

PACS numbers: 07.05.Tp, 61.72.Cc, 64.30.Ef, 64.70.kd, 64.75.-g, 64.75.Op, 81.30.Kf

## **Mathematical Modelling of Primary Recrystallization Kinetics and Precipitation of Carbonitride Particles in Steels.**

### **I. Precipitation**

V. V. Kaverinsky and Z. P. Sukhenko

*I. M. Frantsevich Institute for Problems in Materials Science, N.A.S. of Ukraine,  
3 Academician Krzhyzhanovsky Str.,  
UA-03142 Kyiv, Ukraine*

A mathematical physical-based semi-empirical model and a corresponding computer program are developed for describing recrystallization process and carbonitrides particles precipitation in deformed austenite. The model is suitable for alloyed steels of a wide range of compositions. The model allows calculate a thermodynamic equilibrium for excess carbonitride phases with solid solution, the kinetics of their nucleation and growth, and their effect on recovery and recrystallization. A detailed description is given for each aspect of the model and its physical nature. Verification of the simulation results with the experimental data from published sources confirms the sufficient reliability of the proposed computer model for evaluative calculations. The model's features are demonstrated by an example that simulates influence of Nb content on recrystallization, recovery and nucleation, growth and Ostwald ripening of Nb and Ti carbonitride particles. The simulation shows and allows numerically evaluate the effect of slowing down recrystallization and recovery with increasing in Nb content. This indicates a significant effect of dispersed carbonitrides on recrystallization and recovery. The simulation theoretically predicts an intensification of Ti(C, N) particles precipitation and growth with an increase in the Nb concentration. Another result is an increase of dispersion and number of Nb(C, N) particles with an increase in the Nb concentration owing to more rapid transition to the Ostwald ripening stage, which is characterized by much more slowly average particle size growth than

---

Corresponding author: Vladyslav Volodymyrovych Kaverinsky  
E-mail: [insamhlaithe@gmail.com](mailto:insamhlaithe@gmail.com)

Citation: V. V. Kaverinsky and Z. P. Sukhenko, Mathematical Modelling of Primary Recrystallization Kinetics and Precipitation of Carbonitride Particles in Steels. I. Precipitation, *Metallofiz. Noveishie Tekhnol.*, **43**, No. 1: 27–45 (2021), DOI: [10.15407/mfint.43.01.0027](https://doi.org/10.15407/mfint.43.01.0027).

from a supersaturated solid solution.

**Key words:** recrystallization, kinetics, austenite, steel, modelling.

Розроблено математичну фізично обґрунтовану напівемпіричну модель і відповідну комп'ютерну програму, що описують процес рекристалізації і виділення частинок карбонітридів в деформованому аустеніті. Модель параметризовано для легованих сталей широкого спектру складів. Модель дозволяє розрахувати термодинамічну рівновагу для надлишкових карбонітридних фаз у твердому розчині, кінетику їх зародження і зростання, а також їх вплив на повернення і рекристалізацію. Для кожного з аспектів моделі наведено докладний опис його фізичної суті. Перевірка результатів моделювання експериментальними даними з літературних джерел підтвердила достатню надійність запропонованої комп'ютерної моделі для оціночних розрахунків. Особливості моделі продемонстровані на прикладі моделювання вплив вмісту Nb на рекристалізацію, повернення, а також на зародження, зростання і Оствальдове дозрівання частинок карбонітридів Nb і Ti. Моделювання показало і дозволило чисельно оцінити ефект уповільнення рекристалізації і повернення при збільшенні вмісту Nb. Це свідчить про вплив дисперсних карбонітридів на рекристалізацію і повернення. Моделювання теоретично передбачило інтенсифікацію зародження і зростання часток Ti(C, N) зі зростанням концентрації Nb. Іншим результатом є збільшення дисперсності та кількості частинок Nb(C, N) зі збільшенням концентрації Nb внаслідок більш швидкого переходу до стадії Оствальдового дозрівання, яка характеризується набагато більш повільним зростанням середнього розміру часток, ніж при їх утворенні з пересиченого твердого розчину.

**Ключові слова:** рекристалізація, кінетика, аустеніт, сталь, моделювання.

*(Received March 12, 2020; in final version, November 12, 2020)*

## 1. INTRODUCTION

Physically based mathematical models can be a convenient tool for predicting a structure formation and properties of materials [1–3], while minimizing time-consuming, expensive, and lengthy experimental studies. In our previous works were presented [4–6] mathematical models for thermodynamics of carbonitrides [4, 5] and complex oxides [6] formation, and for kinetics of phase transformations [7, 8]. This serial of articles proposes a physically based mathematical model that describes kinetics of primary recrystallization (after deformation) with the background of carbonitride particles evolution process. These processes influence each other and should be modelled in aggregate. In particular, dispersed particles of carbonitrides slow down the recrystallization, at the same time, the recovery and recrystallization slow

down the nucleation and growth of the carbonitride inclusions [9–11]. The kinetics of carbonitride particles precipitation also requires thermodynamic calculations of the carbonitrides composition and their equilibrium amount. For this purpose was used a modified version of our earlier model [5]. The software implementation of the corresponding module has been completely redeveloped. To implement the model, a special computer program in Python was written.

Models for this purpose were being developed earlier by others, for example [9–12]. In comparison with the above, our model considers the simultaneous of several elements carbonitrides precipitation, their composition is calculated, and the temperature and concentration dependences of a number of intermediate parameters are taken into account.

The present part primary considers on modelling of carbonitride precipitation kinetics for the case of deformed steels. The following one will be devoted to the influence of this process on the recrystallization and recovery phenomena. In spite, the description and analysis of the processes of carbonitride precipitation and recrystallization are given in separate parts of the article they are simulated simultaneously in one computer model because they, as been mentioned, are strong interrelation.

## 2. MATHEMATICAL MODEL

**A thermodynamic model of carbonitrides formation.** The thermodynamic module of our model is based on the method described in [4, 5]. The essence of the method consists in calculating the thermodynamic equilibrium for a group of reactions carbides and nitrides formation from a solid (in this case) solution. In this case, carbonitrides are assumed as a mutual solid solution of the corresponding carbide and nitride. It was taken into account a deviation from the ideality of such solution basing on the method of A. G. Ponomarenko (a method for assessing the thermodynamic functions of systems with collectivized electrons) [13].

