

## Minimization of Ostwald Ripening of Dispersed Particles\*

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It is very important to suppress the coarsening of dispersed particles in heat resisting alloys in order to prevent the deterioration of the high temperature strength. However, the theoretical systematization has not been given adequately.

The purpose of this article is to find out general rules of minimization of the coarsening of dispersed particles on the basis of the thermodynamical equilibrium and the generalized Ostwald ripening equation. It is concluded that the most stable combination is made in the binary alloy in which (1) the main component of the matrix has the least chemical binding force for the formation of dispersed particles and the main component of the dispersed particles has the greatest chemical binding force and (2) the sufficiency ratio of the main metal component of the dispersed particles to the whole dispersed particles is 1/2. These rules agree with the experimental results on some heat resisting alloys.

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### I. Introduction

Fine particles being dispersed and distributed in a metallic material, its strength is improved in general. This phenomenon is utilized not only for the alloys of precipitation hardening and oxide dispersion hardening types but also in the fundamental fields such as precipitation of carbide or nitride in iron and steel very extensively. Accordingly many studies have been carried out on its hardening mechanism itself and in relation to the dispersed states. However, the theoretical systematization has not been established adequately for the phenomenon in which the creep strength is deteriorated due to the aggregation and coarsening of dispersed particles in them as in the case of heat resistant materials.

To cope with increasing demand for the materials of high temperature strength, it is very important for the material development to systematize the theories as a guide to suppress the aggregation and coarsening of dispersed particles in materials and to prevent the deterioration in strength at elevated tempera-

tures.

The purpose of this report is to analyze the Ostwald ripening of dispersed particles on the basis of thermodynamical equilibrium between the dispersed particles and matrix alloy, and to systematize the theories to explain which conditions should be provided for suppressing the coarsening of dispersed particles in materials.

### II. Ostwald Ripening and Strength

The coarsening of dispersed particles occurring after they reached to a stage nearly in thermodynamical equilibrium with the matrix alloy is the phenomenon that "larger dispersed particles ripen and smaller ones disappear" in order to reduce the interfacial energy between them and the matrix alloy, which is known as the Ostwald ripening.

The concept of this Ostwald ripening was introduced originally in relation to the coarsening of dispersed particles in liquid solutions, and its basic theoretical equations were derived by Lifshitz, Slyozov<sup>(1)</sup> and Wagner<sup>(2)</sup>, and the equations for ripening applicable to solid phases in binary alloys were obtained by Oriani<sup>(3)</sup>, Li *et al.*<sup>(4)</sup>.

The present author has given the following equation for the Ostwald ripening in the composition of multiple systems by generalizing it

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in solid phases by paying attention to the stress generated through the volume change at its reaction<sup>(5)</sup>:

$$\bar{r}_a^3 = \frac{8\sigma t}{9(1-\alpha)RT} \left/ \sum \left[ \frac{1}{C_i D_i} (C_i^0 - C_i)^2 \right] \right., \quad (1)$$

where  $\bar{r}_a$  is the mean diameter of dispersed particles;  $t$  is the elapsed time;  $\sigma$  is the interfacial energy between the matrix and dispersed particles;  $\alpha$  is the one-third power of volume ratio at the dispersed particles;  $R$  is the gas constant;  $T$  is the absolute temperature;  $C_i$  is the molar concentration of component  $i$  in the matrix (molar fraction/molar volume);  $C_i^0$  is the molar concentration of component  $i$  in the dispersed particles; and  $D_i$  is the volume diffusion coefficient of component  $i$  in the matrix.

On the basis of this result, the following three means can be considered for suppressing the coarsening of dispersed particles, that is, to make  $\sigma$  smaller, to make  $\alpha$  smaller or to make  $L$  in the following equation larger:

$$L = \sum \left[ \frac{1}{C_i D_i} (C_i^0 - C_i)^2 \right]. \quad (2)$$

Among them, the means of making  $\sigma$  smaller lacks in the degree of freedom from the viewpoint of alloy design, though it can be attained by raising the crystalline conformity between the matrix and dispersed particles. And the means of making  $\alpha$  smaller has only an insufficient effect and causes rather an unfavorable lowering of strength due to the decrease of the dispersed particles, though it can be achieved by reducing the total amount of dispersed particles.

Therefore, the coarsening of dispersed particles at elevated temperatures can be suppressed in practice only by the means of making  $L$  in eq. (2) larger. For this reason, in this report the conditions for maximizing  $L$  are derived on the basis of eq. (1) by introducing the thermodynamical component equilibrium into it.

According to the theory by Orowan<sup>(6)</sup>, the yield strength of the alloy containing dispersed particles  $\tau$  has the following relation with the mean particle distance  $2\bar{r}_b$  and mean particle diameter  $\bar{r}_a$ :

$$\tau \propto 1/(\bar{r}_b - \bar{r}_a) \simeq 1/\bar{r}_b \quad (3)$$

Then if the volume ratio of dispersed particles is taken as  $\psi$ ,

$$\varphi = (\bar{r}_a/\bar{r}_b)^3 \quad (4)$$

and  $\bar{r}_b$  related to the yield strength is given by the following equation:

$$\bar{r}_b^3 = \frac{8\sigma t}{9(1-\alpha)RT} \left/ \varphi \sum \left[ \frac{1}{C_i D_i} (C_i^0 - C_i)^2 \right] \right. \quad (5)$$

Therefore, it is proper to use eq. (2) in the case of dealing with the coarsening of dispersed particles and that (5) in the case of doing with the yield strength. But both of the equations are coincident with each other except for the term of  $\psi$ . For this reason eq. (2) will be used for the following general examinations and eq. (5) only in particular cases.

