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Simulation of the growth of Cu critical nucleus in Fe-Cu alloys

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In Cu bearing steels Cu particles are nucleated as bcc clusters in the ferrite or martensite matrix of Cu bearing steel during aging. The concentration profile of a critical nucleus of coherent bcc Cu was calculated from Cahn-Hilliard non-classical nucleation theory, and the growth of the nucleus was simulated solving Cahn-Hilliard nonlinear diffusion equation. It is found that the Cu concentration at the center of the nucleus increased first to the binodal concentration and then, the increase in particle radius followed. The time for the particle to become essentially pure copper depends considerably on the alloy composition and the aging temperature. These may have to be taken into account in the discussion of experimental observations (e.g. APFIM and positron annihilation) of the concentration of Cu particles.

Key words: Nucleation, precipitation, Fe-Cu alloy, Cahn-Hilliard nucleation theory

1. INTRODUCTION

Cu bearing high strength low alloy steels have the potential of achieving good formability, high strength and weldability by aging. The age hardening characteristics can be improved significantly by prestraining [1]. Accordingly, the mechanism of Cu precipitation in steel has received considerable attention. Presently, different results of Cu concentration in the particles are reported depending on the experimental methods. The positron annihilation [2] and small angle neutron scattering (SANS) tend to support that the particles are pure Cu [3,4]. On the other hand, atom probe field ion microscope (APFIM) [5] reported the concentration of Cu particles to be less than unity.

It is well known that Cu precipitates are formed initially as coherent bcc clusters in the ferrite matrix. Thus, the composition and activation energy of Cu critical nuclei can be calculated from Cahn-Hilliard non-classical nucleation theory [6]. This theory predicts that the composition of nuclei coherent to the matrix varies with the alloy composition and temperature; at lower temperatures and compositions close to the spinodal curve, the concentration of a critical nucleus becomes significantly less than pure Cu [1]. In the above experiments comparisons were made in different alloy compositions and aging temperatures and times as well.

Under this circumstance, the concentration profile of Cu nuclei are first calculated using non-classical nucleation theory and the growth of the nucleus was simulated by means of non-linear Cahn-Hilliard diffusion equation [6]. Then, the variation of the composition and size of Cu nuclei with aging is discussed in conjunction with experimental observations.

2. SIMULATION METHOD

Under the assumption that the Cu nucleus is spherical, the change in free energy accompanying the formation of a critical nucleus is given by the following equation[6]:

$$F(c) = \int_V \{\Delta f + \kappa(\nabla c)^2\} dV \qquad (1)$$

$$\Delta f = f(c) - f(c_0) - (c - c_0)\left(\frac{\partial f}{\partial c}\right)_{c_0} \qquad (2)$$

where $f(c)$ is the free energy per unit volume of a homogeneous solid solution of concentration , c_0 is the bulk composition, and κ is the gradient energy coefficient. The concentration profile of Cu nucleus is calculated from the Euler equation of variational principle,

$$2\kappa\nabla^2 c + \frac{\partial \kappa}{\partial c}(\nabla c)^2 = \frac{\partial \Delta f}{\partial c} \qquad (3)$$

Assuming that κ does not depend on the concentration, eq. (3) becomes

$$2\kappa\frac{\partial^2 c}{\partial r^2} + \frac{4\kappa}{r}\frac{\partial c}{\partial r} = \frac{\partial \Delta f}{\partial c} \qquad (4)$$

with the following boundary conditions

$$\frac{\partial c}{\partial r} = 0 \qquad at\ r = 0 \quad and \quad r = \infty$$
$$c = c_0 \qquad at\ r = \infty \qquad (5)$$

The value of κ depends on the crystal structure. In a bcc matrix, the 1st and 2nd nearest neighbor interactions are taken into account. Under the assumption that the interact energy between the 2nd neighbor is 3/4 of the interaction between the 1st neighbors[7], κ is calculated to be $\kappa \sim 0.28kT_c a^2$, where T_c is the critical temperature(1587 ℃), k is the Boltzmann constant, and a is the lattice parameter [1,7].

