SIMULATION OF EVOLUTION OF CARBONITRIDE PRECIPITATE ENSEMBLES OF SEVERAL COMPOSITIONS IN STEELS DOPED WITH STRONG CARBONITRIDE-FORMING ELEMENTS

PASYNKOV A.Yu.*, POPOV V.V., GORBACHEV I.I.

*M.N. Miheev Institute of Metal Physics, UB RAS, Ekaterinburg, Russian Federation, apasynkov@list.ru**

Abstract

A numerical method of simulation of evolution of complex precipitates in multiphase multicomponent systems is suggested. This method is based on the mean field approximation for the description of evolution of the pre-existing particles and on the classical theory of nucleation for calculation of the rate of formation of new nuclei. It takes into account the polydispersity of precipitate ensembles and can be used at all the stages of precipitates evolution, namely, nucleation, growth, dissolution, coarsening and transition stages between the growth or dissolution and coarsening. The application of this method is demonstrated by an example of carbonitrides evolution in low-carbon steel doped with Ti and Nb.

Keywords: Precipitate evolution, computer simulation, nucleation, multicomponent system

1. INTRODUCTION

The description of precipitate evolution in metal alloys is an extremely intricate problem, and its analytical solution is possible only for the simplest cases. That is why there appeared a wide number of studies dealing with numerical simulation of precipitates evolution and its effect on the structure (see e.g. [1 - 5]). An approach developed in our publications [6 - 7] is more universal compared to those realized in other studies, particularly, in [8 - 10]. In our recent studies this approach was generalized on a case of multiphase multicomponent systems, and calculations of evolution of carbonitrides in steels without considering the possibility of nuclei formation were performed [11, 12].

The goal of the present work is to extend the elaborated method to the case of multiphase multicomponent systems in which the formation of new nuclei is possible in the process of isothermal annealing.

2. FORMULATION

Several assumptions were made in simulation. It was assumed that all precipitates are of spherical shape and constant composition, the local equilibrium is established at interfaces and mass transfer is accomplished by bulk diffusion in the main phase (matrix). Besides, the effect of elastic stresses on the conditions of local equilibrium and mass transfer in the system was not taken into account.

In the proposed model the initial data are composition of an alloy, compositions and volume fractions (Ff) of excess phases and particle size distributions (PSD) at an initial moment for every phase. The PSD for every phase is given by its own histogram. In these histograms particles of k-th size class are related to a fraction of the particles falling into the corresponding size interval. The method is based on the use of the mean field approximation in which it is believed that component concentrations of all the elements at a certain distance from the particles are equal (the same mean environment). The mean field approximation requires certain assumptions, which correlate the extension of transport fields associated particles (i.e., the sizes of their spheres of influence) with the particle sizes and their volume fraction. By now there have been suggested a number of geometrical models for field cells construction. As demonstrated earlier, in a case when the volume fraction of a precipitating phase is relatively low, calculations using different geometrical models of field cells give approximately the same results [13], and the choice of this or that geometrical model is inessential. As it is just the case considered in simulation of carbide evolution in steels (small volume fraction of precipitates), we use the model suggested in [13], in which a field cell radius connected with a particle of phase f in the l-th size interval is proportional to the particle radius ${}^fR_l$ and inversely proportional to a cubic root of the total volume fraction of precipitates:

$$ {}^fR_l^L = {}^fR_l\left(\sum_f F_f\right)^{-1/3} \tag{1} $$

A system of diffusion equations describing substance fluxes in a cell connected with a particle of phase *f* in the *l*-th size interval for a (*N*+1)-component system is:

$$ \frac{\partial C_i^{fl}}{\partial \tau} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \cdot \sum_{j=1}^{N} \tilde{D}_{ij}\frac{\partial C_j^{fl}}{\partial r}\right), \tag{2} $$

where C_j^{fl} $\mathrm{X}_\mathrm{i}^\mathrm{l}$ is concentration of the *i*-th component in field cell of *l*-th size interval for precipitations of *f*-th composition; $\tilde{D}_{ij}$ $\tilde{\mathrm{D}}_{\mathrm{ij}}$ are partial interdiffusion coefficients in a matrix and *r* is a spatial variable.

The stationary field approach was used for determination of concentration distributions of elements in field cells as it was also done in the previous studies [7], [11], [12]. In this case equation (2) takes the form:

$$ \sum_{j=1}^{N} \tilde{D}_{ij}\frac{\partial C_j^{fl}}{\partial r} = \frac{{}^fK_i^l}{r^2}, \tag{3} $$

where ${}^fK_i^l$ is a constant for the *i*-th element in a cell of the *l*-th size interval for precipitates of phase *f*.

