Model of precipitation kinetics of copper and manganese sulfides in ultra low-carbon and interstitial free steels was created on the basis of classical nucleation and growth theory. The model includes homogeneous and heterogeneous schemes for independent nucleation of manganese and copper sulfides and simultaneous growth/ shrinkage of inclusions.

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MODELING OF PRECIPITATION KINETICS OF MANGANESE AND COPPER SULFIDES IN INTERSTITIAL FREE STEELS

Introduction

Low carbon steel production with copper sulfide precipitation strengthening is being now extensively investigated owing to its lower cost as compared to that with steelmaking using Nb and Ti precipitates. Copper is always available in steel scrap. In some cases steels with copper sulfide precipitates have even better mechanical properties than those with Nb/Ti precipitates. Currently such low-carbon steels with high mechanical properties are under active investigation. Precipitation hardening and strengthening have a great effect on mechanical properties of these steels.

Precipitation kinetic is modeled on the basis of classical nucleation and growth theory (CNGT). This method is most widely used for prediction of precipitation behavior. Its success is in its simplicity and a small number of physically transparent parameters. The correct definition of such parameters (by fitting or by atomic simulation and so on) enables obtaining the quantitative results for precipitation kinetic. The basic developments and applications of classical theory are presented in [1–25].

The different numerical schemes and details are presented in [11]. Application for copper precipitation in steel matrix is developed and good agreement with experimental data are presented in [13, 14].

In some cases precipitates such as nickel superalloys, copper HSLA steel, Al–Sc alloys as well as investigated inclusions with cuprum sulfide have low surface energy. Therefore, the coarsening induced by differences in interface surfaces fails to suppress continuous creation of new small subcritical-size inclusions. The majority of solute atoms belongs to low mobile clusters and do not contribute directly to coarsening process. Conventional models of nucleation are valid for systems with high-surface energy and their application to systems with low values may result in erroneous interpretation of experimental data [18].

For many cases the modeling of homogeneous nucleation and growth by CNGT gives satisfactory agreement with experimental data. In some cases fitting of parameters is not used at all, in others one or two parameters are fitted. But as a rule even in the latter cases good agreement is observed for a great number of temperature regimes and initial concentrations of solutes as well as for multi-component and multiphase precipitation.

By now the physical nature of heterogeneous nucleation of copper sulfides is practically unknown. There are many hypotheses about heterogeneous nucleation sites for CuS including grain borders, matrix-MnS inclusion interfaces, dislocations, Cu or S microsegregation and so on. In general, the method considered can be used for describing various models of nucleation, by means of simultaneous following both MnS and Cu_2S nucleation. In this work the assumption is made that precipitations of copper and manganese sulfides are independent. Next we assumed that the diffusions of copper, manganese and sulfur atoms are independent as well.

The only one available work devoted to approximate modeling of copper sulfides precipitation kinetic is presented in [20]. We shall model precipitation using approximately the following composition: copper is 0,07 wt%, sulfur 0,04 wt% and manganese concentration 0,54 wt% for steels with hot and cold rolling.

The considerations accepted here to be used for simulation of precipitation kinetics on the basis of CNGT are as follows.

1. Wholly diffusion-controlled precipitation is assumed for our case on the basis of spherical shapes of inclusions and reported cube-cube orientation between copper sulfide inclusions and matrix [20].

2. All heterogeneous nucleation sites have deformed lattice around nucleation sites and hence have higher mobility of Cu atoms as compared with that in ideal matrix. In this work the model of Cu diffusion near dislocations has been selected for nucleation and initial growth modeling. The characteristic feature of this model is that in the temperature range 200 to 500 °C the Cu diffusion coefficient may be a few orders of magnitude higher than this coefficient in ideal matrix.

3. The estimation of Gibbs free energy change for precipitation of copper sulfides is corrected in as compared with [20] on the basis of more correct equilibrium temperature estimation in [27], since thermodynamic modeling predicts unstable character of copper sulfides in Fe matrix, especially with adding of Mn solute.

MODEL OF PRECIPITATION

Nucleation

CNGT is based on the changes in Gibbs energy ΔG associated with the formation of a precipitate in a supersaturated solid solution. In the case of spherical precipitates of radius R, $\Delta G(R)$ is given by:

$$\Delta G(R) = \frac{4}{3}\pi R^3 \Delta g + 4\pi R^2 \sigma, \qquad (1)$$

where Δg is the chemical Gibbs energy density change and σ the specific interfacial energy.