The nonlinear diffusion equation is given by the following equation [8],

$$\frac{\partial c}{\partial t} = \nabla\{M(c)\nabla\chi\}$$
$$= \nabla M(c)\cdot\nabla\chi + M(c)\nabla^2\chi \quad (6)$$

where $M(c)$ is the mobility, and χ is the diffusion potential defined by

$$\chi = \frac{\partial f}{\partial c} - \left(\frac{\partial f}{\partial c}\right)_{c_0} - 2\kappa\nabla^2 c \quad (7)$$

Eq. (6) means that the concentration c varies with time dictated by the diffusion potential χ and the growth stops if χ is uniform in the system. Eliminating the 2nd term in the r.h.s. of eq.(7), which is constant,

$$\chi = \frac{\partial f}{\partial c} - 2\kappa\nabla^2 c \quad (8)$$

Thus, eq. (6) becomes

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial r}\frac{\partial M(c)}{\partial c}\left(\frac{\partial \chi}{\partial r}\right) + M(c)\left(\frac{\partial^2\chi}{\partial r^2} + \frac{2}{r}\frac{\partial \chi}{\partial r}\right)$$
$$= \left(M(c)\frac{2}{r} + \frac{\partial c}{\partial r}\frac{\partial M(c)}{\partial c}\right)\frac{\partial \chi}{\partial r} + M(c)\frac{\partial^2\chi}{\partial r^2} \quad (9)$$

In a binary Fe-Cu alloy the mobility of the inter diffusion [9] is

$$M(c) = \{M_{Cu}(1-c) + M_{Fe}c\}c(1-c) \quad (10)$$

where $M_{Cu} = D_{Cu}/RT$ and $M_{Fe} = D_{Fe}/RT$, D_{Cu} and D_{Fe} are the intrinsic diffusion coefficient of Cu and Fe, respectively, R is the gas constant; T is the temperature. Eq.(9) is solved using the finite different method with the values of ancillary parameters shown in Table 1.

Table 1. The values of thermodynamic parameters for a Fe-Cu alloy at 550℃

Parameter			Ref.
D_{Fe}	1.0×10^{-17}	cm^2/s	9
D_{Cu}	1.28×10^{-17}	cm^2/s	9
κ	3.56×10^{-16}	$J\,m^2/mol$	1

3. RESULT AND DISCUSSION

Fig.1 illustrates the concentration profiles of a critical nucleus calculated at 550℃ for Fe-1.0 and 3.0 wt% Cu alloys. The composition of a Cu particle in the latter alloy is significantly less than unity at least at the stage of nucleation. For this concentration profile the diffusion potential is zero everywhere in the system. The concentration of the nucleus was then slightly increased or decreased as shown in Fig.2 As expected, the nucleus grew in the former case, whilst it shrank in the latter (not shown here).

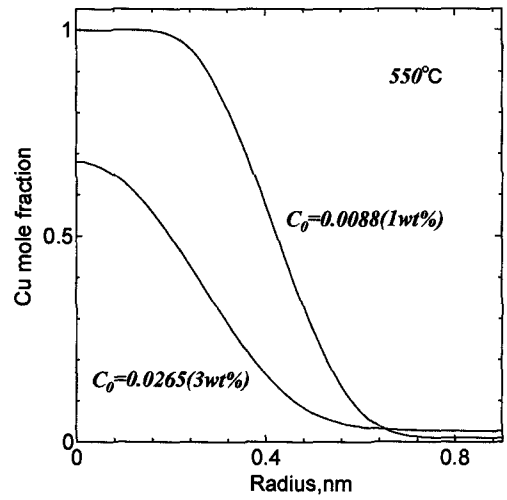

Fig.1 Concentration profile of critical nuclei for the two alloys at 550°C.

