (d) volume fraction, (e) volume number of particles, (f) solid solution, and (g) mean particle composition.

to slow down the nucleation rate. The initial critical radius of nucleation is about 0.3 nm (Fig. 4(c)). After  $\sim 20$  s, the composition of the solid solution reaches a value where the nucleation rate is practically zero and nucleation stops.

From this point, the number of particles begins to decrease (Fig. 4(e)). A transitory coarsening stage occurs, during which the critical radius has not yet reached the average radius (Fig. 4(c)). After  $\sim 35$  s, almost all nitrogen initially in solid solution has been consumed from the matrix and growth now proceeds by precipitation of carbon and vanadium in the form of VC shells (Fig. 4(f)). As a result, the average carbon composition of the precipitates grows slowly.

A time  $t = 500$  s, the critical radius has reached the mean radius of the particles and coarsening develops in a quasi-steady state manner, leading to an endless growth of the mean radius of the particles and a steady decrease of their total number per unit volume (Fig. 4(c) and (e)). The composition of the precipitates reaches its equilibrium value of  $y = 70\%$  after  $10^6$  s of annealing. In the meantime, the volume fraction of the precipitates has increased towards its equilibrium value of 0.3%.

Fig. 4(b) shows the time evolution of the size histogram. Nucleation builds up the histogram initially around small radii. The whole distribution shifts to the right by growth. After a while, coarsening is visible in the decrease of the total number of particles and the shift of the mean radius. The shape of the histograms

at long holding times is qualitatively similar, but not identical to the theoretical LSW distribution. This fact is extensively discussed in [12] and will be published in the future.

Fig. 5 is a schematic representation of the evolution of the successive shell accretions that form the precipitates. Starting from a nitrogen rich core, the successive shells are richer and richer in carbon. The overall composition of the particle is that of a carbonitride V(C,N). During the growth of the precipitates, their composition is likely to homogenise somewhat by internal interdiffusion of carbon and nitrogen. This phenomenon is not taken into account in the model, but it is supposed to have an effect on the kinetics of growth and the final state of precipitation.

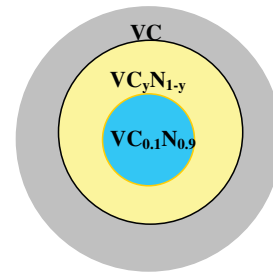


Fig. 5. Schematic representation of the accretion sequence that forms a V(C,N) precipitate.

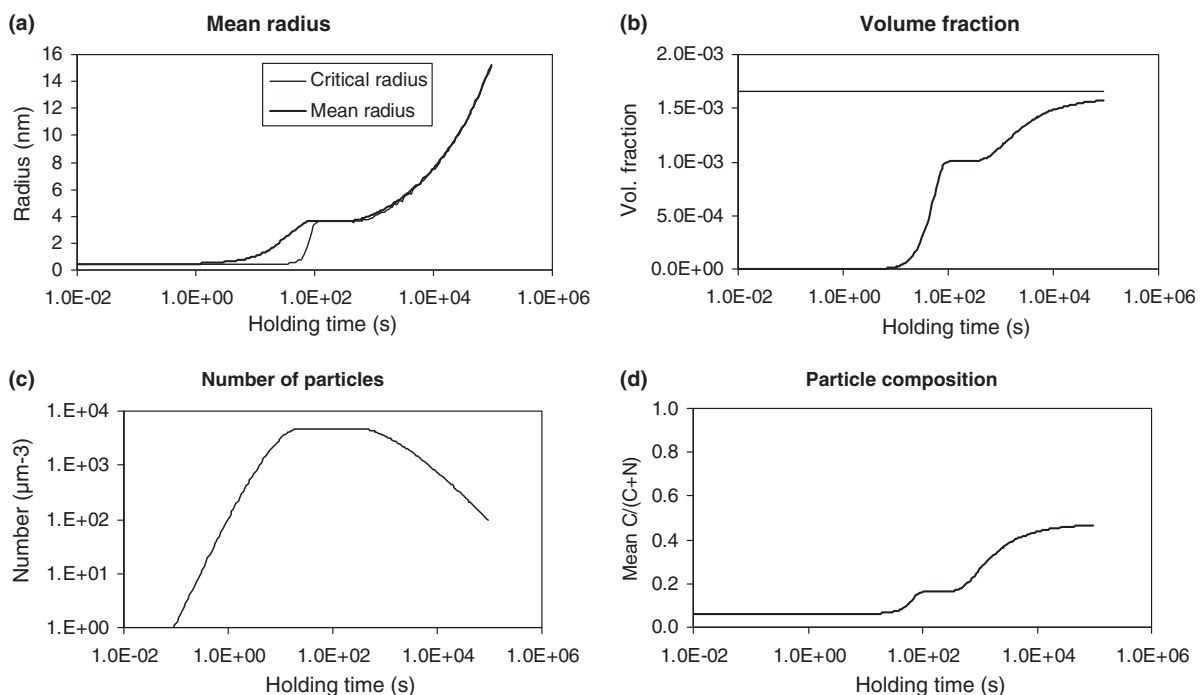


Fig. 6. Results of the calculations for the holding temperature of 900 °C. The entry data are in Table 3: (a) mean radius, (b) volume fraction, (c) volume number of particles, and (d) mean particle composition.



#### 4.3.2. Isotherm of 900 °C

At 900 °C, precipitation occurs in three steps: the first step, corresponding to time  $t < 200$  s, is the nucleation and growth of nitrogen-rich particles (see Fig. 6). A stasis period follows ( $200 \text{ s} < t < 500$  s), during which the size histogram evolves at constant total number and mean radius of the particles. After 500 s, an atypical coarsening phenomenon is at work: indeed, the total number of particles decreases while the mean radius increases, as a result of the growth of the big particles at the expense of the smallest. However, this occurs while in the meantime the mean composition of the particles evolves from  $y = 6\%$  to  $50\%$ , and while the volume fraction increases from  $0.1\%$  towards its equilibrium value of  $0.165\%$ . This leads to a deviation from the usual time-scaling laws of  $R^3 \propto t$  and  $N^{-1} \propto t$ .

### 5. Conclusion

The model presented here proposes a methodology that solves the difficulty of dealing with tri-atomic and composition-varying precipitates. This approach allows for the simple account of nucleation, growth and coarsening of M(C,N)-type carbonitrides. The application of the model to a Fe–V–C–N alloy illustrates the prominent role of nitrogen in the precipitation sequence and kinetics. This approach will be extended in the future

to the case of (M,M')(C,N) mixed carbonitrides (M,M' = V, Nb, Ti).

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