The method for calculating the equilibrium amount of a compound is based on the concept of the equilibrium constant of a compound from a solution formation reaction:

$$K_p = \frac{a_{\text{Me}_n\text{R}_m}}{a_{[\text{Me}]}^n a_{[\text{R}]}^m}, \quad (1)$$

where  $K_p$ —equilibrium constant,  $a_{\text{Me}_n\text{R}_m}$ —an activity of this compound in the carbonitride phase,  $a_{[\text{Me}]}$ —carbide or nitride forming element activity,  $a_{[\text{R}]}$ —activity of carbon or nitrogen,  $n$ ,  $m$ —stoichiometric reaction equation coefficients.

For carbides and nitrides of elements Ti, Nb, Zr, the numbers  $n$  and  $m$  can be considered equal to 1. A compound part in carbonitride can be expressed as follows:

$$x_{\text{MeR}} = K_p \frac{f_{[\text{R}]}f_{[\text{Me}]}}{\gamma_{\text{MeR}}} [\text{R}][\text{Me}], \quad (2)$$

where  $x_{\text{MeR}}$ —a proportion of the carbide or nitride;  $f_{[\text{Me}]}$ ,  $f_{[\text{R}]}$ —respectively, activities coefficients of the carbonitride formers;  $\gamma_{\text{MeR}}$ —an activity coefficient of a resulting compound in the carbonitride phase,  $[\text{Me}]$ ,  $[\text{R}]$ —respectively, mass concentrations of carbonitride-forming element and carbon or nitrogen equilibrium with the formed compounds, %.

In [5, 6], we have obtained the following equations (3)–(7):

$$\begin{aligned} \frac{m_{[\text{Me}]_u} M_{\text{MeR}}}{(m_{\text{carb.}} + m_{\text{nitr.}}) M_{\text{Me}}} = \\ = 10000 K_p \frac{f_{[\text{R}]}f_{[\text{Me}]}}{\gamma_{\text{MeR}}} \frac{m_{[\text{R}]_n} - m_{[\text{R}]_u}}{m_{\text{p}_n} - m_{\text{carb.}} - m_{\text{nitr.}}} \frac{m_{[\text{Me}]_n} - m_{[\text{Me}]_u}}{m_{\text{p}_n} - m_{\text{carb.}} - m_{\text{nitr.}}}, \end{aligned} \quad (3)$$

$$m_{[\text{R}]_u} = M_{\text{R}} \sum \frac{m_{[\text{Me}]_{u_i}}}{M_{\text{Me}_{n_i}}}, \quad (4)$$

$$m_{\text{carb.}} = \sum m_{[\text{Me}]_{u_i}(\text{carb.})} + m_{[\text{C}]_u}, \quad (5)$$

$$m_{\text{nitr.}} = \sum m_{[\text{Me}]_{u_i}(\text{nitr.})} + m_{[\text{N}]_u}, \quad (6)$$

$$m_{[\text{Me}]_u} = m_{[\text{Me}]_{u_i}(\text{carb.})} + m_{[\text{Me}]_{u_i}(\text{nitr.})}, \quad (7)$$

where  $m_{[\text{Me}]_n}$ ,  $m_{[\text{R}]_n}$ —the total mass of a carbide-forming element and carbon or nitrogen in the volume of the system with mass  $m_{\text{p}_n}$ , kg;  $m_{[\text{Me}]_u}$ ,  $m_{[\text{R}]_u}$ —respectively, the mass of a carbide or nitride forming element and carbon or nitrogen spent on the formation of the compound, kg;  $m_{\text{p}_n}$ —a mass of the considered section of the system, kg;  $m_{\text{carb.}}$ ,  $m_{\text{nitr.}}$ —mass of carbides and nitrides formed;  $M_{\text{Me}}$  and  $M_{\text{MeR}}$ —molecular weights of carbide or nitride forming element and the reaction product, kg/mol;  $m_{[\text{Me}]_{u_i}(\text{carb.})}$ ,  $m_{[\text{Me}]_{u_i}(\text{nitr.})}$ —the consumed mass of each of the carbonitride-forming elements, kg;  $m_{[\text{C}]_u}$ ,  $m_{[\text{N}]_u}$ —consumed masses of carbon and nitrogen.

More details about this calculation method are described in [5], some numerical values are also given there.

Having written Eq. (3) for each of the carbides and nitrides in this system, together with Eqs. (4)–(7), we obtain a closed system, which solution allows us to calculate the distribution of elements between carbides, nitrides, and solid solution and the mass of the compounds

formed.

In the model described in [4], carbonitride was considered an ideal solution of the corresponding carbide and nitride, and the activity coefficient was assumed equal to 1. This approximation is not entirely accurate and, as applied to this problem, often led to significant deviations of the result in the direction of nitride or carbide prevalence in the predicted reactions products. In [13, 14], a method was described that allows one to determine the activity of components in systems representing a mutual solution of chemical compounds. In carbonitrides electrons of the atoms form a single quantum-mechanical system, which can be thermodynamically characterized by the chemical potential of electrons (Fermi level). This allows the partial entropy of the mixing to be presented in the form of two components that take into account the excitation of nuclei and electrons separately:  $S_i^M = S_{i(\text{nuc})}^M + S_{i(\text{el})}^M$ . The term  $S_{i(\text{nuc})}^M$  takes into account the component of thermal motion associated with permutations between different atoms,  $S_{i(\text{el})}^M$  takes into account the thermal excitation of electrons. The enthalpy of mixing within the accepted approximation is considered equal to zero. The expression for the chemical potential of an element has the form:

$$\mu_{(i)} = \mu_{(i)}^0 + RT \ln x_{(i)} \psi_i, \quad (8)$$

where  $x_{(i)}$ —an element  $i$  concentration,  $\psi$ —an element activity coefficient.

