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Role of Induced Stress in Ostwald Ripening in Solid Matrices*

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Ostwald ripening in solid matrices is studied theoretically considering the stress around dispersed particles induced by the volume gap.

Under the condition that the diffusion in the matrix compensates the volume gap, a ripening rate equation is derived as follows:

$$\bar{r}_a^3=\frac{8\sigma l}{9(1-\alpha)RT}\Big/\sum_{N}\left[\frac{1}{C_N D_N}(C_N^\theta-C_N)^2\right].$$

The equation is a generalized one for multi-component system and covers all conventional formulas. Under the condition that the creep deformation takes place to compensate the volume gap, the equation is given as follows:

$$\bar{r}_a^n=n\alpha^2 A\exp(-Q_c/RT)\left(\frac{V_\theta}{V_c}\right)\left[\frac{\sigma V_\theta}{3EV_c\ln(1/\alpha)}\right]^n t.$$

The results of calculation have revealed that the creep deformation is more dominant than the iron diffusion to compensate the volume gap for cementite coarsening in ferrite below 973 K.

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Keywords: *Ostwald ripening, cementite, diffusion, precipitation, coarsening*

I. Introduction

The coarsening behavior of precipitated particles in the later stage of aging is well known as Ostwald ripening that larger particles grow and smaller particles shrink so as to decrease the total interfacial energy between the matrix and the particles.

This Ostwald ripening has been known since 1900, but the first theoretical consideration had to wait for Greenwood(1) in 1955. After that, Lifshitz, Slyozov(2) and Wagner(3) presented the fundamental theoretical coarsening equation. However, the application of their theory to the coarsening of precipitates in solid matrices was very limited, because the theory principally dealed with solution of the problems of the coarsening of precipitates in fluid. The precipitation in solid matrices generally produces volume change, and this volume gap should be dissolved by diffusion or plastic deformation.

The first investigation from this view-point was done by Oriani(4). He introduced the volume constraint condition that there be no net volume change when the dislocation loop generation can be shown to be absent. He presented two diffusion mechanisms, i.e. volume coupling diffusion and simple coupling diffusion. Which mechanism takes place depends on the entropy formation rate.

Consecutively, Li *et al.*(5) generalized the theoretical equation introducing "*coupling force*" for the volume constraints. At present, the theoretical coarsening equation by Li *et al.* is usually adopted. But there are some obscurities in the driving force for the dissolution of the volume gap in both treatments by Oriani and Li *et al.* Moreover there are complexities and mistakes in their multi-component treatment.

As well known, diffusion is controlled by chemical potential gradient which includes pressure gradient on the ground of Gibbs-Duhem relation. Precipitation or dissolution in solid matrices generally induces volume

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change and local stress, i.e. pressure. This pressure must be considered to be the driving force of diffusion for the dissolution of the volume gap.

The present paper presents a generalized Ostwald ripening equation for a multi-component system. It starts from Gibbs-Cuhem relation and discusses whether the pressure induced by precipitation or dissolution can cause plastic deformation for the dissolution of the volume gap.

II. Model of Precipitation Field

Conventional theories pay no attention to the relative position of precipitates, but the relative position is important for the treatment of diffusion or plastic deformation in stress field. For convenience' sake precipitated particles and their territories are schematically modeled as shown in Fig. 1. Here, r_a is the radius of a precipitated particle and r_b is the territory radius of the particle. r_a is assumed to be proportional to r_b. Therefore, r_a/r_b is given by the volume fraction of precipitated particles.

Using this model, multi-particle problems can be simplified to be a single particle problem. After this preparation, the author investigated how the pressure induced by the volume change affects the Ostwald ripening in either case with or without plastic deformation. As the most general expression,

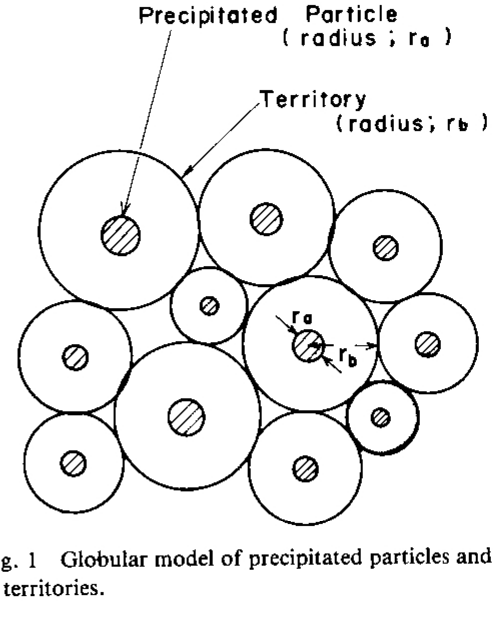

Fig. 1 Globular model of precipitated particles and their territories.

$$a[\mathrm{A}]+b[\mathrm{B}]+c[\mathrm{C}]+\cdots=[A_aB_bC_c\cdots] \quad (1)$$

is used for the precipitation reaction, in which each of A, B, C$\cdots$ stands for each element.

