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Effect of grain size on grain boundary segregation

K. Ishida

Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai 980-77, Japan

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Abstract

A simple thermodynamic calculation to assess the effect of grain size on grain boundary segregation has been performed. It is shown that in binary alloys when the bulk solute content is small, segregation increases with increasing grain size. In ternary alloys, however, intergranular segregation depends both on the magnitude of segregation free energy and the bulk concentrations of the solute. It is pointed out that grain size could play an important role in the segregation phenomena, not only in metallic but also in ceramic systems.

Keywords: Segregation; Grain size; Grain boundary; Interface; Thermodynamics

1. Introduction

Since it is well-known that the origin of intergranular fracture in several materials is due to the segregation of impurities to the grain boundary, manufacturers tend to aim for lower and lower impurity concentration in materials, while, at the same time, reducing the overall grain size of materials to impart better mechanical properties. The control of residual impurities and the grain size is thus a technologically important subject that has engaged the attention of scientists for a long time. As regards impurity segregation to the grain boundaries, recent advances in surface analysis techniques have enabled accurate determinations of the concentration profiles of solute at the grain boundaries or the surfaces of alloys. This has greatly facilitated the quantitative investigation of the segregation process in alloy systems. Quantitative results obtained using such techniques have led to the observation that in many alloys systems [1,2] the equilibrium segregation of solute to the grain boundary can be described by the McLean's equation [3]:

$$\frac{x^{\mathrm{b}}}{1-x^{\mathrm{b}}}=\frac{x^{\mathrm{m}}}{1-x^{\mathrm{m}}}\exp\left(\frac{\Delta G_{x}^{\mathrm{s}}}{RT}\right) \tag{1}$$

where x^{b} and x^{m} are the solute concentrations at the grain boundary and in the matrix respectively, and $\Delta G_{x}^{\mathrm{s}}$ is the segregation free energy. x^{m} has been generally assumed to be equal to the bulk concentration $^{\circ}x$ because the total magnitude of solute atoms segregating to the grain boundary is usually much smaller than the bulk content. This assumption is, however, invalid in the cases where the total number of solute atoms is comparable with the number of positions available for solute atoms to segregate, which is more likely to be the case in very fine grained materials.

Arkharov and Skornyakov [4,5] have shown (Fig. 1) [6], using X-ray diffraction methods, that variation in grain size is accompanied by changes in lattice parameter in alloys that contain impurities which segregate to the grain boundary. Since the principal contribution to the X-ray diffraction lines comes from the scattering of the regular lattice atoms in the interior of the grains, this implies that the magnitude of solute segregation varies with the grain size, causing variation in matrix concentrations, thus clearly indicating that grain boundary segregation is a function of grain size. However, very little is known about the grain size dependence of grain boundary segregation. In the present work, a simple thermodynamic calculation is performed to clarify the effect of grain size on intergranular segregation.

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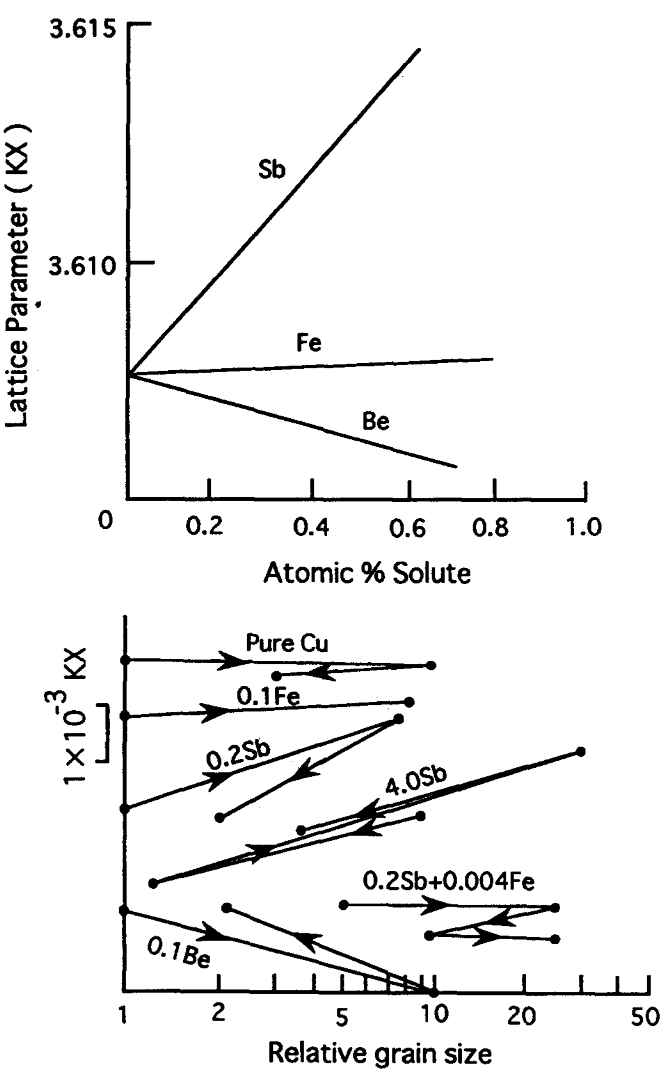