The chemical potential of a compound is by definition equal to:

$$\mu_{(\text{Me}_n\text{R}_m)} = n\mu_{\text{Me}} + m\mu_{\text{R}}, \quad (9)$$

hence

$$\mu_{(\text{Me})} = \mu_{(\text{Me})}^0 + RT \ln x_{(\text{Me})} \psi_{(\text{Me})}, \quad (10)$$

$$\mu_{(\text{R})} = \mu_{(\text{R})}^0 + RT \ln x_{(\text{R})} \psi_{(\text{R})}, \quad (11)$$

$$\mu_{(\text{Me}_n\text{R}_m)} = n\mu_{(\text{Me})}^0 + m\mu_{(\text{R})}^0 + RT \ln x_{(\text{Me})}^n x_{(\text{R})}^m \psi_{(\text{Me})}^n \psi_{(\text{R})}^m. \quad (12)$$

$n\mu_{(\text{Me})}^0$  and  $m\mu_{(\text{R})}^0$  in (12) can be wrapped up to  $\mu_{(\text{Me}_n\text{R}_m)}^0$

$$\mu_{(\text{Me}_n\text{R}_m)} = \mu_{(\text{Me}_n\text{R}_m)}^0 + RT \ln x_{(\text{Me})}^n x_{(\text{R})}^m \psi_{(\text{Me})}^n \psi_{(\text{R})}^m. \quad (13)$$

The chemical potential of a compound is related to its activity:

$$\mu_{(\text{Me}_n\text{R}_m)} = \mu_{(\text{Me}_n\text{R}_m)}^0 + RT \ln a_{(\text{Me}_n\text{R}_m)}. \quad (14)$$

From analogy of (13) and (14), the activity of a single compound in

the carbonitride phase is:

$$a_{(\text{Me}_n\text{R}_m)} = x_{(\text{Me})}^n x_{(\text{R})}^m \psi_{(\text{Me})}^n \psi_{(\text{R})}^m. \quad (15)$$

Formula (16) was proposed to determine the parameters  $\psi$ , [14]:

$$\psi_i = \left[ \left( \frac{\Pi}{e^{\kappa_i}} \right)^{\frac{\Pi}{RT}} \sum_{j=1}^k x_j e^{-\frac{\varepsilon_{ij}}{RT}} \right]^{-1}, \quad (16)$$

where  $\Pi = \prod_{i=1}^k \kappa_i^{x_i} = \kappa_1^{x_1} \kappa_2^{x_2} \dots \kappa_k^{x_k}$ ,  $\varepsilon_{ij}$ —interchange energy of atoms  $i$  and  $j$ :

$$\varepsilon_{ij} = \frac{1}{2} (\kappa_i^{1/2} - \kappa_j^{1/2})^2, \quad (17)$$

where  $\kappa_i, \kappa_j$ —energy parameters of elements  $i$  and  $j$ .

Despite the not very accurate nature of the considered method, the use of activity coefficients determined with it is more correct than assuming them equal to 1.

The values of the energy parameters  $\kappa$  adopted in our model are:  $\kappa_{\text{Ti}} = 134$ ,  $\kappa_{\text{N}} = 732$ ,  $\kappa_{\text{Al}} = 125$ ,  $\kappa_{\text{C}} = 29$ ,  $\kappa_{\text{V}} = 184$ ,  $\kappa_{\text{Nb}} = 280$ ,  $\kappa_{\text{Zr}} = 226$ .

The calculation is carried out in several iterations starting from the approximation of an ideal solution with the refinement of the activity coefficients at each subsequent step, until the gap between the values obtained in the neighbouring iterations becomes less than a certain small value.

**A kinetic model of carbonitride particle precipitation.** The precipitation of Ti, Nb and Zr carbonitrides from a solid solution occurs mainly at dislocations [15, 16]. In [16], equation (18) is given for an excess phase particles stationary nucleation rate:

$$\frac{dN}{dt} = N_n F_Z \beta \exp\left(-\frac{\Delta G_C}{RT}\right), \quad (18)$$

where  $N$ —number of particles per unit volume of material,  $\text{m}^{-3}$ ;  $t$ —time, s;  $N_n$ —bulk density of particle nucleation potential sites,  $\text{m}^{-3}$ ;  $F_Z$ —Zeldovich factor [17];  $\beta$ —rate of diffusion attachment of atoms to a critical-size nucleus;  $\Delta G_C$ —thermodynamic barrier of nucleation for a critical-size nucleus, J/mol;  $T$ —temperature, K;  $R$ —gas constant, J/(mol·K).

The Zeldovich factor  $F_Z$  allows one to take into account the possibility of fluctuation dissolution of nuclei with a size larger than critical. It is calculated by the formula (19) from [17]:

$$F_Z = \sqrt{\Delta G_C / (3\pi R T n_c^2)}, \quad (19)$$

where  $n_c$ —a number of some conventional elementary volumes of carbonitride in the nucleus.

Assuming that the nucleus has a spherical shape, the parameter  $n_c$  is calculated by the formula (20):

$$n_c = \frac{4}{3} \pi \frac{R_c^3}{V_a}, \quad (20)$$

where  $R_c$ —the critical radius of nucleus, m;  $V_a$ —conventional elemental volume of carbonitride,  $m^3$ .

The conditional elementary volume of carbonitride is calculated as the ratio of the molar volume of a given carbonitride to the Avogadro number. The critical radius of the nucleus  $R_c$ , according to [9], is equal to:

$$R_c = - \frac{2\gamma_{p/\gamma}}{\Delta G_p^{\text{Me(C,N)}}}, \quad (21)$$

where  $\gamma_{p/\gamma}$ —particle/matrix specific surface energy,  $J/m^2$ ;  $\Delta G_p^{\text{Me(C,N)}}$  — Gibbs volumetric energy change,  $J/m^3$ .

The value of the specific energy of the particle/matrix interface depends on the temperature of the solvus of the compound [9, 18]:

$$\gamma_{p/\gamma} = 0,09272 + 5,84 \cdot 10^{25} e^{-0,04416T_s}. \quad (22)$$

The thermodynamic barrier of nucleation of a nucleus of critical size, if the shape is assumed to be spherical, is determined by formula (23):

$$\Delta G_c = \frac{4}{3} \pi R_c^2 \gamma_{p/\gamma}, \quad (23)$$

where  $R_c$ —the critical radius of nucleus, m,  $\gamma_{p/\gamma}$ —particle/matrix specific surface energy,  $J/m^2$ .

The change in the Gibbs volumetric energy during the formation of carbonitride depends on the concentration of elements in a solid solution [19] and is calculated by the formula (24):

$$\Delta G_p^{\text{Me(C,N)}} = - \frac{RT}{V_m^{\text{Me(C,N)}}} \ln \frac{X_{\text{Me}} X_{\text{C}}^*}{X_{\text{Me}}^{\text{eq}} X_{\text{C}}^{\text{*eq}}}, \quad (24)$$

where  $V_m^{\text{Me(C,N)}}$  —molar volume of carbonitride,  $m^3/\text{mol}$ ;  $X_{\text{Me}}$  and  $X_{\text{C}}^*$  — respectively, the molar fraction carbonitride forming element and effective molar fraction of carbon;  $X_{\text{Me}}^{\text{eq}}$  and  $X_{\text{C}}^{\text{*eq}}$  —equilibrium molar fractions of the carbide-forming element and carbon in the solid solution.