III. Without Plastic Deformation

We shall start from the Gibbs-Duhem relation,

$$C_A\mathrm{d}\mu_A+C_B\mathrm{d}\mu_B+C_C\mathrm{d}\mu_C+\cdots=\mathrm{d}P, \quad (2)$$

as a basic equation. Here C_A, C_B, $C_C\cdots$ and μ_A, μ_B, $\mu_C\cdots$ stand for the concentrations expressed by moles per unit volume (molar fraction/molar volume) and the chemical potentials of element A, B, C$\cdots$, and P stands for the pressure.

At first, Gibbs-Duhem relation is applied to the matrix part of a growing or shrinking precipitate (r_a) and the matrix part of a steady radius precipitate ($\bar{r}_a$). The difference in Gibbs-Duhem relation between the two parts is given as

$$C_A\Delta\mu_A+C_B\Delta\mu_B+C_C\Delta\mu_C+\cdots=\Delta P. \quad (3)$$

Similarly in the case in which Gibbs-Duhem relation is applied to the precipitate part, the difference in the relation is given as

$$C_A^\theta\Delta\mu_A+C_B^\theta\Delta\mu_B+C_C^\theta\Delta\mu_C+\cdots$$
$$=\Delta P+(2\sigma/r_a-2\sigma/\bar{r}_a), \quad (4)$$

because the surface tension of the curved interface gives rise to a pressure difference, $2\sigma/r$. In eq. (4)

$\Delta\mu_N=\mu_N-\bar{\mu}_N$ is the difference in chemical potential of element N between r_a and $\bar{r}_a$ particles.

$\Delta P=P-\bar{P}$ is the difference in pressure acting on the surface between r_a and $\bar{r}_a$ particles.

σ is the interfacial energy between matrix and precipitate. C_N^θ is the concentration expressed by moles per unit volume (molar fraction/molar volume) of element N in the precipitate.

Now we pay attention to the boundary part of the growing or shrinking precipitate. The diffusive flux of N atoms in matrix resulting from the chemical potential gradient is expressed as

$$J_N = -\frac{C_N D_N}{RT}\left(\frac{d\mu_N}{dr}\right)_{r=r_a}, \tag{5}$$

where R is the gas constant, T is the absolute temperature and D_N is the volume diffusion coefficient of element N in matrix. The flux J_N also satisfies the following equation from flux balance across the interface between matrix and precipitate:

$$J_N = (C_N^\theta - C_N)\frac{dr_a}{dt}. \tag{6}$$

Equating eqs. (5) and (6), we obtain

$$(C_N^\theta - C_N)\frac{dr_a}{dt} = -\frac{C_N D_N}{RT}\left(\frac{d\mu_N}{dr}\right)_{r=r_a}. \tag{7}$$

As the diffusion of each element N toward the particle becomes steady after a short time, the quation,

$$4\pi r^2 \frac{d\mu_N}{dr} = \text{constant}, \tag{8}$$

is satisfied. Introducing the boundary conditions at $r=r_a$ and $r=r_b$ to the eq. (8),

$$\frac{d\mu_N}{dr} = \frac{\Delta\mu_N}{r^2}\left(\frac{r_a r_b}{r_b - r_a}\right), \tag{9}$$

is driven. From the eqs. (7) and (9), the following equations are obtained.

$$\Delta\mu_N = \beta(C_N^\theta - C_N)/C_N D_N \tag{10}$$

and

$$\beta = -(1-\alpha) r_a RT\left(\frac{dr_a}{dt}\right), \tag{11}$$

where α is r_a/r_b which depends on the volume fraction of precipitates.

On the other hand, from the eqs. (3) and (4), we obtain

$$\sum_N (C_N^\theta - C_N)\Delta\mu_N = \frac{2\sigma}{r_a} - \frac{2\sigma}{\bar{r}_a}. \tag{12}$$

Thus substituting the eq. (10) for $\Delta\mu_N$ in the eq. (12), we finally obtain

$$\beta \sum_N \left[\frac{1}{C_N D_N}(C_N^\theta - C_N)^2\right] = \frac{2\sigma}{r_a} - \frac{2\sigma}{\bar{r}_a}, \tag{13}$$

i.e.

$$\frac{dr_a}{dt} = \frac{2\sigma}{(1-\alpha) r_a RT}\left(\frac{1}{\bar{r}_a} - \frac{1}{r_a}\right) \Bigg/ \sum_N \left[\frac{1}{C_N D_N}(C_N^\theta - C_N)^2\right]. \tag{14}$$