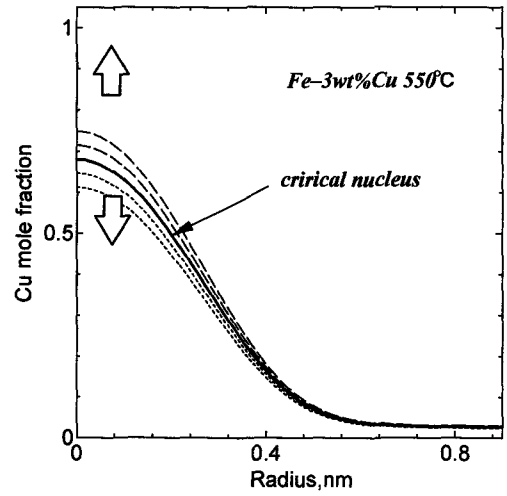

Fig.2 Variation of the concentration profile from the critical nucleus in the growth (dashed line) and the dissolution (dotted line).

Fig.3a and b show the variation of the concentration profile with time. In the 3wt%Cu alloy the concentration at the center of a nucleus increased at first and the increase in the particle radius occurred subsequently. The concentration in the center of the nucleus became

close to unity in 240 sec in this alloy as shown in Fig. 4. In contrast, in the 1wt% Cu alloy the radius of the nucleus increased from the beginning because the concentration in the center of the nucleus already was close to unity.

The variation with time of Cu concentration in the periphery region of the nucleus is shown in Fig. 5. The Cu concentration in this region decreases as the particle grows in order to keep mass balance. This concentration is decreasing toward the equilibrium concentration, but not yet reached it in the time in which simulation was conducted.

Fig. 6 shows the variation of the particle radius, defined by the radius at which the Cu concentration is one-half, with time. Initially the growth rate is very

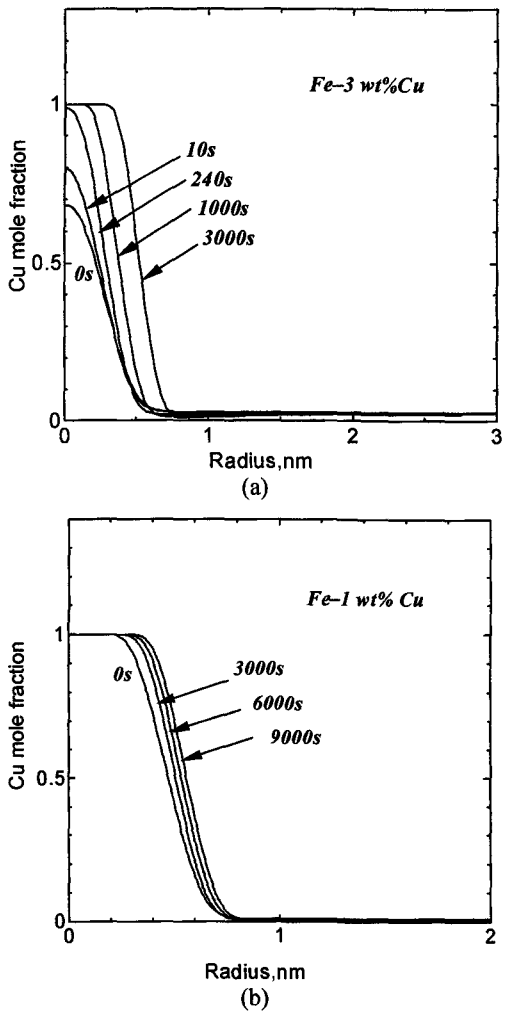

Fig.3 Variation of the concentration profile with aging time (a) in the Fe-3 wt% Cu alloy and (b) in the Fe-1 wt% Cu alloy.

small due to the Gibbs-Thomson effect. Gradually it approaches the $t^{1/2}$ kinetics of diffusion controlled growth as the Cu concentrations in the particle and in the matrix approach the equilibrium concentrations, that is, local equilibrium is a chivied.