The effective molar fraction of carbon in equation (24) is assumed to mean its value that corresponds to the carbon content in the solid solution at which the solvus temperature of the corresponding carbide coincides with the similar temperature for pure carbonitride [20].

Particles of carbonitrides are formed at the nodes of the dislocation net. The volume density of the particles potential nucleation sites  $N_n$  at the initial moment is equal to the total number of these nodes per unit volume, which depends on the dislocation density [15]:

$$N_{n0} = 0,5\rho_d^{1,5}, \quad (25)$$

where  $\rho_d$ —dislocation density.

The average dislocation density can be estimated using formula (26) from [9]:

$$\rho_d = \left( \frac{\sigma - \sigma_{0,2}}{\alpha_p M \mu b} \right)^2, \quad (26)$$

where  $\sigma$ —plastic flow stress, Pa;  $\sigma_{0,2}$ —yield strength at a given temperature, Pa;  $M$ —Taylor factor,  $M = 3.1$  [9];  $\mu$ —shear modulus at a given temperature, Pa;  $b$ —Burgers vector module;  $\alpha_p$ —empirical parameter,  $\alpha_p = 0.15$  [21].

The plastic flow stress of a deformed solid solution  $\sigma$  is the difference between the strain hardening of the material and the stress relaxation due to dynamic recrystallization [22]:

$$\sigma = \sigma_e - \Delta\sigma, \quad (27)$$

where  $\sigma_e$ —strain hardening of metal, Pa;  $\Delta\sigma$ —stress relaxation.

Strain hardening can be estimated by the formula (28) from [22]:

$$\sigma_e = B(1 - e^{-C\varepsilon})^m, \quad (28)$$

where  $\varepsilon$ —degree of plastic deformation;  $B$ —stress corresponding to the maximum strain hardening, Pa;  $C$  and  $m$ —model parameters.

The  $B$ ,  $C$ , and  $m$  in (28) are presented as functions of parameters  $Z$  and  $A$ . The Zener-Hollomon parameter  $Z$  is also called the temperature-velocity parameter [9] and is given by the equation (29):

$$Z = \dot{\varepsilon} e^{\frac{Q_d}{RT}}, \quad (29)$$

where  $\dot{\varepsilon}$ —strain rate, expressed as an additional degree of deformation per unit time,  $s^{-1}$ ;  $Q_d$ —strain activation energy, J/mol.

The effective energy activation of the deformation process  $Q_d$  can be estimated for austenite of known chemical composition according to



the empirical formula (30) from [23]:

$$\begin{aligned} Q_d = & 267000 - 2535.52[\text{C, \%}] + 1010[\text{Mn, \%}] + 33620.76[\text{Si, \%}] + \\ & + 35651.28[\text{Mo, \%}] + 93680.52[\text{Ti, \%}]^{0.5919} + 31673.46[\text{V, \%}] + \\ & + 70729[\text{Nb, \%}]^{0.6549}. \end{aligned} \quad (30)$$

The parameter  $A$  also depends on the strain activation energy [23]:

$$A = (12.197 + 65.590[\text{C, \%}] - 49.052[\text{Nb, \%}])e^{7.076 \cdot 10^{-5} Q_d}. \quad (31)$$

Parameters  $B$ ,  $C$  and  $m$  from formula (28) are expressed in terms of  $Z$  and  $A$  [22, 23]:

$$B = (9.5326 + 0.6196 \ln(Z / A))^2, \quad (32)$$

$$C = 3.9202(Z / A)^{0.0592}, \quad (33)$$

$$m = 0.3449e^{(0.0139\sqrt{Z/A})}. \quad (34)$$

Stress relaxation due to dynamic recrystallization is proportional to the amount of dynamically recrystallized volume (35):

$$\Delta\sigma = B'F_{\text{DRX}}, \quad (35)$$

where  $F_{\text{DRX}}$ —dynamically recrystallized volume fraction;  $B'$ —strain factor, Pa.

The fraction of the dynamically recrystallized volume  $F_{\text{DRX}}$  depends on the degree of deformation and, according to [24], can be calculated by the formula (36):

$$F_{\text{DRX}} = 1 - \exp\left(-k\left(\frac{\varepsilon - \alpha_d \varepsilon_p}{\varepsilon_p}\right)^{m'}\right), \quad (36)$$

where  $\varepsilon$ —deformation degree;  $\varepsilon_p$ —deformation corresponding to the maximum stress on the plastic flow curve;  $k$ ,  $\alpha_d$  и  $m'$ —model parameters.

Parameters  $k$  and  $m'$  depend on  $A$  and  $Z$ . The coefficient  $B'$  from formula (35) depends on them. These empirical dependencies [22, 24] are represented by formulas (37)–(39):

$$B' = 26.031(Z / A)^{0.1351}, \quad (37)$$

$$k = 0.5974 \exp(1.2333(Z / A)^{-0.5}), \quad (38)$$

$$m' = 1.0901 \exp(0.264\sqrt{Z / A}). \quad (39)$$

The value of the coefficient  $\alpha_d$  from (36) according to [22] is 0.95.

Shear modulus  $\mu$  is temperature dependent. An empirical formula (40) is given in [10, 18]:

$$\mu = 8.1 \cdot 10^{10} \left( 0.91 - \frac{T - 300}{1810} \right), \quad (40)$$

where  $T$  — temperature, °C.

The value of the Burgers vector modulus  $b$  in equation (25) depends on the type and parameter of the crystal lattice. In the case of austenite having a face-centred cubic lattice, it is equal to half the lattice parameter. The lattice parameter depends on temperature and chemical composition. Based on a synthesis of literature data, we have proposed an empirical formula (41):

$$a_\gamma = 0.356 + 8.5 \cdot 10^{-6} T + 0.0033[C, \%], \quad (41)$$

where  $a_\gamma$  — austenite lattice parameter, nm,  $T$  — temperature, K.

Parameter  $\beta$  — the diffusion attachment rate of atoms to a critical-size nucleus [18]:

$$\beta = \frac{4\pi R_C^2 D_{Me} X_{Me}}{a_\gamma^4}, \quad (42)$$

where  $R_C$  — critical nucleus radius, m;  $D_{Me}$  — volume diffusion coefficient of carbonitride-forming element atoms,  $\text{m}^2 \cdot \text{s}^{-1}$ ;  $X_{Me}$  — molar concentration of carbonitride-forming element in austenite;  $a_\gamma$  — austenite lattice parameter, m.