ΔP can be also obtained sustituting the eq. (10) for $\Delta\mu_N$ in the eq. (3).

$$\Delta P = \beta \sum_N \left[\frac{1}{D_N}(C_N^\theta - C_N)\right]. \tag{15}$$

From the eqs. (13) and (15), ΔP is rewritten as

$$\Delta P = \left(\frac{2\sigma}{\bar{r}_a} - \frac{2\sigma}{r_a}\right) \sum_N \left[\frac{1}{D_N}(C_N^\theta - C_N)\right] \Bigg/ \sum_N \left[\frac{1}{C_N D_N}(C_N^\theta - C_N)^2\right]. \tag{16}$$

Now, in order to solve the differential eq. (14), we assume the relation between r_a and $\bar{r}_a$ as follows.

$$\rho = r_a/\bar{r}_a. \tag{17}$$

Then the following equation is obtained.

$$\bar{r}_a^3 = 3\left(\frac{\rho - 1}{\rho^3}\right)\frac{2\sigma t}{(1-\alpha)RT} \Bigg/ \sum_N \left[\frac{1}{C_N D_N}(C_N^\theta - C_N)^2\right], \tag{18}$$

where $\bar{r}_a$ has the maximum value at $\rho = 1.5$.

As Wagner[(3)] used $\rho = 1.5$ for his coarsening rate equation after the rigorous analysis, we also set $\rho = 1.5$. Then the generalized Ostwald ripening rate equation is given as

$$\bar{r}_a^3 = \frac{8\sigma t}{9(1-\alpha)RT} \Bigg/ \sum_N \left[\frac{1}{C_N D_N}(C_N^\theta - C_N)^2\right]. \tag{19}$$

1. Comparison with Li *et al.*

Li *et al.*[(5)] gave the solution for the two component system (cementite precipitation in steel) as follows;

$$\bar{r}_a^3 = \frac{8\sigma t}{9RT}\cdot\frac{C_{Fe}D_{Fe}C_C D_C V_\theta^2 V_{Fe}}{C_{Fe}D_{Fe}V_{Fe}^2 + C_C D_C V_C^2}\left[V_{Fe} + \frac{C_C}{C_{Fe}}V_C\right], \tag{20}$$

Where V_{Fe} and V_C are the mole volumes of Fe and C, and V_θ is $3V_{Fe} + V_C$.

In order to make comparison with the results of Li *et al.*, we introduce two equations.

$$V_\theta=aV_A+bV_B+cV_C+\cdots$$
$$(V_\theta=3V_{Fe}+V_C) \tag{21}$$

and

$$C_AV_A+C_BV_B+C_CV_C+\cdots=1$$
$$(C_{Fe}V_{Fe}+C_CV_C=1). \tag{22}$$

Then the eq. (19) is converted to

$$\bar{r}_a^3=\frac{8\sigma t}{9(1-\alpha)RT}\cdot\frac{C_{Fe}D_{Fe}C_CD_CV_\theta^2}{C_{Fe}D_{Fe}V_{Fe}^2+C_CD_CV_C^2}\left(\frac{1}{C_{Fe}-3C_C}\right)^2. \tag{23}$$

On the other hand, the eq. (20) given by Li *et al.* also can be converted to

$$\bar{r}_a^3=\frac{8\sigma t}{9RT}\cdot\frac{C_{Fe}D_{Fe}C_CD_CV_\theta^2}{C_{Fe}D_{Fe}V_{Fe}^2+C_CD_CV_C^2}\cdot\frac{1+C_CV_C}{C_{Fe}^2(1-C_CV_C)}, \tag{24}$$

which is in agreement with the eq. (23) when α and C_c have low values.

2. Comparison with Wey *et al.*

To express the mole fraction in an alloy carbide, it is convenient to use the existence ratios of metal elements except carbon in the Fe-M-C system, such as $(Fe_{(1-y)}M_y)_aC_b$. Then the eq. (19) becomes

$$\bar{r}_a^3=\frac{8\sigma V_\theta^2t}{9(1-\alpha)RT}\Bigg/\Bigg[a^2(y-x)^2\left(\frac{1}{C_{Fe}D_{Fe}}+\frac{1}{C_MD_M}\right)+2a(y-x)(b-C_CV_\theta)\left(\frac{1}{D_{Fe}}-\frac{1}{D_M}\right)+V_C^2(b-C_CV_\theta)^2\left(\frac{1}{D_{Fe}}+\frac{1}{D_M}\right)+\frac{1}{C_CD_C}(b-C_CV_\theta)^2\Bigg]. \tag{25}$$

To simplify the eq. (25), we assume $D_{Fe}=D_M$ and $V_{Fe}=V_M$.

