MODELING OF THE KINETICS OF CARBONITRIDES PRECIPITATION PROCESS IN MICROALLOYED STEELS

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Abstract

Microalloying elements Ti, Nb, V, entered into steel they influence their microstructure and mechanical properties, because formation of carbonitrides, M (C, N), which in the high temperature inhibit the austenite grains growth and during the cooling of the austenite form fine precipitates giving the dispersion precipitation effect in ferrite. Influence of carbonitrides to the microstructure and mechanical properties depends on their basic stereological parameters: volume fraction, V_V, and their size, *r.* In this work the model of the kinetics of the carbonitrides precipitation which enable to predict the chemical composition of austenite as well as the size distribution of carbonitrides formed during isothermal annealing of supersaturated steel is presented. The model is based on the Kampmann and Wagner model developed using the classical theory of nucleation. Examples of applications of developed model are presented.

Keywords: Cellular automata, precipitation, carbonitrides, microalloying elements, microalloyed steel

1. INTRODUCTION

Carbonitrides precipitations of microalloying elements V, Nb and Ti, strongly influence the microstructure and mechanical properties of high strength low alloy steels. To predict the mechanical properties of these steels parameters of precipitates such as size (mean radius) and content (volume fraction) are required. Mathematical models describing the carbonitrides precipitation process enable to calculate these parameters [1, 2]. The development of computer science enables simulations of precipitation process. The models are based on the algebraic equations describing the nucleation and growth kinetics of precipitates.

Important group of structural steels are microalloyed steels with ferrite-pearlite microstructure, where high mechanical properties are achieved through small additions of elements such as Ti, Nb, V, introduced separately or comprehensively. These elements have high chemical affinity for interstitial elements C, N and form sparingly soluble compounds, carbides and nitrides. Due to the similarity of the crystal lattice these compounds exhibit mutual solubility which results in forming complex compounds carbonitrides, M (C, N).

The carbonitrides undissolved at austenitisation temperature inhibit the growth of austenite grains, providing a fine grain of supercooled austenite transformation products.

Effect of the carbonitride parameters, volume fraction, V_v, and the average radius of the precipitations, r, on the average radius of the austenite grains, R_a, describes the Smith-Zener equation [1]:

$$R_a = \frac{4 \cdot r}{3 \cdot V_v} \tag{1}$$

The effect of strengthening of ferrite by dispersed carbonitrides precipitations formed during the transformation austenite-ferrite as a result of reactions between elements dissolved in austenite is the second factor influencing the mechanical properties of microalloyed steel. This effect is described by Ashby-Orowan model [1]:

$$\Delta\sigma_e = \frac{10.8\cdot\sqrt{V_v}}{d}\cdot \ln\left(\frac{d}{6.125\cdot 10^{-4}}\right) \quad (2)$$

where:

$\Delta\sigma_e$ - increase of yield point (MPa)

d - mean diameter of carbonitride particles (μm)

Knowledge of parameters carbonitrides precipitations, both undissolved in austenite at high temperatures and formed in ferrite during phase transformations of undercooled austenite allows to predict the mechanical properties after manufacturing process using the knowledge of the steel chemical composition and process parameters. Carbonitride precipitations parameters, their contents, V_v and size distribution of precipitates can be calculated using mathematical models [3 - 7].

2. MODEL OF THE KINETICS OF CARBONITRIDES PRECIPITATION PROCESS

To calculate the kinetics of the carbonitrides precipitation process in the low alloy steel a model based on the classical theory of nucleation and growth (CNGT) was developed. CNGT is based on the change in free energy ΔG, associated with the formation of an embryo in a supersaturated solid solution. In the process of carbonitrides precipitation there are three stages: nucleation, growth and coalescence, which can occur simultaneously. The nucleation rate V_n, is described by the equation [1]:

$$V_n = \frac{dN}{dt} = N_0 \cdot Z \cdot \beta^* \cdot exp\left(-\frac{\Delta G^*}{k\cdot T}\right)\cdot exp\left(-\frac{\tau}{t}\right) \quad (3)$$

where:

β^* - the condensation rate of solute atoms in cluster of critical size

Z - Zeldovich parameter

N_0 - number of nucleation site per unit volume

ΔG^* - critical Gibbs free energy for nucleus formation

k- Boltzmann constant

T - temperature

τ - incubation time

t - time.