Diffusion coefficients depend on temperature:

$$D_{Nb} = 7.5 \cdot 10^{-5} e^{-\frac{264000}{RT}}, \quad (43)$$

$$D_{Ti} = 1.5 \cdot 10^{-5} e^{-\frac{251000}{RT}}, \quad (44)$$

$$D_V = 2.5 \cdot 10^{-5} e^{-\frac{239180}{RT}}, \quad (45)$$

$$D_{Al} = 9.62 \cdot 10^{-8} e^{-\frac{190940}{RT}}, \quad (46)$$

$$D_{Zr} = 5.63 \cdot 10^{-4} e^{-\frac{198400}{RT}}. \quad (47)$$

Particle growth involves two stages: at the first stage, the equilibrium between the solid solution and the excess phase has not yet occurred; at the second stage, the process of Ostwald ripening actually takes place.

As in [9], our model describes a change in the average particle size.

At the first stage, the growth rate of the average particle radius is described by equation (48) from [21]:

$$\frac{d\bar{R}}{dt} = \frac{D_{\text{Me}}^{\text{eff}}}{\bar{R}} \frac{X_{\text{Me}} - X_{\text{Me}}^{\text{eq}} e^{\frac{R_0}{\bar{R}}}}{\alpha_p X_{\text{Me}}^{\text{p}} - X_{\text{Me}}^{\text{eq}} e^{\frac{R_0}{\bar{R}}}} + \frac{1}{N} \frac{dN}{dt} (R_{\text{C}}^* - \bar{R}). \quad (48)$$

where  $\bar{R}$ —current average particle radius, m;  $D_{\text{Me}}^{\text{eff}}$ —diffusion coefficient taking into account the contribution of volume and dislocation diffusion,  $\text{m}^2 \cdot \text{s}$ ;  $X_{\text{Me}}$ —actual molar concentration of the carbonitride-forming element in the solid solution at a given time;  $X_{\text{Me}}^{\text{eq}}$ —equilibrium molar concentration of carbonitride-forming element in solid solution;  $X_{\text{Me}}^{\text{p}}$ —molar fraction of carbonitride-forming element atoms in carbonitride;  $\alpha_p$ —ratio of atomic volumes in solid solution and in excess phase;  $R_0$ —a capillary radius (the minimum radius of a particle that can grow with a given supersaturation of the solid solution), m;  $R_{\text{C}}^*$ —an effective critical radius of carbonitride particles, m;  $N$ —number of particles.

The capillary radius  $R_0$  is determined by the formula (49) from [9]:

$$R_0 = \frac{2\gamma_{\text{p}/\gamma} V_{\text{a}}^{\text{Me(C,N)}}}{k_{\text{B}} T}, \quad (49)$$

where  $\gamma_{\text{p}/\gamma}$ —particle/matrix surface energy,  $\text{J}/\text{m}^2$ ;  $V_{\text{a}}$ —conventional elemental volume of carbonitride,  $\text{m}^3$ ;  $k_{\text{B}}$ —Boltzmann constant,  $\text{J}/\text{K}$ ;  $T$ —temperature,  $\text{K}$ .

The effective critical radius of a carbonitride particle  $R_{\text{C}}^*$  defined by the formula (50):

$$R_{\text{C}}^* = (1 + \alpha) R_{\text{C}}, \quad (50)$$

where  $R_{\text{C}}$ —critical radius of the nucleus, determined by the formula (21), m;  $\alpha$ —empirical parameter,  $\alpha = 0.03$  [9].

Effective diffusion coefficient  $D_{\text{Me}}^{\text{eff}}$  consists of the coefficient of volume diffusion and the coefficient of dislocation diffusion. According to [17], its value can be calculated on the basis of the volume and dislocation diffusion coefficients according to the formula (51):

$$D_{\text{Me}}^{\text{eff}} = \pi R_{\text{d}}^2 \rho_{\text{d}} D_{\text{Me}}^{\text{dis}} + (1 - \pi R_{\text{d}}^2 \rho_{\text{d}}) D_{\text{Me}}, \quad (51)$$

where  $R_{\text{d}}$ —dislocation core radius, m;  $\rho_{\text{d}}$ —dislocation density,  $\text{m}^{-2}$ ;  $D_{\text{Me}}^{\text{dis}}$ —dislocation diffusion coefficient,  $\text{m}^2 \cdot \text{s}^{-1}$ ;  $D_{\text{Me}}$ —volume diffusion coefficient,  $\text{m}^2 \cdot \text{s}^{-1}$ .

The temperature dependences of the dislocation diffusion coefficients for elements considered in this model are given below:

$$D_{\text{Nb}}^{\text{dis}} = 1.0 \cdot 10^{-4} e^{\frac{-172500}{RT}}, \quad (52)$$

$$D_{\text{Ti}}^{\text{dis}} = 4.5 \cdot 10^{-3} e^{\frac{-170000}{RT}}, \quad (53)$$

$$D_{\text{V}}^{\text{dis}} = 2.5 \cdot 10^{-4} e^{\frac{-160000}{RT}}, \quad (54)$$

$$D_{\text{Al}}^{\text{dis}} = 2.17 \cdot 10^{-4} e^{\frac{-160000}{RT}}, \quad (55)$$

$$D_{\text{Zr}}^{\text{dis}} = 2.53 \cdot 10^{-4} e^{\frac{-132240}{RT}}. \quad (56)$$

The change in the average particle size during Ostwald ripening is given by equation (57) from [17]:

$$\frac{d\bar{R}}{dt} = \frac{4}{27} \frac{X_{\text{Me}}}{\alpha_{\text{p}} X_{\text{Me}}^{\text{p}} - X_{\text{Me}}^{\text{eq}}} \frac{R_0 D_{\text{Me}}^{\text{eff}}}{\bar{R}^2}. \quad (57)$$

The decrease in the total number of particles during the Ostwald ripening process is described by equation (58) [17]:

$$\frac{dN}{dt} = \frac{4}{27} \frac{X_{\text{Me}}}{\alpha_{\text{p}} X_{\text{Me}}^{\text{p}} - X_{\text{Me}}^{\text{eq}}} \frac{R_0 D_{\text{Me}}^{\text{eff}}}{\bar{R}^3} \left[ \frac{R_0 X_{\text{Me}}}{\bar{R} (X_{\text{Me}}^{\text{p}} - X_{\text{Me}}^{\text{eq}})} \left( \frac{3}{4\pi \bar{R}^3} - N \right) - 3N \right]. \quad (58)$$

All the parameters from equations (57) and (58) are described above.