$$\bar{r}_a^3=\frac{8\sigma V_\theta^2t}{9(1-\alpha)RT}\Bigg/\Bigg[\frac{a^2(y-x)^2}{x(x-1)D_M(C_{Fe}+C_M)}+\frac{(C_{Fe}+C_M)(b-C_CV_\theta)^2V_C^2}{D_M}+\frac{(b-C_CV_\theta)^2}{C_CD_C}\Bigg]. \tag{26}$$

If C_CD_C is large enough and

$$\frac{(y-x)^2}{x(1-x)}a^2V_M^2\gg b^2V_C^2, \tag{27}$$

Ostwald ripening is controlled by the diffusion of element M.

$$\bar{r}_a^3=\frac{8\sigma V_\theta^2D_M}{9a^2(1-\alpha)V_MRT}\cdot\frac{x(1-x)}{(y-x)^2}t$$
$$=\frac{8\sigma V_\theta^2D_M}{9a^2(1-\alpha)V_M}\cdot\frac{1-x}{x(K-1)^2}t, \tag{28}$$

where K is y/x.

This result roughly agrees with the ripening rate equation which Björklund *et al.*(6) proposed on the alloy cementite in steel,

$$\bar{r}_a^3=\frac{8\sigma V_\theta D_M}{27RTx(K-1)^2}t, \tag{29}$$

or the ripening rate equation which Wey *et al.*(7) obtained by generalization of the Björklund method,

$$\bar{r}_a^3=\frac{8\sigma V_\theta D_Mx}{9aRT(y-x)^2}t, \tag{30}$$

because

$$(1-x)\left(\frac{V_\theta}{aV_M}\right)=(1-x)\left(\frac{aV_M+V_C}{aV_M}\right)$$
$$=(1-x)\left(1+\frac{V_C}{aV_M}\right) \tag{31}$$

approachs 1, when V_C/aV_M and x are small enough.

IV. With Plastic Deformation

In the preceding chapter the pressure around the precipitate was shown to be the driving force of the diffusion to dissolve the volume gap. If the pressure is large enough to generate plastic deformation, the situation would be quite different. This problem is very important for the precipitation of carbide or nitride in steel, however the quantitative discussion has not been proposed.

In this chapter we discuss the Ostwald ripening with plastic deformation. For this purpose,

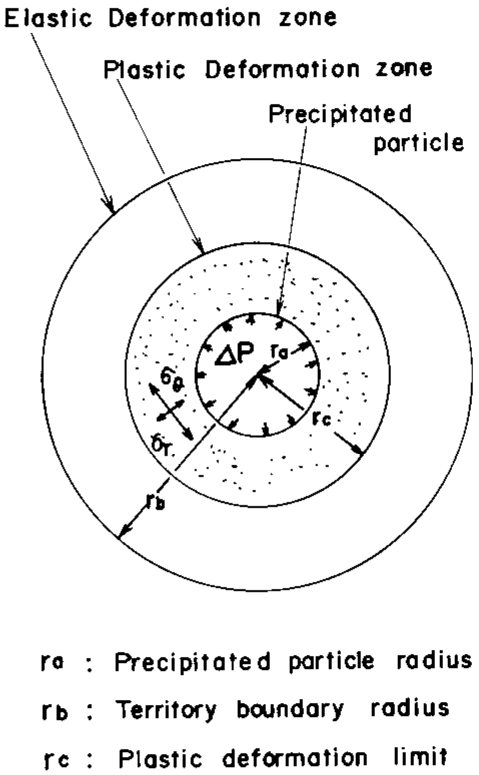

Fig. 2 Plastic deformation and elastic one around a precipitated particle.

we analyze the relation between the stress around the precipitate and the plastic deformation using the schematic representation as shown in Fig. 2.

From the theory of solid mechanics, the relation between the pressure around the precipitate and the plastic deformation is given as

$$\Delta P=2\sigma_s\left[\ln\left(\frac{r_c}{r_a}\right)+\frac{1}{3}\left(1-\frac{r_c^3}{r_b^3}\right)\right] \tag{32}$$

and the displacement is given as

$$\frac{(u)_{r=r_a}}{r_a}=\frac{\sigma_s}{E}\left[(1-\nu)\frac{r_c^3}{r_a^3}-\frac{2}{3}(1-2\nu)\left(1-\frac{r_c^3}{r_b^3}\right)-2(1-2\nu)\ln(r_c/r_a)\right], \tag{33}$$

where σ_s is the elastic limit, i.e. the creep strength, E is the elastic modulus and ν is Poison's modulus. For convenience' sake, we discuss the Fe-C system.