The mass balance at an interface for precipitates of phase *f* in the *l*-th size interval is:

$$ \left[C_i^f\, \upsilon_m^M / \upsilon_m^f - {}^{M/f}C_i^{fl}\right]\frac{d\,{}^fR_l}{d\tau} = \left.\frac{{}^fK_i^l}{r^2}\right|_{r=R_k}, \tag{4} $$

where υ_m^M and υ_m^f are average atom volumes of austenite matrix and excess phases respectively; C_i^f is concentration of the *i*-th element in phase *f*; ${}^{M/f}C_i^{fl}$ is concentration of the *i*-th element in matrix at an interface with particles of phase *f* in the *l*-th size interval.

The local thermodynamic equilibrium conditions at an interphase boundary have the form:

$$ \overline{G}_i^{p/m} + \frac{2\cdot\sigma\cdot\upsilon^p}{R_k} = \overline{G}_i^{m/p}, \tag{5} $$

where $\overline{G}_i^{p/m}$ and $\overline{G}_i^{m/p}$ are chemical potentials of *i*-th element at an interface in particle and matrix respectively; σ is a specific surface energy of an interface; υ^p is volume of one formula unit of precipitate phase.

Additionally, as the quasi-stationary approach is used, the above given set of equations should be supplemented with the mass conservation condition which must be satisfied by calculated average component concentrations in matrix:

$$\sum_f \alpha_f C_i^f + (1-\sum_f \alpha_f)\bar{C}_i = C_i^0 , \tag{6}$$

where α_f are the mole fractions of precipitating phases, $\bar{C}_i$ is average concentration of solute component in the matrix, C_i^0 is concentration of the i-th element in the alloy.

Average values of component concentrations in a matrix are expressed through concentration distributions in cells given by net functions as follows:

$$\bar{C}_i = \frac{\sum_{f=1}^{S}\sum_{l=1}^{m_f} {}^fH_l \sum_{k=1}^{n_f} \frac{\gamma C_i^{fl}(k_f)+C_i^{fl}(k_f-1)}{2}\left({}^f r_l^3(k_f) - {}^f r_l^3(k_f-1)\right)}{\sum_{f=1}^{S}\sum_{l=1}^{m_f} {}^fH_l\left(({}^fR_l^L)^3-({}^fR_l)^3\right)} , \tag{7}$$

where m_f is the number of size intervals for particles of phase f; k_f is node number in a cell associated with precipitate of f-th composition; N_f is the number of particles of phase f in a unit volume; S is the number of excess phases in an alloy; ${}^fH_l$ is the fraction of particles of this phase falling into this interval among the precipitates of all compositions. The value of ${}^fH_l$ is calculated as:

$${}^fH_l = {}^fh_l N_f \Big/ \sum_{f=1}^{S} N_f , \tag{8}$$

where N_f is the number of particles f in a unit volume:

$$N_f = \sum_{l=1}^{m_f} \frac{F_f\,{}^fh_l}{4/3\,\pi\left({}^fR_l\right)^3} \tag{9}$$

The calculation of nucleation rate was performed based on the classical nucleation theory. Nucleation of carbide precipitates in steels was considered by a number of researchers, e.g. by Dutta and Sellars [14], Liu and Jonas [15], [16], Gustafson and Agren [17] and Bhadeshia et al. [18 - 20]. As in [7], we used an approach developed by Liu and Jonas [15], [16], who showed that if the nuclei were formed at dislocations then the rate of nucleation and Gibbs energy of a critical size nucleus can be calculated by the formulas:

$$\mathrm{J} = \rho D_{eff}\, X / a^3 \exp\left(-\frac{\Delta G_{crit}}{RT}\right) \tag{10}$$

$$\Delta G_{crit} = \frac{16\pi\zeta^3\sigma_n^3}{3\left(\Delta G_{chem} + \Delta G_{\varepsilon}\right)} \tag{11}$$

where ρ is the dislocation density; a is matrix lattice period; R is the universal gas constant; T is temperature, K, ΔG_{crit} is the system energy change at the formation of one mole of critical size nuclei of a new phase, D_{eff} and X are effective diffusion coefficient and concentration of an element controlling the nucleation process. In the case considered the latter are concentrations of carbonitride-forming elements in a matrix at interfaces with carbonitride precipitates and effective diffusion coefficients of these elements in austenite. The σ_n is specific surface energy of a nuclei/matrix interface, ς is a correcting multiplier to the surface energy of an interphase boundary connected with the presence of dislocations, the value of which falls between 0 and 1, ΔG_{chem} and ΔG_{ε} are changes of chemical free energy and free energy of stresses at the formation of a new phase unit volume.