### III. Conditions for Minimization of Ostward Ripening

#### 1. In the case of dispersed particles approximating to ideal solution model

A thermodynamical equilibrium exists between the composition  $C_i$  in the matrix and  $C_i^0$  in the dispersed particles in the stage of the Ostwald ripening. Now assuming that the chemical bond of dispersed particles may be carbide, nitride or oxide, it is generalized as  $M_a X_b$ . Here  $M$  indicates that the metal component contained  $i$  in the ratio  $y_i$ , and  $X$  means carbon, nitrogen or oxygen. Expressing in the form of chemical reaction, the following formula is obtained:

$$a \{ y_1 [M_1] + y_2 [M_2] + \dots \} + b [X] = M_a X_b. \quad (6)$$

Namely,  $y_i$  means the molar fraction of the metal component  $i$  in the dispersed particles excepting carbon, nitrogen or oxygen  $X$  from them and has the following relation with  $C_i^0$ , if the molar volume of the metal  $M$  is taken as  $V_\theta$ :

$$y_i = V_\theta C_i^0 \quad (7)$$

$$\sum y_i = 1. \quad (8)$$

And also the molar fraction of metal component  $i$  in the matrix  $x_i$  has the following relation

with  $C_i$ , if the molar volume of matrix is taken to be  $V_m$ :

$$x_i = V_m C_i \quad (9)$$

$$\sum x_i = 1. \quad (10)$$

Then, for the reaction formula shown in (6), at first let us consider the case where the activity of metal compound in the dispersed particles can be approximated by the ideal solution model. In this case the following equation holds for the component  $i$  from the equilibrium between the matrix and dispersed particles, that is, in relation to the common tangential face which touches the free energy curved surface of each phase.

$$RT \ln a_i + \frac{b}{a} RT \ln a_x = \Delta G_i + RT \ln y_i, \quad (11)$$

where  $a_i$ , and  $a_x$  are the activities of component  $i$  and  $X$  in the matrix, and if their activities are taken as  $\gamma_i$  and  $\gamma_x$ ,

$$a_i = \gamma_i x_i \quad (12)$$

$$a_x = \gamma_x x_x. \quad (13)$$

And also  $\Delta G_i$  is the change of Gibbs free energy when the pure metal of component  $i$  reacts with  $X$  and forms  $b/a[M_a X_b]$ . From eqs. (11) and (12), the relation between  $x_i$  and  $y_i$  is given as follows:

$$\begin{aligned} y_i &= a_i \cdot a_x^{(b/a)} \cdot \exp\left(-\frac{\Delta G_i}{RT}\right) \\ &= a_x^{(b/a)} \cdot \gamma_i \cdot \exp\left(-\frac{\Delta G_i}{RT}\right) \cdot x_i. \end{aligned} \quad (14)$$

For simplifying the expression of eq. (14),

$$f = a_x^{(b/a)} \quad (15)$$

and

$$g_i = \gamma_i \exp\left(-\frac{\Delta G_i}{RT}\right) \quad (16)$$

are used, then eq. (14) can be expressed as follows:

$$y_i = f g_i x_i. \quad (17)$$

Accordingly to the relations between eqs. (8) and (10) the following equation can be obtained:

$$f = \frac{1}{\sum g_i x_i} = \sum \frac{y_i}{g_i}. \quad (18)$$

As already mentioned, it is necessary for suppressing the coarsening of dispersed particles to make  $L$  in eq. (2) larger. Assuming the chemical reaction shown in eq. (6) for  $L$ , and separating the terms of the metal component and carbon, nitrogen or oxygen,  $L$  can be expressed as follows:

$$L = \sum \frac{(C_i^\theta - C_i)^2}{C_i D_i} + \frac{(C_x^\theta - C_x)^2}{C_x D_x}. \quad (19)$$

Here, since in general the volume diffusion coefficient  $D_x$  of component  $X$  is considerably larger in comparison with  $D_i$ , the second term of eq. (19) can be neglected. And also it is assumed that the volume diffusion coefficients of metal components  $i$  in the matrix  $D_i$  are approximately equal to each other in order to simplify the computation and the following relation is valid:

$$D_1 \simeq D_2 \simeq D_3 \simeq \dots \simeq D \quad (20),$$

where  $D$  is the value represented by the volume diffusion coefficient of component mainly constituting the dispersed particles. Then  $L$  can be arranged as follows by using the eqs. (8), (10), (17) and (18):

$$\begin{aligned} L &= \sum \frac{(C_i^\theta - C_i)^2}{C_i D_i} \\ &= \frac{1}{D} \sum \left[ \left( \frac{y_i}{V_\theta} - \frac{x_i}{V_m} \right)^2 / \left( \frac{x_i}{V_m} \right) \right] \\ &= \frac{1}{D V_m} \sum \left[ x_i \left( \frac{V_m y_i}{V_\theta x_i} - 1 \right)^2 \right] \\ &= \frac{1}{D V_m} \sum \left[ \left( \frac{V_m}{V_\theta} \right)^2 \frac{y_i^2}{x_i} - 2 \left( \frac{V_m}{V_\theta} \right) y_i + x_i \right] \\ &= \frac{1}{D V_m} \left[ \left( \frac{V_m}{V_\theta} \right)^2 \sum \frac{y_i^2}{x_i} - 2 \left( \frac{V_m}{V_\theta} \right) + 1 \right] \\ &= \frac{1}{D V_m} \left[ \left( \frac{V_m}{V_\theta} \right)^2 \sum g_i y_i \cdot \sum \frac{y_i}{g_i} - 2 \left( \frac{V_m}{V_\theta} \right) + 1 \right] \end{aligned} \quad (21)$$

$$\begin{aligned} &= \frac{1}{D V_m} \left[ \left( \frac{V_m}{V_\theta} \right)^2 \sum g_i^2 x_i / (\sum g_i x_i)^2 \right. \\ &\quad \left. - 2 \left( \frac{V_m}{V_\theta} \right) + 1 \right]. \end{aligned} \quad (22)$$

Based upon the above preparation,  $i=0$  is assigned to the main component constituting the matrix and  $i=1 \sim n$  to the other alloy components. But since for  $i=1 \sim n$  its general character is not lost by ordering of  $g_n$ , it is de-

fined as

$$g_1 \leq g_2 \leq g_3 \leq \dots \leq g_n.$$

Then from eqs. (10) and (22),  $L$  can be expressed as follows:

$$L = \frac{1}{DV_m} \left\{ \left( \frac{V_m}{V_\theta} \right)^2 \left[ g_0^2 + \sum_1^n (g_i^2 - g_0^2) x_i \right] / \left[ g_0 + \sum_1^n (g_i - g_0) x_i \right]^2 - 2 \left( \frac{V_m}{V_\theta} \right) + 1 \right\}, \quad (23)$$