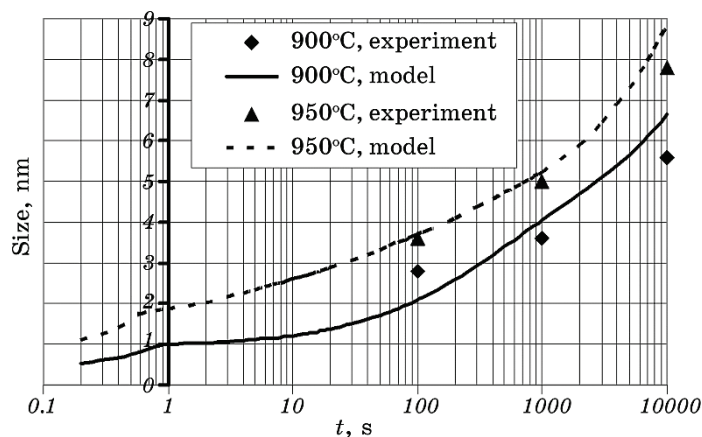
### 3. VERIFICATION OF THE DEVELOPED MODEL

To verify the proposed computer model of carbonitride particle formation, experimental data was used from several published sources [9, 15, 18, 26–32].

Figure 1 shows an example of comparing the experimental data from [15] on the change over time of the average particle size (diameter) of Nb(C, N) with the calculation results. The composition of the steel is given in Table 1. The degree of deformation is 80% and the rate of deformation is  $2.6 \text{ s}^{-1}$ .

The verification study showed that the average deviation of the values predicted by the model from the experimental data for modelling the growth of carbonitride particles is about 13%. Deviations are equally observed both up and down. This allows us to use this model to assess and analyse the nature of the influence of various factors (composition, temperature, degree of deformation) on the kinetics of precipitation of carbonitride particles in steels.

Thus, although the developed computer model is not a complete alternative to experimental studies, it allows one to obtain quickly and



**Fig. 1.** Comparison of experimental data (points) [15] on the change in the average particle size Nb(C, N) with the results of the computer model (curves).

with minimal costs reliable data on precipitation of carbonitride particles in steels sufficient for practical purposes.

#### 4. EXAMPLES OF CALCULATIONS USING THE DEVELOPED COMPUTER MODEL

To illustrate the developed program operating, calculations were performed demonstrating an effect of Nb content on changes in the amount and size of carbonitride particles over time. The steel composition for which the calculations were carried out is given in Table 2. The size of the initial austenite grain was taken to be 100  $\mu\text{m}$ .

The following parameters were taken: temperature 900°C; deformation degree 30%; strain rate 0.1  $\text{s}^{-1}$ .

Of great interest is the change over time of the number of carboni-

**TABLE 1.** Steel composition for verification of modelling changes of the average size of carbonitride particles over time according to [15] (% wt.) and the size of the initial austenite grain ( $\mu\text{m}$ ).

C	Si	Mn	Nb	N	Fe	$d_A, \mu\text{m}$
0.11	0.00	1.35	0.03	0.01	base	100

**TABLE 2.** The steel composition adopted in the simulation, % mass.

C	Si	Mn	Mo	Ti	Nb	N	Fe
0.08	0.20	1.80	0.15	0.025	0.01–0.06	0.005	base

tride particles shown on Fig. 2—Ti(C, N) and Fig. 3—Nb(C, N).

It can be seen from the presented simulation results, an increase in the Nb content has a stimulating effect on the increase in the number of Ti carbonitride particles. At lower Nb content an increase in the number of Ti(C,N) particles over time is quite smoothly and remains small. With an increase in Nb content to 0.04% (Fig. 2, *b*) the amount of Ti(C, N) particles increases by more than an order of magnitude. A shape of the curve changes: an intensive increase in the number of particles is observed during the first 4 s then the nucleation rate decreases markedly.

Comparison with the corresponding plot for Nb(C, N) shows that by this moment the nucleation of Nb(C, N) particles is completed and the process of Ostwald ripening begins for them. For Ti(C, N) particles the number of potential nucleation sites is significantly reduced. This leads to inhibition of the further nucleation of its new particles. Then, due to a decrease in the number of Nb(C, N) particles due to Ostwald ripening, potential sites for the nucleation of new Ti(C, N) particles begin to be released.

With an increase in Nb content to 0.06% the amount of precipitated Ti(C, N) particles increases even more. A shape of the curve also changes. A significant slowdown in a further increase in the number of Ti(C, N) particles is observed after about 1.5 s; a further increase in their number is insignificant. After approximately 200 s Ostwald ripening begins for Ti(C, N) particles, which is expressed in the plot by a

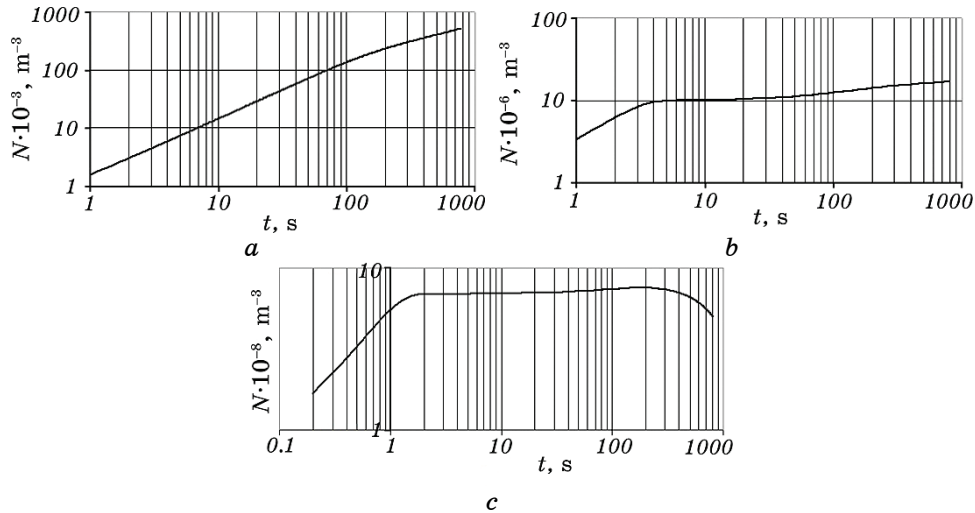


Fig. 2. Results of modelling of the effect of Nb content on the change over time of Ti(C, N) particles number in low-carbon steel: 0.01% Nb (*a*), 0.04% Nb (*b*), 0.06% Nb (*c*).

decrease in their number.