1. C diffusion control

First, we discuss the extreme case in which C can diffuse very fast but Fe can not diffuse entirely. In this case the volume gap must be dissolved only by the plastic and the elastic deformation. This problem is equivalent to calculating the pressure induced by dilating the precipitated ball from

$$r_a(3V_{Fe}/V_\theta)^{1/3}=r_a/(1+V_C/3V_{Fe})^{1/3} \tag{34}$$

to $r=r_a$. As this dilatation corresponds to the volume change, the following relations are obtained from the eq. (33).

$$\frac{u}{r_a}=1-1/(1+V_C/3V_{Fe})^{1/3}\simeq V_C/9V_{Fe}$$
$$=\frac{\sigma_s}{E}\left[(1-\nu)\left(\frac{r_c}{r_a}\right)^3-\frac{2}{3}(1-2\nu)\left(1-\frac{r_c^3}{r_b^3}\right)-2(1-2\nu)\ln\frac{r_c}{r_a}\right]\simeq\frac{\sigma_s}{E}(1-\nu)\left(\frac{r_c}{r_a}\right)^3. \tag{35}$$

Therefore,

$$\Delta P=2\sigma_s\left[\ln\left(\frac{r_c}{r_a}\right)+\frac{1}{3}\left(1-\frac{r_c^3}{r_b^3}\right)\right]\simeq 2\sigma_s\ln\left(\frac{r_c}{r_a}\right)$$
$$=\frac{2}{3}\sigma_s\ln\left[\frac{V_C E}{V_{Fe}(1-\nu)\sigma_s}\right], \tag{36}$$

is obtained from the eqs. (32) and (35). The pressure ΔP is independent of the radius of the particles, so ΔP is zero. Therefore, the Ostwald ripening in this case approaches the Ostwald ripening in fluid matrices, and the rate equation is given as

$$\bar{r}_a^3=\frac{8\sigma V_\theta^2 C_C D_C}{9(1-\alpha)RT}t. \tag{37}$$

Therefore, in the case in which Fe cannot diffuse and plastic deformation may occur, the coarsening rate is only controlled by C diffusion.

The situation is similar, when Fe can diffuse slightly. In order to know the situation, we calculate how fast ΔP decays by diffusion of Fe. In this case diffusion is only maintained in the elastic deformation field ($\bar{r}_c<r<\bar{r}_b$). From the balance between the displacement u and the flux of Fe

$$\frac{\mathrm{d}u}{\mathrm{d}t}=-\frac{1}{C_{\mathrm{Fe}}}\left(\frac{\bar{r}_{\mathrm{c}}}{\bar{r}_{\mathrm{a}}}\right)^2\frac{C_{\mathrm{Fe}}D_{\mathrm{Fe}}}{RT}\left(\frac{\mathrm{d}\mu_{\mathrm{Fe}}}{\mathrm{d}r}\right)_{r=\bar{r}_{\mathrm{c}}}$$
$$=-\frac{2\sigma_{\mathrm{s}}D_{\mathrm{Fe}}\bar{r}_{\mathrm{b}}\bar{r}_{\mathrm{c}}}{3C_{\mathrm{Fe}}RT\bar{r}_{\mathrm{a}}^2(\bar{r}_{\mathrm{b}}-\bar{r}_{\mathrm{c}})} \tag{38}$$

is obtained.

From the eq. (33)

$$\frac{u}{\bar{r}_{\mathrm{a}}}\simeq\frac{\sigma_{\mathrm{s}}}{E}(1-\nu)\left(\frac{\bar{r}_{\mathrm{c}}}{\bar{r}_{\mathrm{a}}}\right)^3 \tag{39}$$

is obtained, and differentiating the eq. (39) we obtain

$$\frac{\mathrm{d}u}{\mathrm{d}t}=\frac{3\sigma_{\mathrm{s}}(1-\nu)}{E}\left(\frac{\bar{r}_{\mathrm{c}}}{\bar{r}_{\mathrm{a}}}\right)^2\frac{\mathrm{d}\bar{r}_{\mathrm{c}}}{\mathrm{d}t}. \tag{40}$$

So

$$\bar{r}_{\mathrm{c}}=(\bar{r}_{\mathrm{c}})_0-\frac{2ED_{\mathrm{Fe}}}{9(1-\nu)C_{\mathrm{Fe}}RT}\cdot\frac{\bar{r}_{\mathrm{b}}}{(\bar{r}_{\mathrm{c}})_0[\bar{r}_{\mathrm{b}}-(\bar{r}_{\mathrm{c}})_0]}\,t \tag{41}$$

is given, where $(\bar{r}_{\mathrm{c}})_0$ is the initial value of $\bar{r}_{\mathrm{c}}$ and given from the eq. (35).

