

MODELLING OF THE KINETICS OF MX-TYPE CARBIDES PRECIPITATION PROCESS IN LOW – CARBON BAINITIC STEELS

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Abstract

The paper focuses on the modelling of MX-type carbides precipitation processes in low-carbon precipitation-strengthened bainitic steels. The precipitation of these carbides allows the lowering of carbon content in bainitic steels, while maintaining their strength. In this way, high strength and ductility in long and flat products can be developed by means of proper thermo-mechanical processing. Deschamps model was employed to simulate the precipitation kinetics under the assumption that the diffusion along dislocation line is the rate controlling process. The elaborated model was used to evaluate the effect of steel composition and process parameters on the precipitation strengthening effect.

Key words: ultra-high strength low-carbon bainitic steels, precipitation strengthening, precipitation kinetics

1. INTRODUCTION

The bainitic steels were first developed by Irvine and Pickering (Irvin and Pickering, 1957). The physical metallurgy principles established during their development have been applied in the metallurgical design of a wide range of bainitic steels. The strong interest in bainitic steels has started when it was confirmed that ductility and toughness can be significantly improved by reducing the carbon content while maintaining its strength using other strengthening mechanisms (Pickering, 1977). Carbon strengthening is undesirable as it deteriorates ductility, toughness and weldability.

The strength of bainite is composed of five major components:

- The intrinsic strength of iron - $\Delta\sigma_{Fe}$
- Solid solution - $\Delta\sigma_{ss}$
- Precipitation - $\Delta\sigma_p$
- Grain size - $\Delta\sigma_{gs}$

- Dislocations - $\Delta\sigma_d$

The principles for novel bainitic steels lies in low and ultra-low carbon, low alloys steels, containing small amounts of boron and other bainite promoting elements to increase bainitic hardenability and suppress allotriomorphic ferrite formation as well as microalloying elements to provide precipitation strengthening. Precipitation strengthening allows a decrease in carbon content which gives the lowest transition temperature at a given strength and improves formability. By retarding the growth of brittle cementite, microalloying additions minimise low temperature embrittlement caused by the formation and growth of cementite. The formation of dispersed microalloy carbides in bainitic ferrite, instead of cementite, will give optimum impact properties and formability in high strength bainitic steels. The rejection of impurities from grain boundaries, which are associated with the classical site competition

effects, is also influenced by microalloying additions.

The main objective of the research presented in the paper is to develop the model capable of predicting the kinetics of the MX-type carbides or nitrides precipitation in bainitic ferrite.

2. EXPERIMENTAL

The low-carbon ($C < 0.1\%$) bainitic steel was investigated whose chemical composition was built upon Cr-Mo ($Cr + Mo \approx 0.4\%$) system as bainite promoting elements and V ($\approx 0.2\%$) as the element causing the precipitation strengthening in ferrite. The samples machined from the bars of experimental steel, having the dimensions: $20 \times 25 \times 35 \text{ mm}$, were reheated in the Gleeble 3800 simulator to 1180°C , held for 300 seconds at this temperature, cooled at a rate of approximately 20°C/s to the isothermal holding temperatures below B_s , and held for varying time intervals. After isothermal holding, the samples were immediately quenched with water. The schematic characterisation of the experiments conducted using the Gleeble 3800 simulator is given in figure 1.

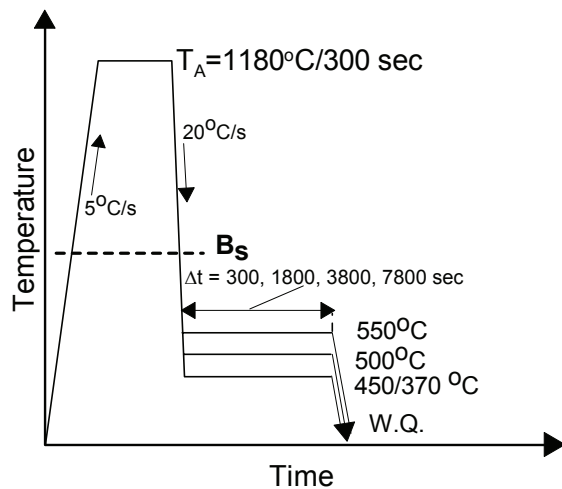


Fig. 1. Schematic depiction of the experiments conducted using Gleeble 3800 simulator for the investigation of the MX-type carbides precipitation kinetics in the experimental steel.