3. NUMERICAL CALCULATIONS PROCEDURE

The procedure of numerical calculations is to a great extent similar to that used in [7]. The main difference is that in the present case we consider evolution of precipitates of several phases of complex composition.

The calculation order is as follows.

1) Calculation of field cell sizes connected with particles of all excess phases for different size intervals by the formula (1).
2) Construction of spatial nets in field cells for all phases and all size intervals.
3) Calculation of concentration of elements at cell boundaries corresponding to the mass conservation condition (6).
4) Calculation of component concentration distributions in cells and velocities of interphase boundaries for particles of all excess phases in all size intervals by the equations (3)-(5).
5) Calculation of precipitate nucleation rate for all excess phases by the equations (10)-(11).
6) Calculation of particle size distributions and volume fractions of all excess phases at a new time layer without consideration for the formation of new nuclei.
7) Calculation of particle size distributions and volume fractions for all excess phases at a new time layer with consideration for nucleation processes.

The equations (3)-(6) were solved numerically by Newton's method for systems of equations using the finite difference method to calculate the distributions of concentrations of the components in the cells. The as-determined values of volume fractions of excess phases and their PSDs were used as the initial ones for calculations at a new time layer, etc. This procedure was repeated till the required time was reached.

Separate steps of these calculations are described in more detail in [7], [11], [12].

4. CALCULATION RESULTS

As an example, in the present study the calculations were performed for precipitate evolution in low-carbon steels, doped with Nb and Ti, under their holding in the austenite region. The steel composition was as follows (wt. %): 0.1C, 0.008N, 0.02Nb and 0.015Ti. The calculations were done for a temperature range of 900-1000 °C.

According to thermodynamic calculations performed with our program IMP Equilibrium, there are two carbonitrides in equilibrium with austenite in this temperature range. Composition of the first is $Nb(C_{0.77}N_{0.23})_{0.97}$ and of the second is $(Ti_{0.85}Nb_{0.15})(C_{0.01}N_{0.99})$. For convenience, they can be denoted as Nb(CN) and (Ti,Nb)N. So, it was assumed in the simulation that the excess phases are absent at the initial state, and nucleation, growth and coarsening occur under further isothermal annealing. **Figure 1** demonstrates temporal dependences of precipitates volume fractions and average radii at 900, 950 and 1000 °C for a case of complete absence of excess phases at the initial state. The volume fraction of Nb(CN) grows quite slowly with increasing temperature, compared to the (Ti,Nb)N. About 40 000 seconds are required to achieve the volume fraction of this phase close to equilibrium one at 900 °C. With further annealing the volume fraction of these precipitates is not changed and the coarsening stage begins, during which the particle radii increase significantly slower than at the growth stage. Both time to reach the equilibrium value and the equilibrium volume fraction itself of Nb(CN) decrease with temperature increasing.