$$(\bar{r}_{\mathrm{c}})_0=\bar{r}_{\mathrm{a}}\left[\frac{V_{\mathrm{C}}E}{9V_{\mathrm{Fe}}(1-\nu)\sigma_{\mathrm{s}}}\right]^{1/3}. \tag{42}$$

Therefore, ΔP is given from the eqs. (32) and (42) as follows.

$$\Delta P\simeq2\sigma_{\mathrm{s}}\ln\left(\frac{\bar{r}_{\mathrm{c}}}{\bar{r}_{\mathrm{a}}}\right)\simeq2\sigma_{\mathrm{s}}\ln B$$
$$-\frac{4\sigma_{\mathrm{s}}ED_{\mathrm{Fe}}}{9(1-\nu)C_{\mathrm{Fe}}RT}\cdot\frac{t}{\bar{r}_{\mathrm{a}}^2B^2(1-\alpha B)}, \tag{43}$$

where

$$B=\frac{(\bar{r}_{\mathrm{c}})_0}{\bar{r}_{\mathrm{a}}}=\left[\frac{V_{\mathrm{C}}E}{9V_{\mathrm{Fe}}(1-\nu)\sigma_{\mathrm{s}}}\right]^{1/3}. \tag{44}$$

For the Fe-C system, as E/σ_{s} is 1000-5000, B is 5-6. So C diffusion control is effected under the condition that the change in ΔP with the lapse of time is relatively smaller than the difference in the interfacial tension, i.e.

$$\frac{2\sigma}{\bar{r}_{\mathrm{a}}}-\frac{2\sigma}{r_{\mathrm{a}}}=\frac{2\sigma}{3\bar{r}_{\mathrm{a}}}>\frac{4\sigma_{\mathrm{s}}ED_{\mathrm{Fe}}}{9(1-\nu)C_{\mathrm{Fe}}RT}\cdot\frac{t}{\bar{r}_{\mathrm{a}}^2B^2(1-\alpha B)} \tag{45}$$

and

$$\frac{\bar{r}_{\mathrm{a}}}{t}>\frac{2\sigma_{\mathrm{s}}ED_{\mathrm{Fe}}V_{\mathrm{Fe}}}{3\sigma(1-\nu)RTB^2(1-\alpha B)}, \tag{46}$$

where αB should be less than 1.

2. Creep deformation control

In the case in which the eq. (46) can not be effective or αB is greater than 1, the pressure around the steady particle becomes zero while the pressure around the growing or shrinking particle reaches the level for the plastic deformation to occur.

From the eqs. (3) and (4), the following equations are obtained.

$$C_{\mathrm{Fe}}\Delta\mu_{\mathrm{Fe}}+C_{\mathrm{C}}\Delta\mu_{\mathrm{C}}=\Delta P \tag{47}$$

and

$$3\Delta\mu_{\mathrm{Fe}}+\Delta\mu_{\mathrm{C}}=V_\theta(\Delta P+2\sigma/r_{\mathrm{a}}-2\sigma/\bar{r}_{\mathrm{a}}). \tag{48}$$

As C_{C} is small enough, we obtain

$$\Delta\mu_{\mathrm{C}}\simeq2\sigma V_\theta(1/r_{\mathrm{a}}-1/\bar{r}_{\mathrm{a}})+V_{\mathrm{C}}\Delta P. \tag{49}$$

We assume that ΔP is large enough for the plastic deformation to occur in the entire territory of the growing particle ($r=r_{\mathrm{a}}$), i.e.

$$\Delta P=2\sigma_{\mathrm{s}}\ln\left(\frac{r_{\mathrm{b}}}{r_{\mathrm{a}}}\right)=2\sigma_{\mathrm{s}}\ln\left(\frac{1}{\alpha}\right). \tag{50}$$

Simultaneously we assume that $\Delta\mu_{\mathrm{C}}$ is nearly zero not to delay the C diffusion with the existance of this pressure. We obtain

$$2\sigma V_\theta\left(\frac{1}{\bar{r}_{\mathrm{a}}}-\frac{1}{r_{\mathrm{a}}}\right)\simeq V_{\mathrm{C}}\Delta P=2\sigma_{\mathrm{s}}V_{\mathrm{C}}\ln\left(\frac{1}{\alpha}\right) \tag{51}$$

and

$$\bar{r}_{\mathrm{a}}\simeq\frac{\sigma V_\theta}{3\sigma_{\mathrm{s}}V_{\mathrm{C}}\ln(1/\alpha)}, \tag{52}$$

where $r_{\mathrm{a}}=1.5\bar{r}_{\mathrm{a}}$.