After the treatment presented in figure 1, the samples were examined using advanced experimental techniques, including: FEG SEM, TEM and X-ray analysis of residues produced by electrochemical dissolution of the matrix.

3. EXPERIMENTAL OBSERVATIONS

The detailed examination of the experimental samples revealed the presence of very small particles of MX-type carbides or carbonitrides that precipi-

tated in bainitic ferrite. An example of such particles is shown in figure 2.

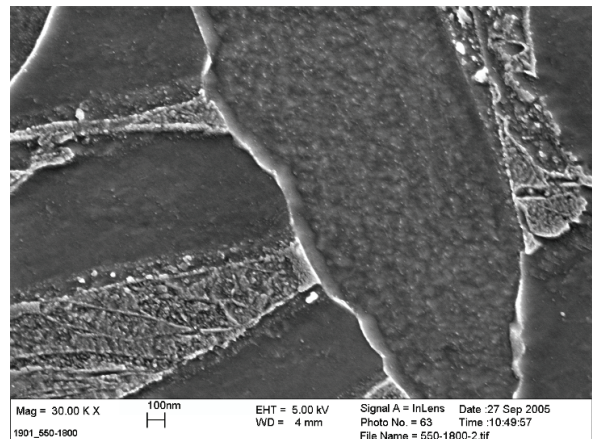


Fig. 2. MX-type precipitates in the bainitic ferrite of the sample held at 450°C for 1800 seconds. FEG SEM.

Detailed investigation has shown that the particles contained both, vanadium and chromium, in the mass proportions being approximately 1:1. Observations using transmission electron microscopy have shown that the nucleation of the precipitates was connected with dislocations present in the bainitic ferrite as a result of the glissile nature of the phase transformation. This feature of the precipitation process is shown in figure 3 and will be used as a main assumption in mathematical modelling of this process.

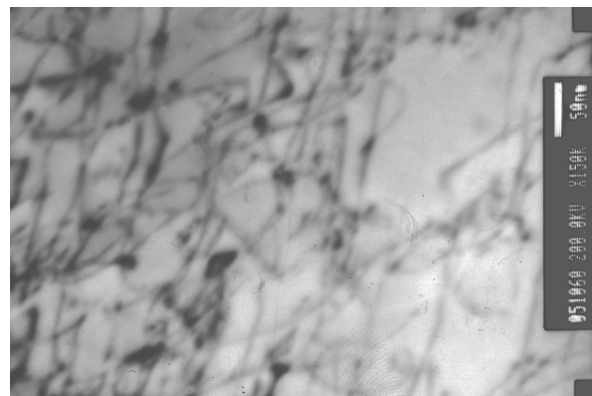


Fig. 3. MX-type precipitates in the sample of experimental steel held at 550°C for 1800 seconds. TEM.

4. MATHEMATICAL MODEL

The bainitic transformation proceeds under para-equilibrium conditions. This means that only carbon is allowed to segregate at the interface between parent and product phase. Based upon the thermodynamics calculation and the experimental observations, we have assumed that two factors account for the MX-type precipitation in the bainitic ferrite: (1) extremely high driving force for this process; (2)



lower activation energy for pipe diffusion compared to the volume one. The classical model formulations were adopted for the purpose of the precipitation process simulations (Maugis and Gouné, 2005):

- The precipitates are spherical.
- The thermodynamics of complex (V,Cr)(C,N) is an ideal solid solution.
- Nucleation occurs heterogeneously on the dislocation nodes.
- Growth is limited by the pipe diffusion along dislocation lines.
- Coarsening is driven by the Gibbs-Thompson effect.

Driving force for precipitation is given by the following equation (Maugis and Gouné, 2005):

$$\Delta G_V = -\frac{RT}{V_m} \ln \left(\frac{C_M C_X}{C_M^e C_X^e} \right) \quad (1)$$

where: R is universal gas constant, T is temperature in absolute scale, V_m is the molar volume of the precipitate, C_M and C_C are instantaneous concentrations of M (V , Nb , Ti) and X (C , N) in mol fraction, while C_M^e and C_X^e are the equilibrium concentrations of M and X calculated using the solubility product given by equation:

$$\log_{10} \left([C_M^e][C_X^e] \right) = A - \frac{B}{T} \quad (2)$$

According to the classical nucleation theory, the critical radius for nucleation, r_c , is calculated using the following equation:

$$r_c = -\frac{2\gamma}{\Delta G_V} \quad (3)$$

where: γ is the surface energy of the precipitate typically in the range of 0.2-0.3 J/m² for coherent and 0.5 J/m² for incoherent particles.