Embryo critical radius r^*, and parameters β^* and Z represent the following equations [1]:

$$r^* = -\frac{2\cdot\gamma}{\Delta G_v} \quad (4)$$

$$\beta^* = \frac{4\cdot\pi\cdot(r^*)^2\cdot D\cdot X}{a^4} \quad (5)$$

$$Z = \frac{v_{at}^p}{2\cdot\pi\cdot(r^*)^2}\cdot\sqrt{\frac{\gamma}{k\cdot T}} \quad (6)$$

The incubation time τ, is given by equation [1]:

$$\tau = \frac{4}{2\cdot\pi\cdot\beta^*\cdot Z^2} \quad (7)$$

where:

γ - interphase boundaries energy

ΔG_v - the driving force for precipitation per unit volume

D - diffusion coefficient of the metallic element

X - a fraction of the atomic metallic element dissolved in matrix

a- lattice parameter

V_{at}^{p} - the average volume of an atom in precipitation

In the case of the formation of precipitates of carbonitrides, described by formula MC_yN_{1-y} driving force of nucleation is equal to [1]:

$$\Delta G_v = -\frac{R \cdot T}{V_{MCN}} \cdot \left[\ln\left(\frac{X_M^S}{X_M^e}\right) + y \cdot \ln\left(\frac{X_C^S}{X_C^e}\right) + (1-y) \cdot \ln\left(\frac{X_N^S}{X_N^e}\right) \right] \quad (8)$$

where:

X_i^S - the atomic fraction of the component X in the solution

X_i^e - equilibrium atomic fraction of component X in solution

Growth rate V_{gr} is described by equation [1]:

$$V_{gr} = \frac{dr}{dt} = \frac{D}{r} \cdot \left(\frac{X - X^i(r)}{\alpha \cdot X^p - X^i(r)}\right) \quad (9)$$

where:

D - diffusion coefficient of metal M

X, X^p - atomic fractions of X in matrix and in precipitate

X^i(r) - equilibrium solute fraction of X at precipitate/matrix interface taking into account the Gibbs-Thomson effect

α - ratio of matrix to precipitate volumes

In the last stage the precipitations undergo the coagulation process involving of dissolution of small precipitates and growing of large precipitation at constant V_v and $r = r^*$. The coarsening process of precipitates is described by equation [1]:

$$V_{coarse} = \frac{dr}{dt} = \frac{4}{27} \cdot \left(\frac{X^i}{\alpha \cdot X^p - X^i}\right) \cdot \frac{2 \cdot \gamma \cdot v_{at}^p}{k \cdot T} \cdot \frac{D}{r^2} \quad (10)$$

Consequently, mean radius, r, of precipitates is an increasing function of time. As a result, the particle density N_v, decreases and size distribution as a probability density function, g(r), with a negative asymmetry moves toward larger particle size.

3. RESULTS

In C# was written and implemented in the Visual Studio 2010 the MPCA program (Marynowski Przemysław Cellular Automata). Graphical interface was added. The following input data are introduced through the interface: the chemical composition of steel, supersaturation, precipitation temperature and time isothermal heating. The following parameters are calculated by the model: nucleation rate, the chemical composition of the matrix, distribution function for the size of precipitates and an average size of precipitates.

Steel containing 0.84 % C, 0.06 % Nb and 0.015 % N subjected to heat treatment austenitization at 1200 °C with following isothermal holding at 980 °C for 20 h time was considered.