It can be differentiated with respect to  $x_n$  in order to obtain the condition for its maximum value:

$$\frac{dL}{dx_n} = \frac{1}{DV_m} \left( \frac{V_m}{V_\theta} \right)^2 \left\{ (g_n^2 - g_0^2) \left( \sum_0^n g_i x_i \right)^2 - 2(g_n - g_0) \sum_0^n g_i x_i \cdot \sum_0^n g_i^2 x_i \right\} / \left( \sum_0^n g_i x_i \right)^4 = 0. \quad (24)$$

Therefore,

$$(g_n + g_0) \sum_0^n g_i x_i = 2 \sum_0^n g_i^2 x_i. \quad (25)$$

By arranging this equation,

$$g_n x_n = \sum_0^{n-1} g_i x_i - 2 \sum_1^{n-1} \frac{(g_i - g_0) g_i x_i}{g_n - g_0}. \quad (26)$$

Also by introducing eq. (17) into the above equation,

$$y_n = \sum_0^{n-1} y_i - 2 \sum_1^{n-1} \frac{(g_i - g_0) y_i}{g_n - g_0}. \quad (27)$$

Then by using eq. (8) the following equation is obtained:

$$y_n = \frac{1}{2} - \sum_1^{n-1} \frac{(g_i - g_0) y_i}{g_n - g_0}. \quad (28)$$

By substituting this into eq. (21), the maximum value of  $L$  can be obtained as follows:

$$L_{\max} = \frac{1}{DV_m} \left\{ \left( \frac{V_m}{V_\theta} \right)^2 \left( \frac{g_n + g_0}{2} \right) \left[ \frac{1}{2} \left( \frac{1}{g_n} + \frac{1}{g_0} \right) - \sum_1^{n-1} \frac{(g_n - g_i)(g_i - g_0)}{g_0 g_n g_i} y_i \right] - 2 \left( \frac{V_m}{V_\theta} \right) + 1 \right\}. \quad (29)$$

It is apparent from this result that in the case of  $g_i > g_0$ ,  $L$  can be made much larger when the value of  $y_i (i=1 \sim n-1)$  is minimized, or no alloying element is contained. On the contrary, in the case of  $g_i < g_0$ , the value of  $y_i$  should be

as large as possible, indicating the preferability of replacing the main component in the matrix. Accordingly, in short, it is suitable for  $L$  to choose the minimum composition of  $g_i$  for the main component of the matrix and the maximum one of  $g_i$  for that of dispersed particles. In this case, regardless of the values of  $g_0$  and  $g_n$ ,  $y_0$  and  $y_n$  are given from eqs. (8) and (28)  $g_n$  to be

$$y_0 = y_n = 0.5, \quad (30)$$

and from eq. (29)

$$L_{\max} = \frac{1}{DV_m} \left[ \frac{1}{4} \left( \frac{V_m}{V_\theta} \right)^2 \left( \frac{g_n}{g_0} + \frac{g_0}{g_n} + 2 \right) - 2 \left( \frac{V_m}{V_\theta} \right) + 1 \right] \quad (31)$$

If  $g_n \gg g_0$ ,

$$L_{\max} = \frac{1}{4DV_m} \left( \frac{V_m}{V_\theta} \right)^2 \left( \frac{g_n}{g_0} \right). \quad (32)$$

However, in general the third element is added in the case of heat-resistant materials for the purpose of improving its oxidation resistance or the strength of its matrix. Even in such a case, if  $g_n \gg g_i$ ,  $g_0$  holds, the maximum value of  $L$  is given at  $y_n = 0.5$ , and it is expressed from eq. (29) as follows:

$$L_{\max} \simeq \frac{1}{4DV_m} \left( \frac{V_m}{V_\theta} \right)^2 \left( \frac{g_n}{g_0} \right) \times \left[ 1 - 2 \sum_1^{n-1} \left( 1 - \frac{g_0}{g_i} \right) y_i \right]$$

$$\begin{aligned}
&= \frac{1}{4DV_m} \left( \frac{V_m}{V_\theta} \right)^2 \left( \frac{g_n}{g_0} \right) \cdot 2g_0 \sum_1^n \left( \frac{y_i}{g_i} \right) \\
&= \frac{1}{4DV_m} \left( \frac{V_m}{V_\theta} \right)^2 \left( \frac{g_n}{g_0} \right) \cdot 2g_0 \left/ \sum_0^n g_i x_i \right. \quad (33)
\end{aligned}$$

And also from the relation  $y_n = \sum_0^{n-1} y_i = 0.5$  and eq. (17),

$$g_n x_n = \sum_0^{n-1} g_i x_i. \quad (34)$$

Then the equation can be simplified into the form

$$\begin{aligned}
L_{\max} &= \frac{1}{4DV_m} \left( \frac{V_m}{V_\theta} \right)^2 \left( \frac{g_i}{g_0} \right) \left/ \sum_0^{n-1} \left( \frac{g_i}{g_0} \right) x_i \right. \\
&= \frac{1}{4DV_m} \left( \frac{V_m}{V_\theta} \right)^2 \left/ x_n \right. \quad (35)
\end{aligned}$$

But while  $x_0 \sim x_{n-1}$  can have arbitrary values as the alloy components,  $x_n$  is limited to the value so that  $y_n = 0.5$  holds. The above results may be summarized as follows;

(1) When the main component ( $i=0$ ) of the matrix has the composition which minimizes  $g_i$  and the main component ( $i=n$ ) of the dispersed particles is the second element which maximizes  $g_i$ , the Ostwald ripening is suppressed most intensively. In such a case the composition in which the Ostwald ripening is minimum is  $x_n = g_0/g_n$  and  $y_0 = y_n = 0.5$ .

(2) Even if it is required for improving the heat resistance of strength of matrix to add the third element, the Ostwald ripening is minimum at  $x_n = (g_0 x_0 + g_1 x_1 + g_{n-1} x_{n-1})/g_n$  and  $y_n = 0.5$  where  $g_n \gg g_i$ ,  $g_0$  holds.

(3) Namely, the Ostwald ripening is minimum in general at  $y_n = 0.5$ , if  $g_n \gg g_i$ ,  $g_0$  holds.