The interaction between the dislocation and the precipitates is very complex. For simplicity, an assumption is made that the dislocation core energy over the precipitate radius is spent for the nucleation event. Under this assumption, the Gibbs energy, ΔG , for the formation of a spherical nucleus of radius r is:

$$\Delta G = \Delta G_{chem} + \Delta G_{int} + \Delta G_{disl} \quad (4)$$

where: ΔG_{chem} is the chemical free energy given by the equation:

$$\Delta G_{chem} = -\frac{4}{3}\pi r^3 \Delta G_V \quad (5)$$

ΔG_{int} is the interfacial free energy given by the equation:

$$\Delta G_{int} = 4\pi r^2 \gamma \quad (6)$$

and ΔG_{disl} is the dislocation core energy:

$$\Delta G_{disl} = -0.4\mu b^2 r \quad (7)$$

where: μ is the shear modulus, b is Burgers vector of the matrix.

Thus, the activation energy for the critical nucleus formation is given by the equation:

$$\Delta G = \pi \frac{16}{3} \frac{\gamma^3}{\Delta G_V^2} - 0.8\mu b^2 \frac{\gamma}{\Delta G_V} \quad (8)$$

It is assumed for the bainitic steels that the precipitation occurs through the nucleation and growth mechanism. The variation in the precipitate density is given by the nucleation rate, and the evolution of mean precipitate radius is a combination of the growth of existing precipitates and the formation of new precipitates of critical radius. For the nucleation rate calculation, a Becker-Döring law can be used (Deschamps and Brecht, 1999):

$$\left. \frac{dN}{dt} \right|_{nucleation} = N_0 Z \beta^* \exp\left(-\frac{\Delta G}{kT}\right) \exp\left(-\frac{\tau}{t}\right) \quad (9)$$

where: Z is the Zeldovich parameter ($\approx 1/20$), k is Boltzmann constant, β^* is atomic impingement rate and τ is the incubation time.

The parameter β^* can be estimated as:

$$\beta^* = \frac{4\pi r_c^2 D_d C_M}{a_0^4} \quad (10)$$

The incubation time is given by:

$$\tau = \frac{1}{2\beta^* Z} \quad (11)$$

where: D_d and C_M are the pipe diffusivity and concentration of the element which is rate controlling the nucleation process and a_0 is the lattice constant of the matrix.

The parameter N_0 , representing the number of available sites for the heterogeneous nucleation, is the number of nodes in the dislocation network that can be estimated as:

$$N_0 = 0.5\rho^{1.5} \quad (12)$$

where ρ is the dislocation density estimated as (Enamoto, 2005):

$$\log_{10}(\rho) = 9.2848 + \frac{6880.73}{T} - \frac{1780360}{T^2} \quad (13)$$

The evolution of the precipitate radius during the nucleation and growth stage is governed by the equation (Deschamps and Brecht, 1999):



$$\left. \frac{dr}{dt} \right|_{\text{nucl+growth}} = \frac{D_d}{r} \frac{C_M - C_M^e \exp\left(\frac{r_0}{r}\right)}{C_M^p - C_M^e \exp\left(\frac{r_0}{r}\right)} + \frac{1}{N} \frac{dN}{dt} \left(\alpha \frac{r_0}{\ln\left(\frac{C_M}{C_M^e}\right)} - r \right) \quad (14)$$

where: C_M^e is the concentration of M in the precipitate, α is the numerical factor accounting for the fact that nucleated precipitates can grow only if their radius is slightly larger than the nucleus critical radius. Since the value of this factor does not have a significant effect on the result of the calculation, typically it is taken as 1.05. The r_0 parameter is calculated as:

$$r_0 = \frac{2\gamma V_m}{RT} \quad (15)$$

In the late stage of the precipitation, the nucleation rate in the depleted solid solution progressively decreases, and the pure growth equations are valid provided that the mean precipitate radius is much larger than the critical radius:

$$\left. \frac{dr}{dt} \right|_{\text{growth}} = \frac{D_d}{r} \frac{C_M - C_M^e \exp\left(\frac{r_0}{r}\right)}{C_M^p - C_M^e \exp\left(\frac{r_0}{r}\right)}$$

and: (16)

$$\left. \frac{dN}{dt} \right|_{\text{growth}} = 0$$

Nucleation on dislocation ends when the following condition is satisfied (Deschamps and Brecht, 1999):

$$N^3 = \frac{1}{4D_d} \frac{dN}{dt} \quad (17)$$

when the mean particle radius is equal to the critical radius, the coarsening regime holds and the evolution of precipitate radius is given by the equation:

$$\left. \frac{dr}{dt} \right|_{\text{coars}} = \frac{\gamma V_m C_M^e D_d r_{\text{core}}^2}{25kT} \frac{1}{r^4} \quad (18)$$

In order to change continuously from the growth stage to the coarsening stage, the coarsening function is defined:

$$\frac{dr}{dt} = (1 - f_{\text{coars}}) \left. \frac{dr}{dt} \right|_{\text{growth}} + f_{\text{coars}} \left. \frac{dr}{dt} \right|_{\text{coars}} \quad (19)$$

$$\frac{dN}{dt} = f_{\text{coars}} \left. \frac{dN}{dt} \right|_{\text{coars}}$$

where:

$$f_{\text{coars}} = 1 - \text{erf} \left(4 \left(\frac{r}{r_0} \ln \left(\frac{C_M C_X}{C_M^e C_X^e} \right) - 1 \right) \right) \quad (20)$$

Finally, the solute balance gives the following equation:

$$C_M = \frac{C_M^0 - f_V C_M^p}{1 - f_V} \quad (21)$$

where C_M^0 is the mean concentration of element in a steel and f_V is volume fraction of particles. f_V is given by the following equation:

$$f_V = \frac{4}{3} \pi N r^3 \quad (22)$$

5. MODEL RESULTS

The results of the evolution of MX-type precipitates in the bainitic ferrite in the course of isothermal experiments, described in Chapter 3, were used for the model parameter adjustment. The set of the model coefficients is given in table 1.

Table 1. Model parameters for the calculation of MX-type precipitation kinetics in the bainitic ferrite.

Name parameter	Symbol	Value
Coefficients of equation (2)	A	6.561
	B	13097.94
Shear modulus	M [GPa]	64000
Burgers vector	b [m]	$2.5 \cdot 10^{-8}$
Diffusion coefficient	$D_d = D_0 \exp\left(-\frac{Q}{RT}\right)$	
	D_0 [m ² /s]	$0.15 \cdot 10^{-4}$
Molar volume	V_m [m ³ /mol]	$6.10 \cdot 10^{-6}$

Only two model parameters, activation energy for the diffusion and interface energy, were adjusted in the calculation. The activation energy for the pipe diffusion of vanadium was estimated to be less by 20% from the activation energy for volume diffusion. Higher interface energy, namely 0.43 J/m², gave better results of the calculation for higher temperatures compared to the results pertaining to lower temperatures for which the relevant parameter was taken as 0.2 J/m². This may mean that at higher temperatures, the precipitates lose coherency immediately after the nucleation process completion.