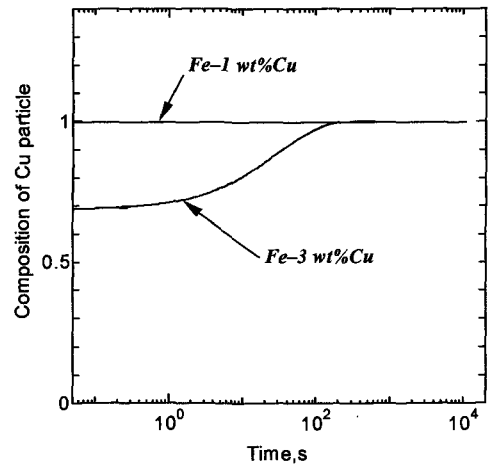

Fig.4 Variation of the concentration of the center of the particle with aging time in the Fe-3 wt% Cu and Fe-1 wt% Cu alloys.

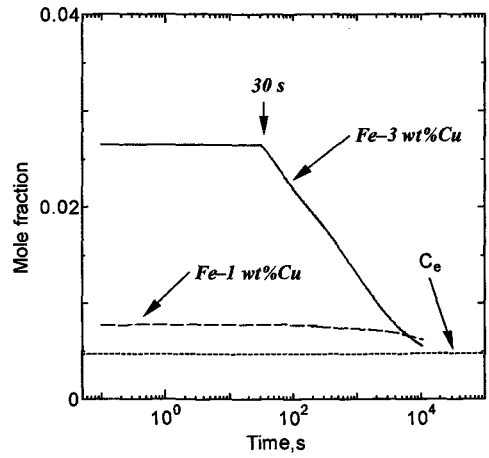

Fig.5 Variation of the concentration at the boundary in the matrix with aging time in the Fe-3 wt% Cu (solid line) and Fe-1 wt % Cu (dash line) alloys. c_e is the concentration at the boundary in the matrix at equilibrium.

4. SUMMARY

The growth of a Cu nucleus at 550℃ in Fe-1 wt% and 3 wt%Cu alloys was simulated by solving the Cahn-Hilliard non-linear diffusion equation by the finite difference method. The initial concentration profile of critical nucleus was calculated from non-classical nucleation theory [6].

In the 3wt%Cu alloy the concentration at the center of the Cu nucleus first increased and an increase in the particle radius occurred subsequently. The time spent by this increase was 240 sec for the diffusivities used in the calculation. It appears that the Cu particles are not always pure Cu especially at early growth stages. At a lower temperature the Cu concentration in the nucleus is

smaller and the time for the particle to reach pure Cu may become large due to sluggish diffusivity.

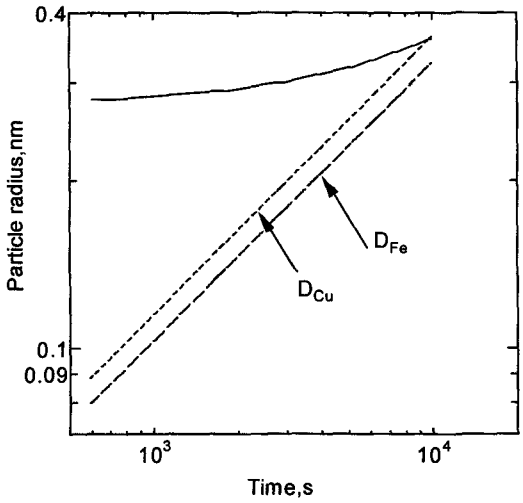

Fig.6 Variation of the size of the particle with aging time in the Fe-1 wt% Cu alloy. The growth by the self diffusion of only Fe (dash line) or Cu (short dash line) is drawn in the classical theory.

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