Under the above conditions, let us make test computation by assuming a binary or ternary alloy. In this case the direct computation of  $L$  requires the evaluation of diffusion coefficient  $D$  and molar volumes of dispersed particles  $V_m$  and  $V_\theta$ , and is too complicated. For this reason, a part of eq. (22) is defined as follows:

$$L_0 = \sum g_i^2 x_i / (\sum g_i x_i)^2. \quad (36)$$

Then all the changes of  $L$  caused by the component can be integrated to  $L_0$ .

On the other hand, as shown in eq. (3), when

the creep strength is taken into consideration, the value of  $\bar{r}_b$  is a most interesting factor. Now, if the amounts of the components  $n$  and  $X$  which constitute the dispersed particles and are fixed in them are taken to be  $\bar{x}_n$  and  $\bar{x}_X$ , the total amounts of  $n$  and  $X$  including those in a state of solid solution in the matrix are:

$$u_n = x_n + \bar{x}_n = x_n + (a/b)y_n \bar{x}_X \quad (37)$$

$$u_X = x_X + \bar{x}_X. \quad (38)$$

Since the volume ratio of dispersed particles  $\varphi$  is proportional to  $(a/b)\bar{x}_X$ , the creep strength  $\tau$  can be expressed from eqs. (3) and (5) as follows:

$$\tau \propto 1/\bar{r}_b \propto (\varphi L)^{1/3} \propto \left[ \left( \frac{a}{b} \right) \bar{x}_X L_0 \right]^{1/3}. \quad (39)$$

And when the effect of composition on the creep strength is indicated, the sufficiency ratio of the component  $n$  to that  $X$ ,

$$\eta = \frac{u_n}{u_X} \left( \frac{b}{a} \right) = \frac{(b/a)x_n + y_n \bar{x}_X}{x_X + \bar{x}_X} \quad (40)$$

can be used in many cases. For illustrating by a diagram, therefore,  $[a/b \cdot \bar{x}_X L_0]^{1/3}$  as the corresponding value to the creep strength will be taken as the ordinate and  $\eta$  as the abscissa.

For a binary alloy, the cases of  $g_n/g_0 = 2000, 4000, 6000, 8000$  and  $10000$  are shown in Fig. 1 and for a ternary alloy the cases of  $x_i = 0, 0.1, 0.2$  and  $0.4$  at  $g_n/g_0 = 1000$  and  $g_i/g_0 = 10$  in Fig. 2. In either cases the values are computed assuming that  $x$  is sufficiently small and  $(a/b)u_X = 0.005$ . As is obvious from the figure,  $\tau_0$  is not so much affected by  $g_n/g_0$  or the presence of the third element and shows a maximum value at  $\eta = 0.5$ . Furthermore, when  $x_X$  is relatively large, the main component of matrix does not form dispersed particles and only the alloying element  $n$  forms them. In this case  $\eta$  can be computed by introducing the relation derived from eqs. (13), (15) and (17),

$$\begin{aligned}
x_X &= \frac{1}{\gamma_X} (y_0/g_0 x_0)^{(a/b)} \\
&= \left( \frac{y_0}{x_0} \right)^{(a/b)} / \gamma_X g_0^{(a/b)} \simeq y_0^{(a/b)} / \gamma_X g_0^{(a/b)}, \quad (41)
\end{aligned}$$

into eq. (35). For simplifying the computation, the cases of  $g_n/g_0 = 10000$  and  $\gamma_X g_0 = 0, 0.0025,$

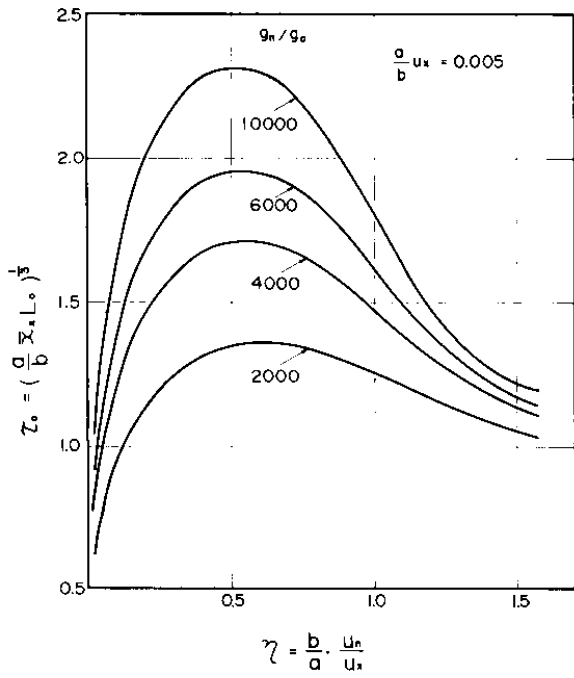


Fig. 1 Relation between the sufficiency ratio of n component to X component and the creep strength factor varying  $g_n/g_0$  in the binary system.

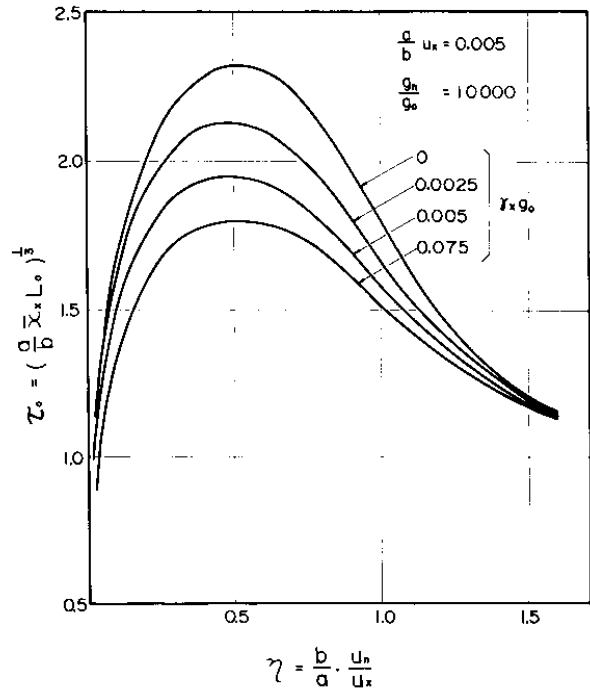


Fig. 3 Relation between the sufficiency ratio of n component to X component and the creep strength factor when X component is soluble in matrix.