According to CNGT the nucleation rate is given by:

$$J^* = N_{tot}\beta^* Z \exp\left(-\frac{\Delta G^*}{kT}\right)\exp\left(-\frac{t_{inc}}{t}\right), \qquad (2)$$

where N_{tot} is the overall number of potential nucleation sites; β^* the frequency factor; Z the Zeldovich factor; ΔG^* the activation energy barrier and t_{inc} the incubation time. They are calculated as:

$$\beta^* = \frac{4\pi D\bar{c}R^{*2}}{a^4}, \qquad (3)$$

$$Z = \frac{v_A}{2\pi R^{*2}}\sqrt{\frac{\sigma}{kT}}, \qquad (4)$$

$$\Delta G^* = \frac{4\pi}{3}R^{*2}\sigma = \frac{16\pi\sigma^3}{3\Delta g^2} = -\frac{\Delta G_0}{S^2}, \qquad (5)$$

$$t_{inc} = \frac{2kTa^4 R^{*2}}{Dv_A\bar{c}\sigma}, \qquad (6)$$

where v_A is the volume of precipitate molecule, a the lattice parameter of matrix, D the diffusivity of solute atoms (Cu or Mn) and $\bar{c}$ the corresponding initial concentration:

$$R^* = \frac{R_0}{S}, \qquad (7)$$

$$R_0 = \frac{2\sigma v_A}{kT}, \qquad (8)$$

$$S = \ln\left(\frac{c_{Cu}^2 c_S}{c_{Cu_2S}}\right), \qquad (9)$$

$$\Delta g = \frac{kT}{v_A}S, \qquad (10)$$

in which it is assumed, that precipitate has stoichiometric composition Cu_2S, and c_{Cu_2S} is the product of solubility for equilibrium concentrations c^e:

$$c_{Cu_2S} = (c_{Cu}^e)^2 c_S^e. \qquad (11)$$

Sometime the critical radius is defined as

$$R = R^* + \sqrt{\frac{kT}{8\pi\sigma}},$$

taking into account the fact that a particle with a radius exactly equal to R^* can not grow.

Gibbs energy

Expression (10) for chemical bulk energy may be estimated by two different ways. Experimental data concerning solubility product for Cu_2S in silicon steel matrix are presented [20]:

$$\log\left([\%Cu]^2[\%S]\right) = -44971/T + 26,31. \qquad (12)$$

The following linear approximation is possible for small supersaturations:

$$\Delta g = Q\frac{\Delta T}{T_e}\frac{1}{V_m}, \qquad (13)$$

where $Q = 860700$ J/mol-molecule of Cu_2S and equilibrium temperature is estimated as $T_e = 1196$ °C (derived from solubility product (12) for concentrations of S equal to 0,01 and Cu 0,07 mass%). ΔT is overcooling below equilibrium temperature, V_m is molar volume of precipitates.

In [27] the thermodynamic calculation resulted in obtaining the dependence of driving force Δg for Cu_2S on temperature. The equilibrium temperature is about 740 °C for 0,0015C–0,2Mn–0,06Si–0,01S–0,06P–0,02Nb–0,05Cu–0,035Al (wt %) steels assuming the absence of sulfur reactions with manganese and iron.

The equilibrium temperature in (13) may depend on initial solute concentration, phase transition pa-

rameters and others. An insignificant error made in experimental measurement of copper solubility in matrix may actually lead to substantial deviation from correct equilibrium temperature. This inaccuracy is less important for estimation of phase transition enthalpy. On assumption that solubility product depends only on temperature as in (12), the Q value would depends only on enthalpy of phase transition [28], and Q can be estimated as in [20].

The equilibrium temperature for 0,05%Cu and 0,01%S is estimated as 740 °C according to [27].

It should be noted that this "combined" estimation ensures metastable behavior of copper sulfide in presence of manganese sulfide for temperatures usually used for annealing. Such approach makes reasonable evaluation of driving force possible. In other words, the accuracy of (13) when using more correct equilibrium temperature is higher than that with direct use of (12).

Then we can equalize Gibbs energies (10) and (13):

$$Q\frac{\Delta T}{T_e} = R_g T \ln\left(\frac{\tilde{c}_{Cu}^2 \tilde{c}_S}{c_{Cu_2S}}\right), \quad (14)$$

where $\tilde{c}$ are the solute concentrations for which equilibrium temperature has been evaluated and R_g the gas constant. Then we have:

$$\ln c_{Cu_2S} = \frac{-Q}{R_g T} + \frac{Q}{R_g T_e} + \ln\left(\tilde{c}_{Cu}^2 \tilde{c}_S\right). \quad (15)$$

As a result, (15) allows finding the corrected estimation of solubility product c_{Cu_2S} for any temperature without direct using of approximation (12). For instance, at 650°C $c_{Cu_2S} = 1,57 \cdot 10^{-15}$. Due to assumption, that such solubility product depends only on temperature, this value may be further used for another concentrations for calculation of Gibbs energy on the basis of (9) and (10).