More Nb(C, N) particles are formed than Ti(C, N) ones. They quickly nucleate in large quantities over the volume of the metal, fixing the nodes of the dislocation grid. With a lower Nb content (0.01%) the number of Nb(C, N) particles increases throughout the entire considered period of 800 s. This suggests that all this time the solid solution remains supersaturated, and enough potential nucleation sites remain in the dislocation grid. With Nb content of 0.02% or more the plots clearly show the moment when the period of Ostwald ripening begins. The time required for the transition to Ostwald ripening depends on Nb content. At 0.02% Nb it takes about 40 s, at 0.04% Nb—about 4 s, and about 0.06 s at 0.06% Nb.

Let us consider the effect of Nb on the change in the average particles size of Ti and Nb carbonitrides over time. The corresponding plots are shown on Fig. 4—Ti (C, N) and Fig. 5—Nb(C, N).

From the presented results is seen that an increase in Nb content not only leads to an increase in the number of Ti(C, N) particles, but also contributes to an increase in their growth rate. A simultaneous increase in the number and size of Ti(C, N) particles explains the transition to Ostwald ripening of these particles after about 200 s when 0.06% Nb (Fig. 2, c). The transition to Ostwald ripening is also visible on the plot in Fig. 4 (curve 4)—after about 200 s a convex curve is replaced by a concave one.

The Nb(C, N) particles are much smaller. An increase in Nb content, on the contrary, in the considered interval leads to a decrease in their

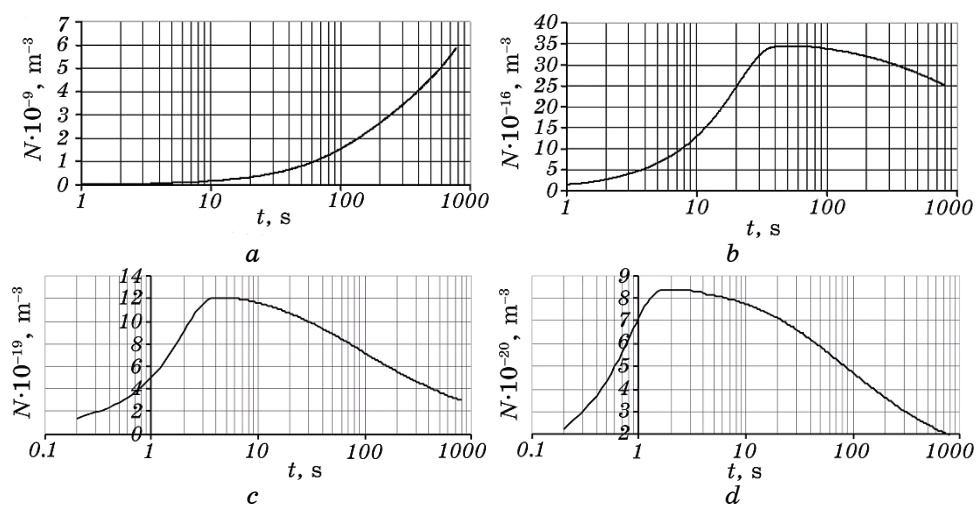
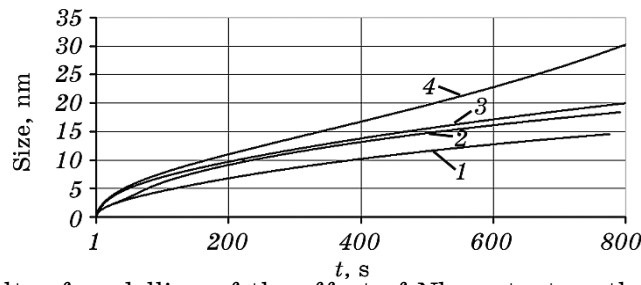


Fig. 3. Results of modelling of the effect of Nb content on the change over time of Nb(C, N) particles number in low-carbon steel: 0.01% Nb (a), 0.02% Nb (b), 0.04% Nb (c), 0.06% Nb (d).



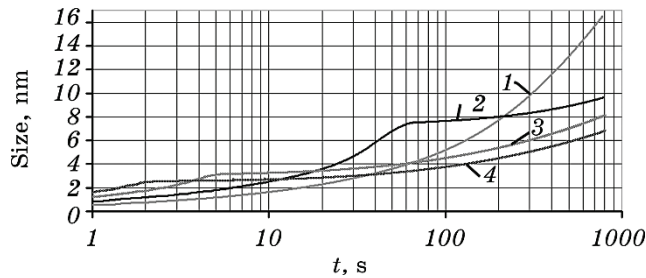
**Fig. 4.** Results of modelling of the effect of Nb content on the change over time of the average Ti(C,N) particles size: 1—0.01% Nb, 2—0.02% Nb, 3—0.04% Nb, 4—0.06% Nb.

size. This is explained by the fact that most of the considered time for these particles is during Ostwald ripening period (except curve 1, Fig. 5). This period begins earlier with a higher Nb content. The growth rate of the average particle size during the period of Ostwald ripening is much lower than the growth rate during precipitation from a supersaturated solid solution. This explains the fact that with a higher Nb content over the same period, the average particle size grows to smaller values.

Significant coarsening of Ti(C, N) particles is an undesirable effect leading to a decrease in the ductility of the metal. Therefore, the optimum Nb content in this case seems to be about 0.04%. With this value the number of Nb(C, N) particles is already quite large, and the size is quite small. At values of 0.02% and lower substantial coarsening of Nb(C, N) particles is possible with simultaneous insufficient their quantity.

## 5. CONCLUSIONS

1. A mathematical model is developed that allows one to describe the



**Fig. 5.** Results of modelling the effect of Nb content on the change over time of Nb(C, N) average particle size: 1—0.01% Nb, 2—0.02% Nb, 3—0.04% Nb, 4—0.06% Nb.



precipitation and Ostwald ripening of dispersed particles of excess phases, in particular carbonitrides, in steels micro alloyed with Nb, Ti, V, Zr and Al. The main features of our model are the ability to describe the simultaneous precipitation of carbonitrides of several elements and the thermodynamic assessment of the N and C content in these carbonitrides.

2. The results of computer simulation are compared with the published experimental data on the kinetics of carbonitride particles average size. The experimental results confirmed the reliability and practical applicability of the developed computer model for evaluative calculations.