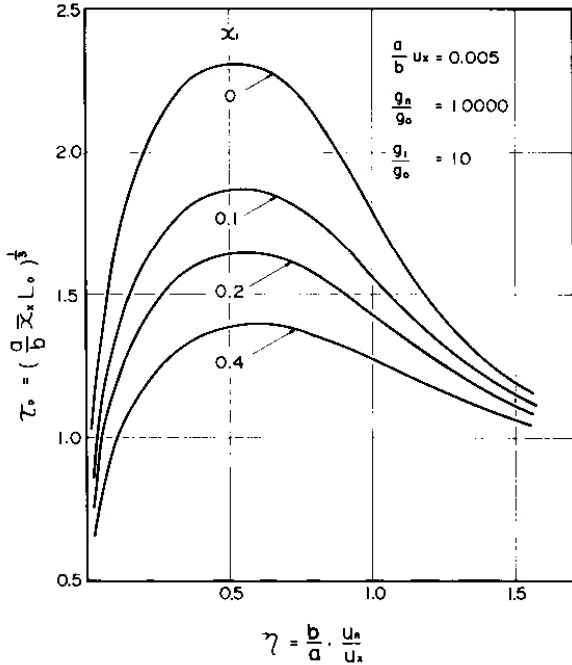


Fig. 2 Relation between the sufficiency ratio of n component to X component and the creep strength factor in the ternary system.

0.005 and 0.0075 are computed under the assumption of  $(a/b)=1$  as shown in Fig. 3. In this case  $\tau_0$  is also found to show the maximum

value at  $\eta=0.5$ .

### 2. In the case of a dispersed particles approximating to regular solution model

Up to now the case in which the dispersed particle can be approximated to the ideal solution model has been discussed, but the approximation to the regular one based on the interaction between the component elements into consideration is more practical. In the following for the sake of simply, a binary alloy will be considered. In such a case the following equilibrium equation holds instead of eq. (11):

$$RT \ln a_0 + (b/a)RT \ln a_x = \Delta G_0 + RT \ln y_0 + \Omega y_n^2 \quad (42)$$

$$RT \ln a_n + (b/a)RT \ln a_x = \Delta G_n + RT \ln y_n + \Omega y_n^2 \quad (43)$$

Here  $\Omega$  denotes the parameter of the interaction. Therefore, from the equilibrium relation as is the case with eqs. (14)-(18), the following equations can be obtained:

$$f g_0 x_0 = y_0 \exp\left(\frac{\Omega}{RT} y_n^2\right)$$

$$= (1 - y_n) \exp\left(\frac{\Omega}{RT} y_n^2\right) \quad (44)$$

$$\begin{aligned} fg_n x_n &= y_n \exp\left(\frac{\Omega}{RT} y_n^2\right) \\ &= y_n \exp\left[\frac{\Omega}{RT} (1 - y_n)^2\right]. \end{aligned} \quad (45)$$

Then

$$fg_0 x_n = \left(\frac{g_0}{g_n}\right) y_n \exp\left[\frac{\Omega}{RT} (1 - y_n)^2\right]. \quad (46)$$

Accordingly, the following equation can be obtained;

$$\begin{aligned} x_n &= \frac{fg_0 x_n}{fg_0 x_0 + fg_0 x_n} = y_n \exp\left[\frac{\Omega}{RT} (1 - y_n)^2\right] \\ &\quad \left/ \left[ \frac{g_n}{g_0} (1 - y_n) \exp\left(\frac{\Omega}{RT} y_n^2\right) \right. \right. \\ &\quad \left. \left. + y_n \exp\left[\frac{\Omega}{RT} (1 - y_n)^2\right] \right] \end{aligned} \quad (47)$$

For the relation between  $\eta$  and  $\tau_0$ , the computation is carried out for the cases of  $\Omega/RT = -1, 0$  and  $1$  on condition of  $g_n/g_0 = 8000$  and the results are shown in Fig. 4. When  $\Omega > 0$ , the two kinds of metal in the dispersed particles are repulsive, the maximum value of  $L$  shifts to the range of  $\eta > 0.5$ , and when  $\Omega < 0$ , that is, two kinds of metal in the dispersed particles are attractive, the maximum value of  $L$  shifts to the range of  $\eta < 0.5$ .

### 3. In the case of coexistence of two kinds of dispersed particle

Up to now the case only one kind of dispersed particles exists has been discussed. In effect, however, there are cases where two kinds of dispersed particle such as MC and  $M_{23}C_6$  coexist in the component equilibrium state. If two kinds of dispersed particles are taken to be  $M_a M_b$  and  $M'_a X'_b$ , the case would be in an equilibrium state shown as follows (returning

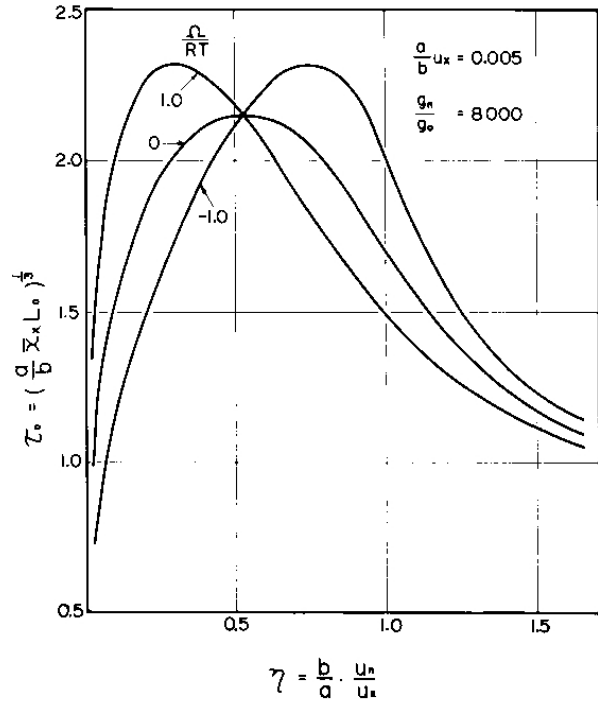


Fig. 4 Relation between the sufficiency ratio of  $n$  component to  $X$  component and the creep strength factor when matrix and  $n$  component have mutual interaction in dispersed particles.