Example of analysis of carbonitride Nb(C,N) precipitation process in the low alloy steel is presented in **Figures 1, 2, 3, 4** and **5.**

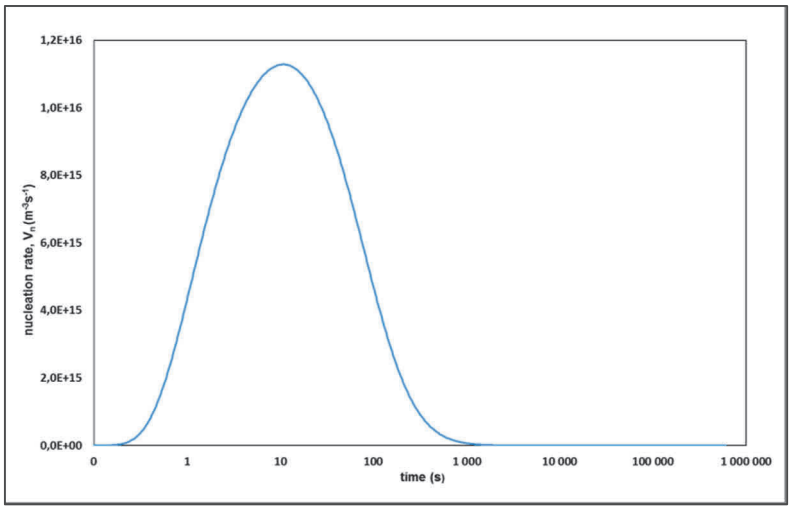

Figure 1 Relationships between nucleation rate and time at T = 980 °C

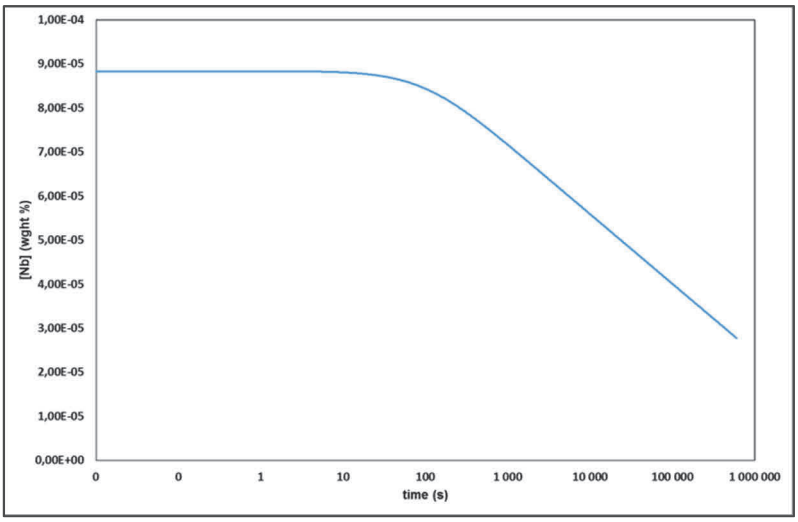

Figure 2 Relationships between dissolved niobium content and time at T = 980 °C

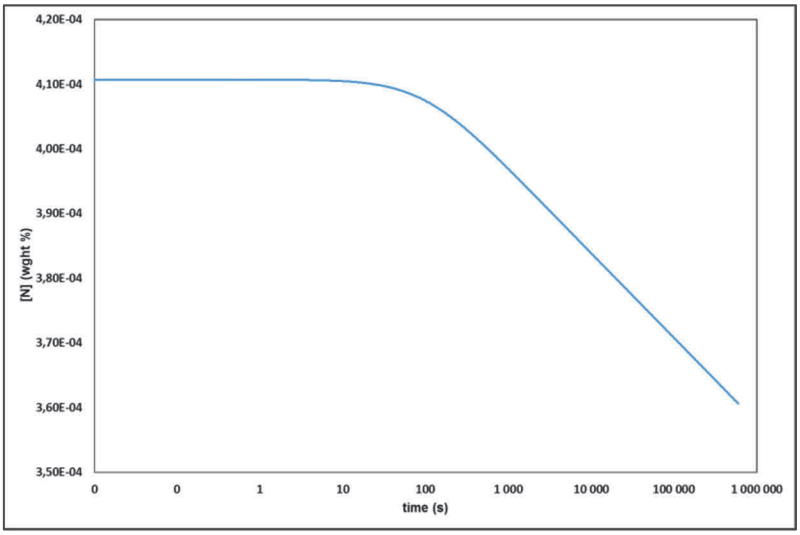

Figure 3 Relationships between dissolved nitrogen content and time at T = 980 °C

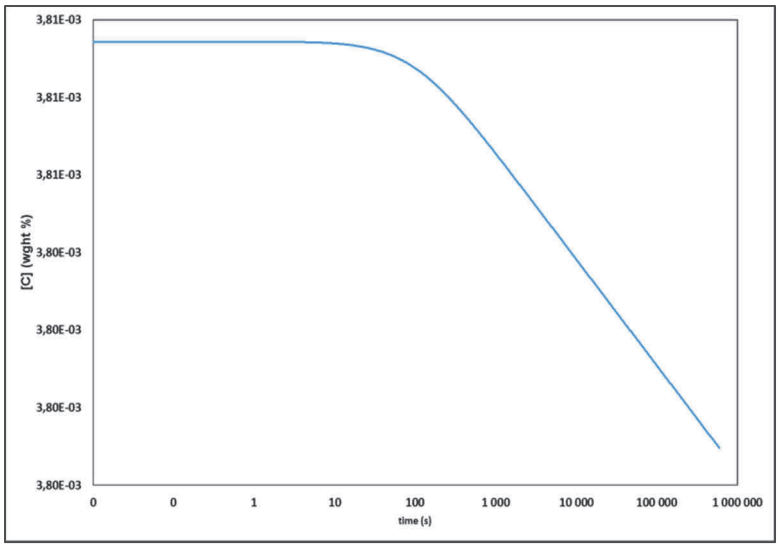

Figure 4 Relationships between dissolved carbon content and time at T = 980 °C

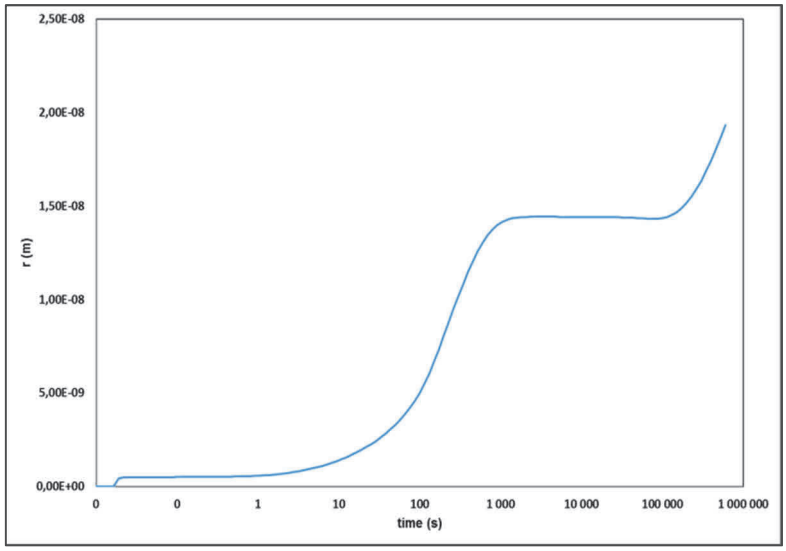

Figure 5 Relationships between radius, *r*, of precipitates and time at T = 980 °C

4. CONCLUSION

A particular advantage of the model is the ability to distinguish and track the individual stages of the carbonitride precipitation process (nucleation, growth, coagulation). It enables to calculate the size distribution of carbonitrides existing in austenite and influencing its grain size as well as size distribution of carbonitrides precipitated in ferrite during decomposition of undercooled austenite and influencing the mechanical properties of ferrite by the strengthening precipitation effect.

Derived model can be a useful tool for chemical composition of steel and heat treatment parameters optimization for obtaining the required high mechanical properties.

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