3. A series of demonstration calculations was carried out for low-carbon structural steel microalloyed with Nb and Ti in order to demonstrate the capabilities of the developed model. In particular, the effect of changes in the Nb content on the process of carbonitride phases precipitation and Ostwald ripening is analysed.

4. An increase in the number and size of Ti(C, N) particles with an increase in the Nb content is theoretically predicted by the simulation. In this case, the dispersion of Nb(C, N) particles increases, which is associated with a more rapid transition to the stage of Ostwald ripening, which occurs much more slowly than growth from a supersaturated solid solution. It was shown that in the case of deformation and carbonitride precipitation at 900°C the optimum Nb content seems to be more than 0.02%, but not more than 0.04%. This contributes to the formation of a sufficiently large number of small Nb(C, N) particles, but at the same time reduces the size and quantity of large Ti(C, N) precipitates.

## REFERENCES

1. V. M. Golod and K. D. Savel'ev, *Vychislitel'naya Termodinamika v Materialovedenii* [Computational Thermodynamics in Material Science] (St. Petersburg: Polytechnic University: 2010) (in Russian).
2. D. F. Sokolov, *Razrabotka Modeley Raspada Austenita i Prognozirovaniya Mekhanicheskikh Svoystv pri Kontroliruemoy Prokatke Staley* [Development of Austenite Decay Models to Predict the Mechanical Properties of Controlled Rolled Steel] (Thesis of Dissert. for Cand. Tech. Sci.) (St. Petersburg: Polytechnic University: 2013) (in Russian).
3. N. Saunders and A. P. Miodownik, *CALPHAD. Calculation of Phase Diagrams* (Guildford: Pergamon Press: 2005).
4. A. I. Trotsan, V. V. Kaverynsky, and I. L. Brodetsky, *Metallofiz. Noveishie Tekhnol.*, **35**, No. 7: 919 (2013) (in Russian).
5. A. I. Trotsan, V. V. Kaverynsky, and I. L. Brodetsky, *Metal ta Lyttya Ukrayiny*, **22**, No. 3: 3 (2014) (in Russian).
6. A. I. Trotsan, V. V. Kaverynsky, I. L. Brodetsky, B. F. Belov, and A. I. Itsenko, *Chernaya Metallurgiya. Byulleten' Nauchno-Tekhnicheskoy i*

- Ekonomicheskoy Informatsii*, No. 5: 62 (2014) (in Russian).
7. V. V. Kaverynsky, A. I. Trotsan, and Z. P. Sukhenko, *Metallofiz. Noveishie Tekhnol.*, **39**, No. 8: 1051 (2017) (in Russian).
  8. V. V. Kaverynsky, *Int. J. Information Content and Processing*, **6**, No. 1: 49 (2019).
  9. S. F. Sokolov, *Issledovanie i Modelirovanie Evolyutsii Mikrostruktury i Soprotivleniya Deformatsii Staley pri Goryachey Obrabotke Davleniem* [Investigation and Modelling of the Evolution of the Microstructure and Deformation Resistance of Steels during Hot Processing] (Thesis of Disser. for Cand. Tech. Sci.) (St. Petersburg: Polytechnic University: 2013) (in Russian).
  10. H. S. Zurob, Y. Bbrechet, and G. A. Purdy, *Acta Mater.*, **49**: 4183 (2001).
  11. H. Buken and E. Kozeschnik, *Metall. Mater. Trans. A*, **48**: 2812 (2017).
  12. H. S. Zurob, S. V. Subramanian, G. Purdy, C. R. Hutchison, and Y. Brechet, *ISIJ Int.*, **45**, No. 5: 713 (2005).
  13. A. G. Ponomarenko, *Zhurnal Fizicheskoy Khimii*, **48**, No. 7: 1668 (1974) (in Russian).
  14. V. A. Grigoryan, A. Ya. Stomachin, and A. G. Ponomarenko, *Fiziko-Khimicheskie Raschety Elektrostaleplavil'nykh Protsessov* [Physicochemical Calculations of Electric Steel Smelting Processes] (Moscow: Metallurgia: 1989) (in Russian).
  15. B. Dutta, E. J. Palmiere, and C. M. Sellars, *Acta Mater.*, **49**, No. 5: 785 (2001).
  16. R. Kampmann and R. Wagner, *Decomposition of Alloys: The Early Stages* (Oxford: Pergamon Press: 1994).
  17. M. Perez, M. Dumont, and D. Acevedo-Reyes, *Acta Mater.*, **56**, No. 9: 2119 (2008).
  18. H. S. Zurob, C. R. Hutchison, Y. Brechet, and G. Purdy, *Acta Mater.*, **50**, No. 12: 3075 (2002).
  19. K. Xu, B. G. Thomas, and R. Malley, *Metal. Mater. Trans. A*, **42**, No. 2: 524 (2011).
  20. A. J. De Ardo, *Int. Materials Reviews*, **48**, No. 6: 371 (2003).
  21. M. Verdier, Y. Brechet, and P. Guyot, *Acta Mater.*, **47**, No. 1: 127 (1999).
  22. S. F. Medina and C. A. Hernandez, *Acta Mater.*, **44**, No. 1: 165 (1996).
  23. S. F. Medina and C. A. Hernandez, *Acta Mater.*, **44**, No. 1: 137 (1996).
  24. S. F. Medina and C. A. Hernandez, *Acta Mater.*, **44**, No. 1: 165 (1996).
  25. V. M. Vorotyntsev and V. D. Skupov, *Bazovye Tekhnologii Mikro- i Naoelektroniki* [Basic Technologies of Micro- and Nanoelectronics] (Moscow: Prospect: 2017) (in Russian).
  26. H. S. Medina and J. E. Mancilla, *ISIJ Int.*, **36**, No. 8: 1070 (1996).
  27. H. S. Medina and A. Quispe, *ISIJ Int.*, **41**, No. 7: 774 (2001).
  28. H. S. Medina, J. E. Mancilla, and C. A. Hernandez, *ISIJ Int.*, **34**, No. 8: 689 (1994).

29. H. S. Medina and A. Quispe, *ISIJ Int.*, **36**, No. 10: 1295 (1996).
30. H. S. Medina and J. E. Mancilla, *ISIJ Int.*, **36**, No. 8: 1063 (1996).
31. M. Gomez, H. S. Medina, and A. Quispe, *ISIJ Int.*, **42**, No. 4: 423 (2002).
32. M. Gomez, L. Rancel, and S. F. Medina, *Met. Mater. Int.*, **15**, No. 4: 689 (2009).