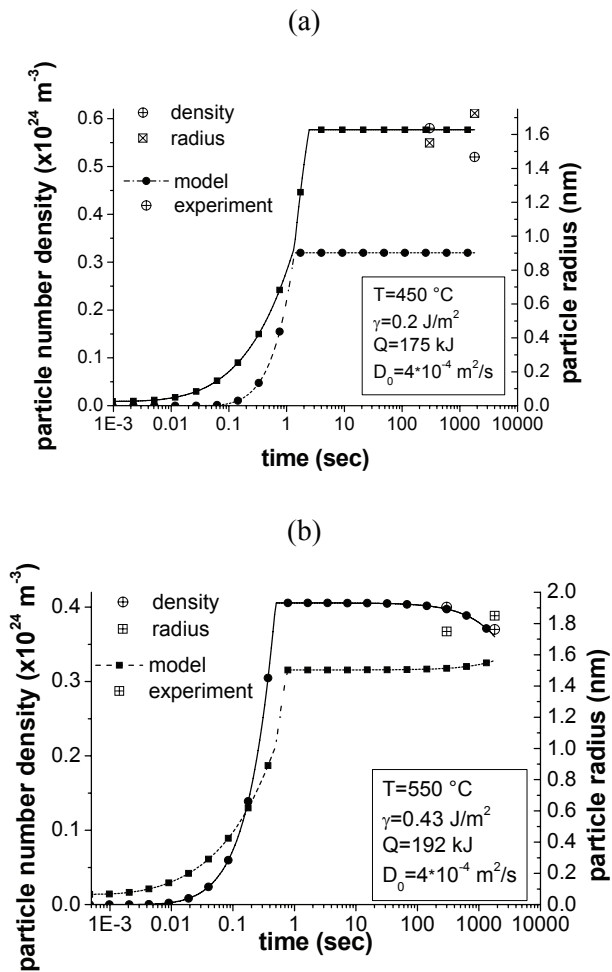


Fig. 4. Calculated versus measured changes of particle radius and number of particles in unit volume as a function of time: (a) for the experiment conducted at 450 °C; (b) for the experiment conducted at 550 °C.

The results of the model predictions and measurement are shown in figure 4. The full symbols in this figure pertain to the results of the calculation whilst the open ones to the results of the measurement. Due to the inaccuracy in the particle size measurement during the initial stage of the precipitation process, connected to the extremely small particle radius, only the results of such a measurement after long holding time were used to scale up the model coefficients. The measured values of the particle radius coincide well with the results of the calculation. The measured number of particles in the unit volume of the material lies outside the calculated line, however, due to the very high value of this parameter, the error in the predictions is acceptable. A higher value of the interfacial energy that had to be used for the calculation at temperature 500 °C compared with the value used at 450 °C may be associated with the fact that at higher temperature, precipitates lose coherency with the matrix at early stage of the precipitation process. From the

theoretical point of view, it is noteworthy that good results of the calculation were obtained with physically justified values of the model coefficients. Thus the observed precipitation process can be accounted for without changing our views regarding the bainitic transformation and using the classical nucleation and growth theory.

It seems, however, that depending on the precipitation temperature range, and thus the bainite morphology, this process may be influenced by the specific features of the bainitic transformation. Thus, perhaps no unique theory describing the precipitation process in the entire temperature range of the bainitic transformation can be formulated without the simultaneous analysis of the conditions of bainite sub-unit formation.

6. SUMMARY

The investigation presented in this paper shows that the MX-type precipitation process occurring in bainitic steels can be accounted for using classical nucleation and growth theory with physically meaningful model parameters. Main factors allowing for such a process occurrence comprise high thermodynamics driving force for the precipitation and pipe diffusion along dislocation lines. According to the model predictions and experimental results, MX-type precipitates in bainitic ferrite are extremely fine. Typically, their mean size is less than 5 nm. This means that their contribution to the strength of steel is less compared to the precipitates in proeutectoid ferrite. Despite this, the adequate steel chemistry design can provide the precipitation strengthening contribution of MX-type particles in the bainitic ferrite as high as 200 MPa.

Acknowledgement. The authors wish to acknowledge Dr. Stanislaw Zajac of KIMAB for his assistance in the investigation.

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**MODELOWANIE KINETYKI PROCESU
WYDZIELENIOWEGO WĘGLIKÓW TYPU MX
W NISKOWĘGLOWYCH STALACH BAINITYCZNYCH**

Streszczenie:

Praca dotyczy modelowania procesów wydzieleniowych węglików typu MX w niskowęglowych stalach bainitycznych umacnianych wydzieleniowo. Występowanie efektu umocnienia wydzieleniowego w tych stalach pozwala obniżyć w nich

zawartość węgla przy zachowaniu ich wysokiej wytrzymałości. W takim przypadku, wyrób charakteryzuje się również bardzo dobrą ciągliwością. Do modelowania kinetyki procesu wydzieleniowego zastosowano model Deschamps'a przy założeniu, że proces ten jest kontrolowany dyfuzją wzdłuż linii dyslokacji. Opracowany model zastosowano do analizy wpływu składu chemicznego i parametrów procesu na efekt umocnienia wydzieleniowego ferrytu bainitycznego.

Submitted: October 31, 2006

Submitted in a revised form: November 13, 2006

Accepted: November 24, 2006