to the conditions of approximation to ideal solution model):

$$RT \ln a_m + (b/a)RT \ln a_x = \Delta G_m + RT \ln y_m \quad (48)$$

$$RT \ln a_n + (b/a)RT \ln a_x = \Delta G_n + RT \ln y_n \quad (49)$$

$$RT \ln a_m + (b'/a')RT \ln a_x = \Delta G'_m + RT \ln y'_m \quad (50)$$

$$Rt \ln a_n + (b'/a')RT \ln a_x = \Delta G'_n + RT \ln y'_n. \quad (51)$$

Here,  $b/a' < b'/a'$ , i.e.  $a'b < ab'$ . From eqs. (48)–(51) the following relation can be obtained:

$$\frac{y_n y'_m}{(1 - y_n)(1 - y'_m)} = \exp\left(\frac{\Delta G_n - \Delta G'_m + \Delta G'_n - \Delta G_n}{RT}\right). \quad (52)$$

Since the left side has the value generally smaller enough than unity, the approximation  $y_n, y'_m \ll 1$  holds. Then  $y_n$  and  $y'_m$  can be obtained as follows (the deriving process of equations omitted here):

$$y_n = a_m^{(ab'/a'b-1)} \exp \left[ \frac{-(ab'/a'b-1)\Delta G_m - \Delta G_n + \Delta G'_n}{RT} \right] \quad (53)$$

$$y'_m = a_m^{-(ab'/a'b-1)} \exp \left[ \frac{(ab'/a'b)\Delta G_m - \Delta G'_m}{RT} \right]. \quad (54)$$

Namely, while the two kinds of dispersed particles coexist,  $x_n$  and  $x_x$  or  $y_n$  and  $y'_m$  do not change, and only the quantitative relation between  $M_aX_b$  and  $M'_aX'_b$  do, even though the added amount of component n increases. Are  $M_aX_b$  and  $M'_aX'_b$  subjected to the Ostwald ripening according to eq. (1), holding the component equilibrium between them? If both are subjected to ripening, only  $M_aX_b$  takes part in its ripening and disappearance and  $M'_aX'_b$  is left in a stable state. However, from the positional relation between the two kinds of dispersed particles, the following four kinds of ripening and disappearing phenomena may occur:

- (1)  $M_aX_b$  ripens and  $M_aX_b$  disappears
- (2)  $M_aX_b$  ripens and  $M'_aX'_b$  disappears
- (3)  $M'_aX'_b$  ripens and  $M_aX_b$  disappears
- (4)  $M'_aX'_b$  ripens and  $M'_aX'_b$  disappears.

As already explained, while these two kinds of dispersed particles coexist, with the amount change of component n,  $x_n$  and  $x_x$  in a state of solid solution in the matrix and  $y_n$ ,  $y_m$ ,  $y'_n$  and  $y'_m$  of the respective dispersed particles do not change and only the amounts of  $M_aX_b$  and  $M'_aX'_b$  do. Then  $L_0$  shows a constant value for  $M_aX_b$  and  $M'_aX'_b$  of the dispersed particles as shown in eq. (36). As defined by  $b/a < b'/a'$  for  $M_aX_b$  and  $M'_aX'_b$ , the ripening of  $M'_aX'_b$  is slower than that of  $M_aX_b$ . Therefore,  $L_0$  shows the maximum value when the additive amount of component n is increased up to the point where the existence ratio of  $M'_aX'_b$  comes to have the maximum value, that is, the existence of  $M_aX_b$  approaches zero. The value of  $\eta$  is nearly equal to  $y'_n = 1 \sim y'_m$ . Since  $y'_m$  is the value obtained from eq. (54) and is small enough,  $L_0$  shows the maximum value when  $\eta$  has a

value a little smaller than unity (for instance, 0.8–1.0). This is the characteristic feature of the case where the two kinds of dispersed particles coexist. And it shows the same tendency that metals forming the dispersed particles are repulsive.

#### 4. Conditions for solid solution treatment

In the above study the general conditions for suppressing the Ostwald ripening of dispersed particles are made clear. In each case  $g_n/g_0$  plays an important role. And the larger the following formula at  $\eta \approx 0.5$ , the more ripening is suppressed:

$$\frac{g_n}{g_0} = \frac{\gamma_n}{\gamma_0} \exp \left( \frac{\Delta G_0 - \Delta G_n}{RT} \right).$$

However, needless to say, this rule becomes significant only when particles can be dispersed finely at the initial stage. As recognized in some of oxide dispersion hardening alloys, it is preferable to make the particles disperse finely by the mechanical alloying method, but in the case where the precipitation reaction is utilized, there is another limitation. Namely, for the utilization of the precipitation reaction, it is necessary to carry out solution treatment of the components constituting the dispersed particles in the alloy. In this case, the indefinite enlargement of  $g_n$  to results in loss of ways to bring them into the solid solution state. To have a suitable solubility product is a necessary condition in this case. For reference, for the representative carbide and nitride in iron and steel their solubility products are shown in Table 1<sup>(7)(8)</sup>.

Table 1 Solubility products of typical carbide and nitride in steel (Narita<sup>(7)(8)</sup>).

Temp./K	[V][C]	[Nb][C]	[Ta][C]	[Ti][C]	[Zr][C]	[V][N]	[Nb][N]	[Ta][N]	[Ti][N]	[Zr][N]
1573	—	$7.0 \times 10^{-6}$	$4.0 \times 10^{-6}$	$9.8 \times 10^{-6}$	$3.2 \times 10^{-6}$	$5.7 \times 10^{-6}$	$7.4 \times 10^{-7}$	$1.1 \times 10^{-6}$	$8.8 \times 10^{-10}$	$3.9 \times 10^{-10}$
1373	$3.2 \times 10^{-4}$	$1.3 \times 10^{-6}$	$9.0 \times 10^{-7}$	$1.1 \times 10^{-6}$	$1.3 \times 10^{-6}$	$8.8 \times 10^{-7}$	$1.2 \times 10^{-7}$	$7.0 \times 10^{-8}$	—	—
1173	$2.1 \times 10^{-5}$	$1.3 \times 10^{-7}$	$1.2 \times 10^{-7}$	$4.4 \times 10^{-8}$	$1.2 \times 10^{-7}$	$7.0 \times 10^{-8}$	$1.1 \times 10^{-8}$	$1.8 \times 10^{-9}$	—	—



#### IV. Comparison with Practical Materials

Since the relation between the Ostwald ripening of dispersed particles and the components constituting them has been systematized, it will be applied here after to the examples of practical high temperature strength materials. Of course, the Ostwald ripening under creep is somewhat different from the above observation because of the nonuniform diffusion induced by excess vacancies or dislocation migrations under the stress. However, the relative performance can be roughly similar.