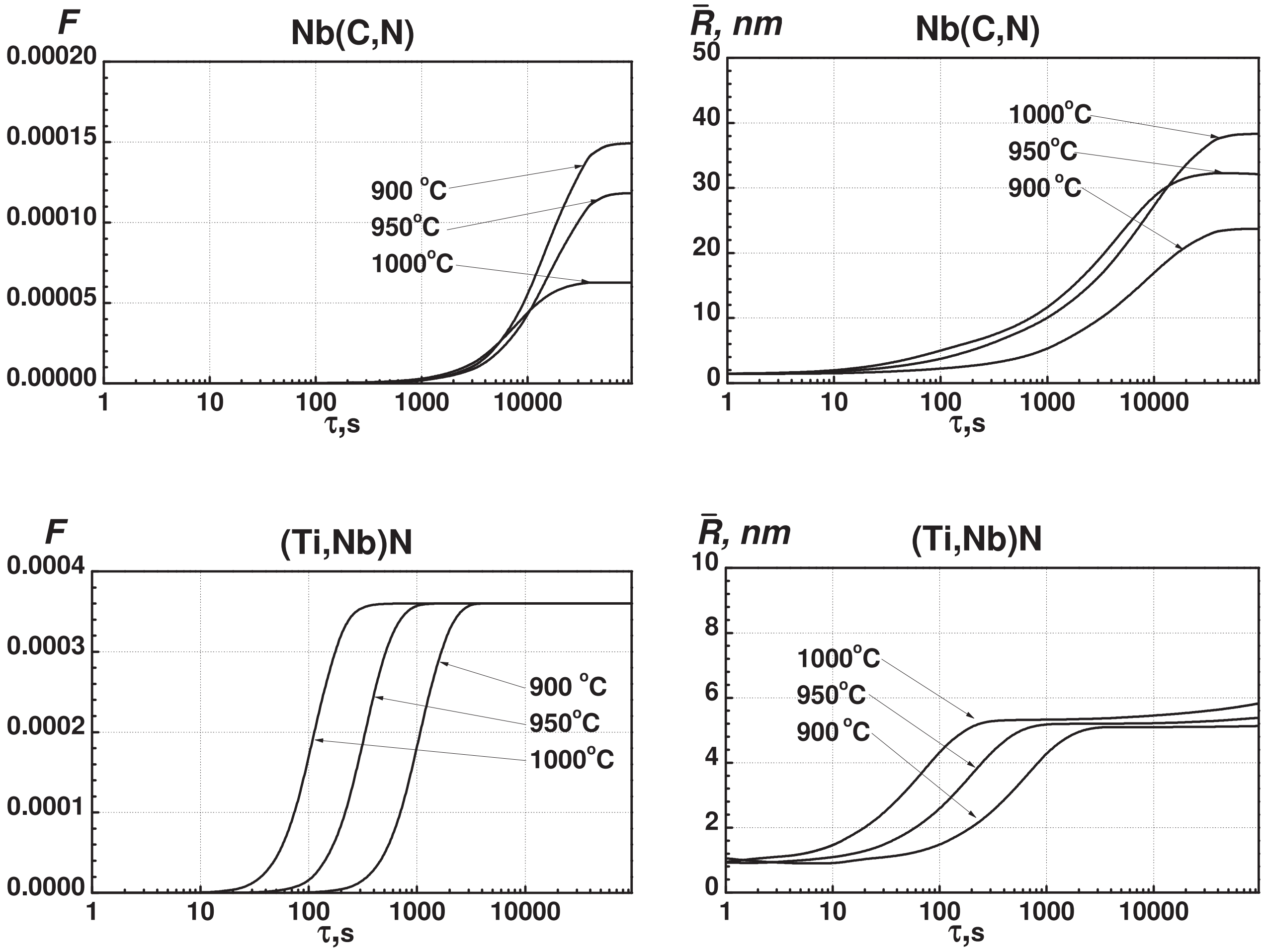

Figure 1 Change in volume fraction and average radius of the precipitates under annealing at different temperatures of steel having following composition (wt. %): 0.1C, 0.008N, 0.02Nb and 0.015Ti

The equilibrium volume fraction of another carbonitride phase (Ti,Nb)N is almost independent of annealing temperature in the temperature range 900 - 1000 °C. However, the time to reach the equilibrium volume fraction of this phase and, respectively, the start of coarsening stage decrease with increasing temperature. The latter begins after 300 seconds for (Ti,Nb)N at the highest temperature of the calculations.

5. CONCLUSION

A method of simulation of precipitate evolution in multiphase multicomponent systems based on the use of the mean field approach has been suggested. This method is a development of the approach worked out previously for two-phase systems. The method suggested enables in the framework of one approach to simulate evolution of complex precipitate ensembles of several phases at different stages, such as nucleation, growth, dissolution, coarsening and intermediate stages. It takes into account finite volume fraction of precipitates, polydispersity of precipitates ensemble and diffusion interaction of elements in the matrix phase. On the basis of the proposed method simulation of evolution of precipitates of two compositions was performed for the system Fe-Ti-Nb-C-N, modelling a real low-carbon low-alloyed steel.

ACKNOWLEDGEMENTS

This work was performed in the framework of the state assignment of FASO of Russia (theme "Spin" No. 01201463330) and supported in part by the Program of Fundamental Research of UB RAS (grant No. 15-9-2-44) and RFBR (grant No. 16-38-00164).

REFERENCES

[1] VOORHEES, P.W., GLICKSMAN, M.E. Solution to the multi-particle diffusion problem with applications to Ostwald ripening-I. Theory. *Acta Metallurgica*, 1984, vol. 32, pp. 2001-2011.