Now, the elastic limit σ_{s} should be taken to equal the creep strength when the deformation speed is very low. The relation between the deformation speed $\dot{\varepsilon}$ and the creep strength is shown as follows.

$$\dot{\varepsilon}=A(\sigma_{\mathrm{s}}/E)^n\exp(-Q_{\mathrm{C}}/RT). \tag{53}$$

As the limit of the plastic deformation field is r_{b}, the deformation speed at r_{b} can be connected with the growing rate of the particle. So we obtain

$$\dot{\varepsilon}=\frac{1}{r_{\mathrm{b}}}\left(\frac{r_{\mathrm{b}}}{r_{\mathrm{a}}}\right)^3\frac{\mathrm{d}r_{\mathrm{a}}}{\mathrm{d}t}\left(\frac{V_{\mathrm{C}}}{V_\theta}\right)=\frac{1}{r_{\mathrm{b}}\alpha^3}\left(\frac{V_{\mathrm{C}}}{V_\theta}\right)\frac{\mathrm{d}r_{\mathrm{a}}}{\mathrm{d}t}. \tag{54}$$

From the eqs. (52), (53) and (54), we obtain

$$\sigma_s^n = \frac{E^n}{\alpha^3 r_b}\left(\frac{V_C}{V_\theta}\right)\frac{dr_a}{dt}\Big/ A\exp(-Q_C/RT) \simeq \left[\frac{\sigma V_\theta}{3\bar{r}_a V_C \ln(1/\alpha)}\right]^n = \left[\frac{\sigma V_\theta}{2 r_a V_C \ln(1/\alpha)}\right]^n. \quad (55)$$

Integrating dr_a, we obtain

$$r_a^n \simeq n\alpha^2 A\exp(-Q_C/RT) \times\left(\frac{V_\theta}{V_C}\right)\left[\frac{\sigma V_\theta}{2EV_C\ln(1/\alpha)}\right]^n t, \quad (56)$$

where n, A and Q_C are constant values given by Sakurai *et al.*(8). Substituting $1.5\bar{r}_a$ for r_a, we obtain

$$\bar{r}_a^n \simeq n\alpha^2 A\exp(-Q_C/RT) \times\left(\frac{V_\theta}{V_C}\right)\left[\frac{\sigma V_\theta}{3EV_C\ln(1/\alpha)}\right]^n t. \quad (57)$$

V. Consideration of Cementite Growth

The experimental coarsening rates of cementite particles have been reported by Bannyh(9), Airey *et al.*(10) Mukherjee *et al.*(11), Vedula *et al.*(12) and Sakuma *et al.*(13).

Sakuma(14) resumed the experimental data and gave the comment that the actual Ostwald ripening rate is too small for C diffusion control and too large for the coupling diffusion control given by Li *et al.*(5). He estimates that the volume gap is dissolved by the formation of both dislocations (plastic deformation) and the coupling diffusion. This is probably correct but not enough to explain the actual phenomena.

Here we calculate the coarsening rates under the following conditions and compare them with the actual coarsening rates.

(1) C diffusion control

[*condition*]

$$\alpha^3 V_C E/9V_{Fe}(1-\nu)\sigma_s < 1$$

$$\frac{\bar{r}_a}{t} > \frac{2\sigma_s E D_{Fe} V_{Fe}}{3\sigma(1-\nu)RTB^2(1-\alpha B)},$$

where

$$B = [V_C E/9V_{Fe}(1-\nu)\sigma_s]^{1/3}.$$

[*coarsening rate equation*]

$$\bar{r}_a^3 = \frac{8\sigma V_\theta^2 C_C D_C}{9(1-\alpha)RT}t.$$

(2) Creep deformation control

[*coarsening rate equation*]

$$\bar{r}_a^n \simeq n\alpha^2 A\exp(-Q_C/RT) \times\left(\frac{V_\theta}{V_C}\right)\left[\frac{\sigma V_\theta}{3EV_C\ln(1/\alpha)}\right]^n t.$$

(3) Fe diffusion control (Coupling diffusion control)

[*coarsening rate equation*]

$$\bar{r}_a^3 = \frac{8\sigma V_\theta^2 D_{Fe}}{9(1-\alpha)RT}\left(\frac{V_{Fe}}{V_C^2}\right)t.$$

Numerical values used for the calculation are shown in Table 1 and hereinafter.

$\sigma = 0.7$ J/m^2.

$V_{Fe} = 7.1\times10^{-6}$ m^3/mol.

$V_C = 2.1\times10^{-6}$ m^3/mol.

$V_\theta = 23.4\times10^{-6}$ m^3/mol.

$\alpha = r_a/r_b =$ (mole fraction of C in steel $\times V_\theta/V_{Fe})^{1/3}$.

$n = 4.9$(8).

$A = 3\times10^{26}$ s^{-1}(8).

$Q_C = 218000$ J/mol(8).