At first the well-known TD nickel and the like in which oxides of Th, Y, etc. are finely dispersed in Ni or Co base by the coprecipitation method or the mechanical alloying method are given as an example utilizing the principle "the particle ripening becomes minimum when the ratio of  $g_0$  of the main component in the matrix to  $g_n$  of the main component in the dispersed particles,  $g_0/g_n$ , is maximum". While Th, Y, etc. form the most stable oxides, Ni and Co are difficult to form their oxides and representative high melting point substances having superior heat resistance. Therefore, TD nickel and the like are the material in which  $g_0/g_n$  is highest among the practical materials.

On the other hand, in the iron base alloys there are some examples of oxide dispersion hardening, but they are not practical, and the precipitation hardening type utilizing the solid solution and precipitation treatments is mainly brought into practice. For instance, the austenitic stainless steel or heat resistant steel is alloyed with Cr for improving its heat resistance or with Ti and Nb and TiC, NbC or  $Cr_{23}C_6$  containing Ti and Nb for improving its creep strength. As such materials hold an important position as practical ones, there are many papers on the relation between the additive amount of Ti, Nb or C and their creep strength. The main results of the previous papers are compared with those obtained in this work.

At first Shinoda *et al.*<sup>(9)</sup> directed their attention to the fact that the creep strength of austenitic stainless steel changes remarkably with to the charges and ascertained that small

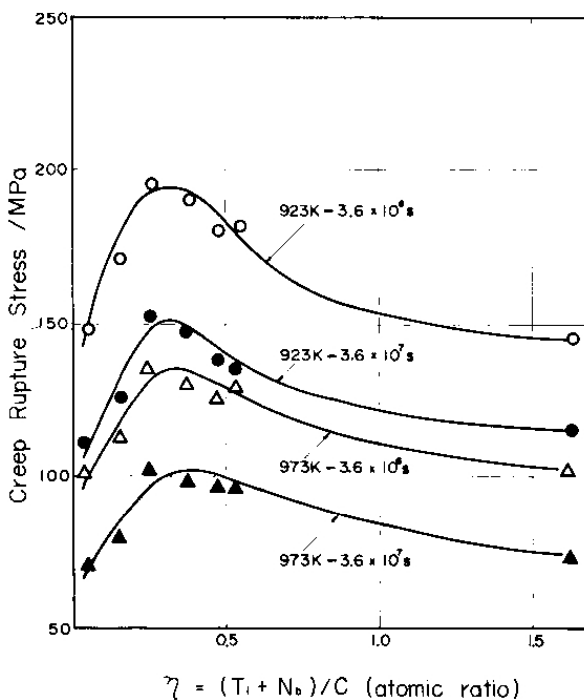


Fig. 5 Relation between  $(Ti+Nb)/C$  and creep rupture stress in 18-8 stainless steel. (Shinoda *et al.*<sup>(9)</sup>)

additions of Ti and Nb are effective, showing that the creep rupture strength reached a maximum at  $(Ti+Nb)/C$  (atomic ratio)=0.25. The relation of creep rupture stress with  $C/(Ti+Nb)$  in their paper is converted to  $(Ti+Nb)/C$  for comparison with Figs. 1-4 as shown in Fig. 5.

Mimino *et al.*<sup>(10)</sup> added Nb and Ti simultaneously to 18Cr-8Mn-6Ni steel and showed that the creep strength reached a maximum at  $(Ti+Nb)/C$  (atomic ratio)=0.2. Then Tanaka *et al.*<sup>(11)(12)</sup> investigated the effect of a separate addition of Ti and Nb to 304 type stainless steel and showed that the creep strength reached a maximum at  $Ti/C$  (atomic ratio)=0.8 and  $Nb/C$  (atomic ratio)=0.2-0.4.

On the other hand, Yamada *et al.*<sup>(13)(14)</sup> investigated the effect of a separate addition of Ti to 15Cr-14Ni steel and showed that the creep strength reached a maximum at  $(Ti+Nb)/C$  (atomic ratio)=0.5-1.0. At the same time they considered that the carbide distribution state was related to the improvement of creep strength by the addition of Ti and gave the relation between the distribution density of dis-

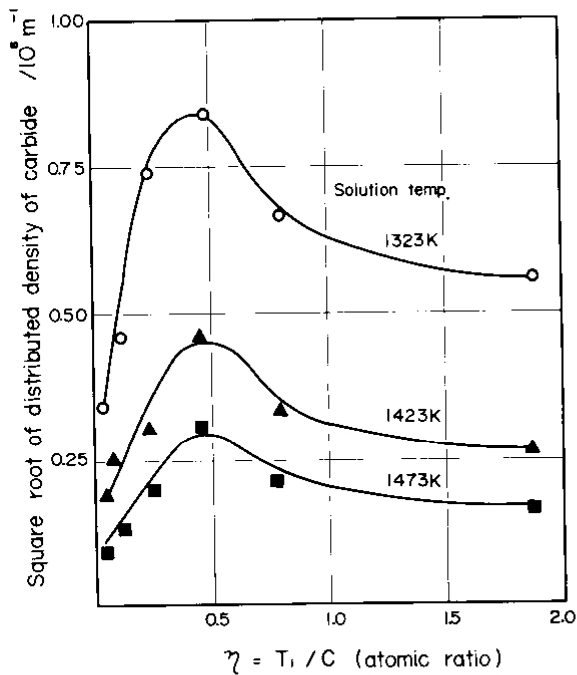


Fig. 6 Relation between Ti/C and square root of distributed density of carbide in 15Cr-14Ni stainless steel. (Yamada *et al.*<sup>(13)</sup>)

persed particles in the heat treatment 1323–1573 K and Ti addition as shown in Fig. 6. Although in the original report the number of dispersed particles per  $\mu\text{m}^2$  on a log scale is taken as the ordinate and the amount of Ti as the abscissa, in Fig. 6 the root of number of dispersed particles per  $\text{m}^2$  (proportional to the mean distance between the dispersed particles) is taken as the ordinate and Ti/C (atomic ratio) as the abscissa for comparison with Figs. 1–4.