Growth

The equilibrium concentrations c^i of solutes in matrix at the matrix-precipitate boundary are increased owing to the curvature of surface between matrix and precipitate. It is assumed that the inclusion has spherical shape with current radius R. As to binary alloys new solute equilibrium concentration is defined by precipitate radius. With two-component precipitates the product of new equilibrium concentrations is defined by radius:

$$\exp\left(\frac{R_0}{R}\right) = \left(\frac{[c_{Cu}^i]^2 c_S^i}{c_{Cu_2S}}\right). \quad (16)$$

The second equation for determination of c_{Cu}^i and c_S^i can be derived from the fact, that diffusion flux of both species should lead to identical growth of

crystal. As to frequently used Zener approximation growth/shrinkage of inclusion is determined by supersaturation and is given by:

$$v = \frac{dR}{dt} = \frac{D_{Cu}}{R}\frac{c_{Cu} - c_{Cu}^i}{\alpha c_{Cu}^p - c_{Cu}^i} = \frac{D_S}{R}\frac{c_S - c_S^i}{\alpha c_S^p - c_S^i}, \quad (17)$$

where c_{Cu}^p and c_S^p are the fractions of Cu and S in precipitate, α the ratio of atomic volumes of this specie in matrix and precipitate and c_{Cu} and c_S the current fractions of solutes in matrix. Two equations (17) give the second equation for definition of concentrations c_{Cu}^i and c_S^i and are simultaneously used for growth speed determination.

The average precipitate radius is little dependent on critical radius for sufficiently long time of precipitation, but activation barrier, precipitation rate and inclusions density may considerably depend on critical radius.

Distinctive features of nucleation and growth on dislocations

The previous model describes homogeneous nucleation. As to heterogeneous nucleation some parameters in equations must de modified. The heterogeneous nucleation of Cu$_2$S is expected to be mainly located on dislocations as soon as the density of dislocations rises to high values following hot and cold rolling.

As regards heterogeneous nucleation the interface energy is decreased by the value that depends on a particular nucleation type. In this work it is approximately assumed, that in accordance with [20] the value of σ must be multiplied by a factor of 0,7.

The significant feature of growth on dislocations is rapid diffusion of copper atoms in a small zone around dislocation. In order to exactly consider this phenomenon the conception of depleted zone is introduced [2, 13]. The activation energy of pipe diffusion has been estimated as 0,73 of matrix diffusion, and around dislocation the diffusion coefficient D_d may be evaluated as [13]:

$$D_d = (D_V^2 D_p)^{1/3}, \quad (18)$$

where D_p and D_V are the pipe diffusion and volume diffusions, respectively.

In this work simpler models without depleted zone calculation are used. Value D_d is used for nucleation and growth at initial stage. With increasing the inclusion radius the coefficient of diffusion decreases to D_V value by linear law. In such approach the mobility of Cu atoms is sufficiently high to ensure nucleation and initial growth of precipitates even for relatively low temperatures of 300–500 °C. This mobility of copper

atoms at small distances around dislocation is comparable with that of sulfur atoms.

Numerical method

The solute balance equations are used for estimation of current concentrations of Cu and S i. e. c_{Cu} and c_S. In this approximation it is assumed, that the solute fraction distribution is uniform in matrix. Then, if matrix volume change is neglected in precipitation process we have:

$$c = \overline{c} - V_p n_p \frac{\rho_p}{\rho_m} \frac{M_{Fe}}{M_{Cu_2S}}, \qquad (19)$$

where $\overline{c}$ is the initial solute molar fraction, V_p the volume fraction of precipitate, n_p the number of atoms of relevant specie in molecule of precipitate (for Cu $n_p = 2$, for S n_p is 1), ρ_p and ρ_m are the densities of precipitate and matrix and M its molecular weights.

N – model [11] will be used for describing the evolution of precipitate size distribution. In this model the particle size distribution function (PSD) is discretized into N_c number of size classes. The class is defined by radius R_i and the number of inclusions with radius size between $R_i - \Delta R/2$ and $R_i + \Delta R/2$. The total number of particles is:

$$N = \sum_i N_i,$$

the average radius is:

$$R = \frac{\sum_i R_i N_i}{N}$$

the precipitate volume fraction is:

$$V_p = \frac{4}{3} \pi \sum_i N_i R_i^3.$$

In case of using "Euler like" method for calculation the boundaries of classes are fixed and fluxes of particles between classes are estimated. The details are presented in [11].

The initial distribution for N_i is null or known (for example experimental data) distribution.

The adaptive step time Δt is used because the radius change during Δt time has not been above $\Delta R/2$. This limitation eliminates the possibility to "jump" across one or more classes. The maximum speed v has classes with small R, according to (17).

New size classes are created for high R values during inclusion growth. And quite the contrary, if the number of particles in a class with small radius is less than 1 it will be excluded from calculation. This makes it possible to increase step time Δt and to calculate particle growth during long annealing periods.

Conclusions

Model for nucleation and growth the precipitation of manganese and copper sulfides inclusions are developed. New estimation of Gibbs free energy change for precipitation of copper sulfides is used. Model of nucleation and growth of copper sulfides precipitates on dislocations are used for heterogeneous nucleation. Numeric model, based on "Euler like" method, are developed for calculations.

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