Each calculation result is shown in comparison with the actual values(9)-(13) in Figs. 3

Table 1 σ_s, E, D_C, D_{Fe} and C_C in iron for calculation.

Temp. K	σ_s J/m^3	E J/m^3	ν	D_C m^2/s	D_{Fe} m^2/s	C_C mol/m^3
773	11×10^7	11×10^{10}	0.33	4×10^{-12}	5×10^{-23}	0.3×10^{-10}
873	8×10^7	8×10^{10}	0.33	2×10^{-11}	1×10^{-20}	0.6×10^{-10}
973	5×10^7	5×10^{10}	0.33	8×10^{-11}	5×10^{-16}	1.1×10^{-10}

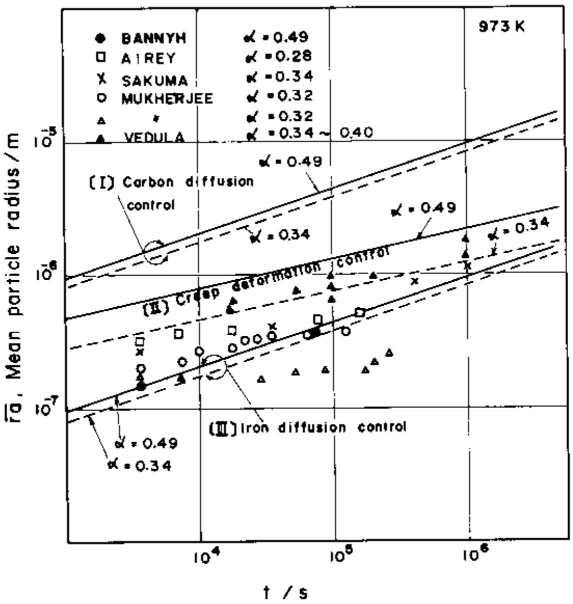

Fig. 3 Comparison between experimental coarsening and calculated one of cementite particles (973 K).

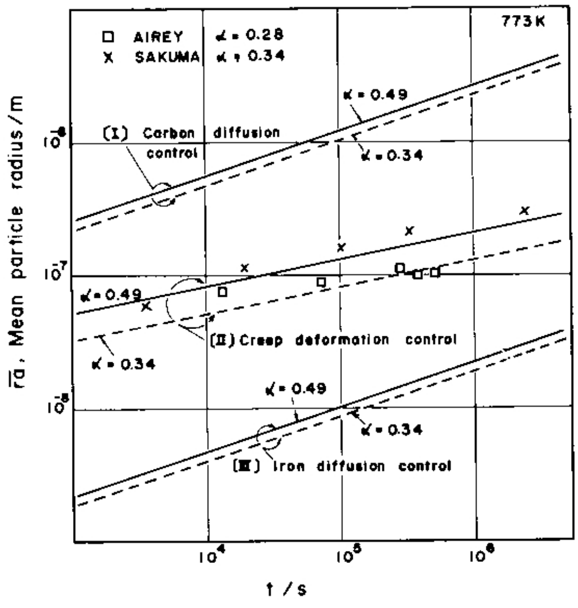

Fig. 4 Comparison between experimental coarsening and calculated one of cementite particles (773 K).

and 4.

From this comparison, at 973 K we can think that the volume gap is dissolved either by the coupling diffusion, i.e. Fe diffusion, or by creep deformation. But at 773 K, we must think that the volume gap is dissolved by creep deformation only.

VI. Summary and Conclusion

Ostwald ripening in solid matrices is studied theoretically considering the stress around dispersed particles induced by the volume gap.

The summary and conclusion are as follows;

(1) It is very important to correctly understand the stress status in solid matrices, whenever the volume gap is dissolved by diffusion or plastic deformation.

(2) For this purpose, starting from Gibbs-Duhem relation, the relation between the stress around particles and the diffusion was investigated, and under the condition that the diffusion in matrix compensates the volume gap, a ripening rate equation is derived as follows;

$$\bar{r}_a^3=\frac{8\sigma t}{9(1-\alpha)RT}\Big/\sum_{N}\left[\frac{1}{C_N D_N}(C_N^\theta-C_N)^2\right].$$

The equation is a generalized one for multicomponent systems and covers solutions of Li *et al.*, Bjorklund *et al.* and Wey *et al.*

(3) Under the condition that the creep deformation takes place to compensate the volume gap the equation is given as follows;

$$\bar{r}_a^n=n\alpha^2A\exp(-Q_c/RT)\times\left(\frac{V_\theta}{V_c}\right)\left[\frac{\sigma V_\theta}{3EV_c\ln(1/\alpha)}\right]^n t.$$

(4) The results of calculation have revealed that the creep deformation is more dominant than the Fe diffusion to compensate the volume gap for cementite coarsening in ferrite below 973 K.

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