Then Kaneko *et al.*<sup>(15)</sup> investigated the effects of addition of Ti to 304 type stainless steel and obtained the results as in the past. And Ohta *et al.*<sup>(16)</sup> investigated also the effects of addition of Ti to 15Cr-15Ni-2.5Mo steel and obtained the results as shown in Fig. 7 for the relation between the creep strength and Ti/C.

Furthermore, these effects of addition of Ti or Nb can be observed not only on austenitic stainless steels but also on 12Cr heat resistant steel, and Takahashi *et al.*<sup>(17)</sup> showed that the creep strength reached to the maximum at Nb/C (atomic ratio) of 0.15.

As mentioned above, it is widely known that

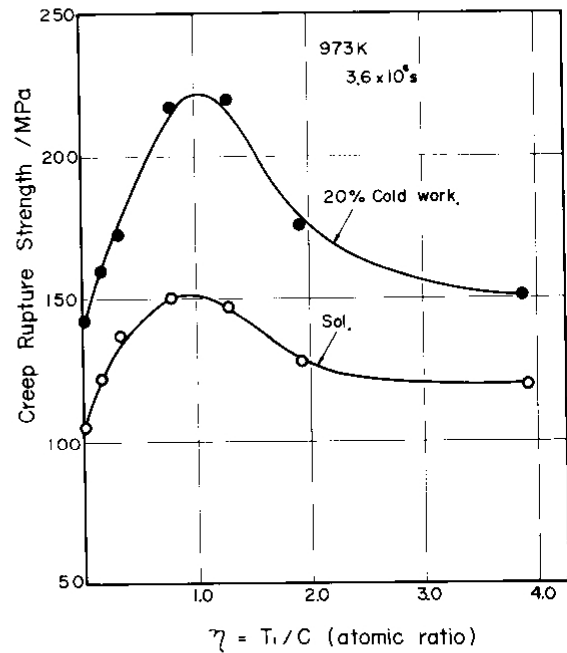


Fig. 7 Relation between Ti/C and creep rupture strength in 15Cr-15Ni-2.5Mo stainless steel. (Ohta *et al.*<sup>(16)</sup>)

the creep strength reaches the maximum at Ti/C or Nb/C of 0.2–0.8. The causes of this phenomenon seem to be related to the carbide distribution state as pointed out in the literature, and it is considered that the present investigation on the ripening rule of dispersed particles is useful in a certain extent, in view of the similarity between Figs. 1–4 obtained theoretically and Figs. 5–7 obtained by the arrangement of practical examples.

## V. Conclusion

For the coarsening phenomenon of dispersed particles in heat resistant materials strengthened by them theoretical systematization is tried on the basis of the thermodynamical equilibrium and generalized Ostwald ripening equation, and the following conclusions are obtained:

- (1) In order to suppress the coarsening of carbide, nitride or oxide, it is preferable for the main component of the matrix to be the composition of the least chemical binding force and for that of the dispersed particles to be the composition of the greatest binding force to carbon, nitrogen or oxygen.

(2) In such a case, the coarsening of dispersed particles can be suppressed to the maximum extent generally at the sufficiency ratio of metal constituting the main component of dispersed particles to carbon, nitrogen or oxygen  $\eta$  of 0.5, which is supported by the relation between the amount of Ti, Nb and C additions in austenitic stainless steel or heat resistant steel and its creep strength.

(3) However, when the dispersed particles exist in two kinds of the chemically binding states or a repulsive interaction acts between the metals constituting the dispersed particles, the coarsening of dispersed particles becomes minimum at  $\eta$  of 0.5–1.0.

## REFERENCES

- (1) I. M. Lifshitz and V. V. Slyozov: *J. Phys. Chem. Solids*, **19** (1961), 35.
- (2) C. Wagner: *Z. Electrochem.*, **65** (1961), 581.
- (3) R. A. Oriani: *Acta Metall.*, **12** (1964), 1399.
- (4) Che-Yu Li, J. M. Blakely and A. H. Feingold: *Acta Metall.*, **14** (1966), 1397.
- (5) H. Arai: *Trans. JIM*, **27** (1986), 151.
- (6) E. Orowan: *Dislocation in Metals*, AIME, (1954), p. 128.
- (7) K. Narita and S. Koyama: *Kobe Steel Tech. Rep.*, **67** (1966), 179.
- (8) K. Narita: *Bulletin Japan Inst. Metals*, **8** (1969), 49.
- (9) T. Shinoda, T. Mimino, K. Kinoshita and I. Minegishi: *J. ISIJ (Tetsu-To-Hagané)*, **54** (1968), 1472.
- (10) T. Mimino, K. Kinoshita, I. Minegishi and T. Shinoda: *ibid.*, **55** (1969), 901.
- (11) R. Tanaka, T. Shinoda, T. Ishii, T. Mimino, K. Kinoshita and I. Minegishi: *Rep. 123 Committee (Japan Society for Promotion of Science)*, **12** (1971), 93.
- (12) R. Tanaka, T. Shinoda, T. Ishii, T. Mimino, K. Kinoshita and I. Minegishi: *J. ISIJ (Tetsu-To-Hagané)*, **57** (1971), S535.
- (13) T. Yamada and T. Fujita: *ibid.*, **59** (1973), 58.
- (14) T. Yamada, T. Fujita and K. Nakamura: *ibid.*, **59** (1973), 1948.
- (15) H. Kaneko and H. Ichinose: *Rep. 123 Committee (Japan Society for Promotion of Science)*, **18** (1977), 51.
- (16) S. Ohta, H. Uchida and M. Fujiwara: *ibid.*, **24** (1983), 35.
- (17) N. Takahashi, K. Tokuda and T. Fujita: *ibid.*, **11** (1970), 33.