[2] ENOMOTO, Y., KAWASAKI, K., TOKUYAMA, M. Computer modelling of Ostwald ripening. *Acta Metallurgica*, 1987, vol. 35, pp. 907-913.

[3] MANDYAM, H., GLICKSMAN, M.E. Late-stage coarsening dynamics in phase separating systems: simulation results. *Materials Science and Engineering*, 1997, A238, pp. 121-127.

[4] SHAHANDEH, S., MILITZER, M. Grain boundary curvature and grain growth kinetics with particle pinning. *Philosophical Magazine*, 2013, vol.93, pp. 3231-3247.

[5] ARDELL, A.J. The effects of elastic interactions on precipitate microstructural evolution in elastically inhomogeneous nickel-base alloys. *Philosophical Magazine*, 2014, vol.94, pp. 2101-2130.

[6] POPOV, V.V., GORBACHEV, I.I. Simulation of the Evolution of Precipitates in Multicomponent Alloys. *The Physics of Metals and Metallography*, 2003, vol. 95, pp. 417-426.

[7] POPOV, V.V., GORBACHEV, I.I., ALYABIEVA, J.A. Simulation of VC precipitate evolution in steels with consideration for the formation of new nuclei. *Philosophical Magazine*, 2005, vol.85, pp. 2449-2467.

[8] SVOBODA, J., FISCHER, F.D., FRATZL, P., KOZESCHNIK, E. Modelling of kinetics in multi-component multi-phase systems with spherical precipitates: I: Theory. *Materials Science and Engineering*, 2004, A385, pp. 166-174.

[9] KOZESCHNIK, E., SVOBODA, J., FISCHER, F.D. Modified evolution equations for the precipitation kinetics of complex phases in multi-component systems. *CALPHAD*. 2004, vol. 28, pp. 379-382.

[10] SRINIVAS, P.B., RAJKUMAR, V.B., HARI, K.K.C. Numerical simulation of precipitate evolution in ferritic-martensitic power plant steels. *CALPHAD*, 2012, vol.36, pp.1-7.

[11] POPOV, V.V., GORBACHEV, I.I., PASYNKOV, A.YU. Simulation of evolution of precipitates of two carbonitride phases in Nb- and Ti- containing steels during isothermal annealing. *The Physics of Metals and Metallography*, 2013, vol.114, pp. 741-751.

[12] POPOV, V.V., GORBACHEV, I.I., PASYNKOV, A.YU. Simulation of Precipitate Ensemble Evolution in Steels with V and Nb. *The Physics of Metals and Metallography*, 2015, vol.116, pp. 356-366.

[13] TSUMURAYA, K., MIYATA, Y. Coarsening models incorporating both diffusion geometry and volume fraction of particles. *Acta Metallurgica*, 1983, vol.31, pp. 437-453.

[14] DUTTA, B., SELLARS, C.M. Effect of composition and process variables on Nb(C, N) precipitation in niobium microalloyed austenite. *Materials Science and Technology*, 1987, vol.3, pp. 197-206.

[15] LIU, W.J., JONAS, J. Characterisation of critical nucleus/matrix interface: application to Cu-Co alloys and microalloyed austenite. *Materials Science and Technology*, 1989, vol. 5, pp. 8-9.

[16] LIU, W.J., JONAS, J. Nucleation kinetics of Ti carbonitride in microalloyed austenite. *Metallurgical and Materials Transactions A*, 1989, vol. 20, pp. 689-697.

[17] GUSTAFSON, A., AGREN, J. Modelling of carbo-nitride nucleationin 10% Cr steel. *Acta Materialia*, 1998, vol.46, pp. 81-90.

[18] YAMASAKI, S., BHADESHIA, H.K.D.H. Modelling and characterisation of V_4C_3 precipitation and cementite dissolution during tempering of Fe-C-V martensitic steel. *Materials Science and Technology*, 2003, vol.19, p. 1335- 1343.

[19] SOURMAIL, T., BHADESHIA, H.K.D.H. Modelling simultaneous precipitation reactions in austenitic stainless steels. *CALPHAD*, 2003, vol. 27, pp. 169-175.

[20] FUJITA, N., BHADESHIA, H.K.D.H., KIKUCHI, M. Precipitation sequence in niobium-alloyed ferritic stainless steel. *Modelling and Simulation in Materials Science and Engineering*, 2004, vol. 12, pp. 273-284.