Fig. 1. Solute segregation in copper alloys as revealed by the grain size dependence of the lattice parameter [4,5].

2. Calculation of the grain size dependence of intergranular segregation

2.1. Binary system

In the basic formulation of Eq. (1) that describes the equilibrium segregation of solute X in the A–X binary system, the relation between the matrix and the bulk concentrations of the solute is expressed by

$$x^{\mathrm{b}} f + x^{\mathrm{m}}(1-f) = {}^{\mathrm{o}}x \tag{2}$$

where f is the fraction of the grain boundary volume and is estimated as $f = [(t/2)(4\pi\bar{R}^2)]/4/3\pi\bar{R}^3 = 3t/2\bar{R}$, where t is the grain boundary thickness and $\bar{R}$ is the average grain radius. The mathematical treatment of this kind of mass balance has also been made for surface segregation in small particles [7], impurity segregation to different segregation sites [8] and the grain size dependence on the diffusivity [9].

Substituting for x^{m} in Eq. (1) yields

$$\frac{x^{\mathrm{b}}}{1-x^{\mathrm{b}}} = \frac{{}^{\mathrm{o}}x - \dfrac{3t}{2\bar{R}}x^{\mathrm{b}}}{1 - {}^{\mathrm{o}}x - \dfrac{3t}{2\bar{R}}(1-x^{\mathrm{b}})} \exp\left(\frac{\Delta G_x^{\mathrm{s}}}{RT}\right) \tag{3}$$

Since $3t/2\bar{R} \ll 1$ in most cases, Eq. (3) can be approximated by

$$\frac{x^{\mathrm{b}}}{1-x^{\mathrm{b}}} \approx \frac{{}^{\mathrm{o}}x - \dfrac{3t}{2\bar{R}}x^{\mathrm{b}}}{1 - {}^{\mathrm{o}}x} \exp\left(\frac{\Delta G_x^{\mathrm{s}}}{RT}\right) \tag{4}$$

The matrix concentration is equal to the bulk composition when ${}^{\mathrm{o}}x \gg (3t/2\bar{R})x^{\mathrm{b}}$, but is quite different from that in cases where ${}^{\mathrm{o}}x$ is comparable with $(3t/2\bar{R})x^{\mathrm{b}}$. The calculated effect of grain size on the magnitude of grain boundary segregation in A–X binary system for ${}^{\mathrm{o}}x = 10^{-5}$ is shown in Fig. 2, where the solid and dotted lines represent the results for $\Delta G_x^{\mathrm{s}} = 100$ kJ mol^{-1} and $\Delta G_x^{\mathrm{s}} = 50$ kJ mol^{-1} respectively. In these calculations, the boundary thickness is assumed to be 1 nm [10,11]. If $t = 0.5$ nm is used instead of 1 nm, the intergranular concentrations are about double, as seen from Eq. (4). It can be seen from Fig. 2 that the grain size effect on intergranular segregation is quite marked at lower temperatures. When the grain size is large ($\bar{R} > 300$ µm in Fig.2), the extent of variation in the grain boundary concentration due to variation in grain size is small. At lower

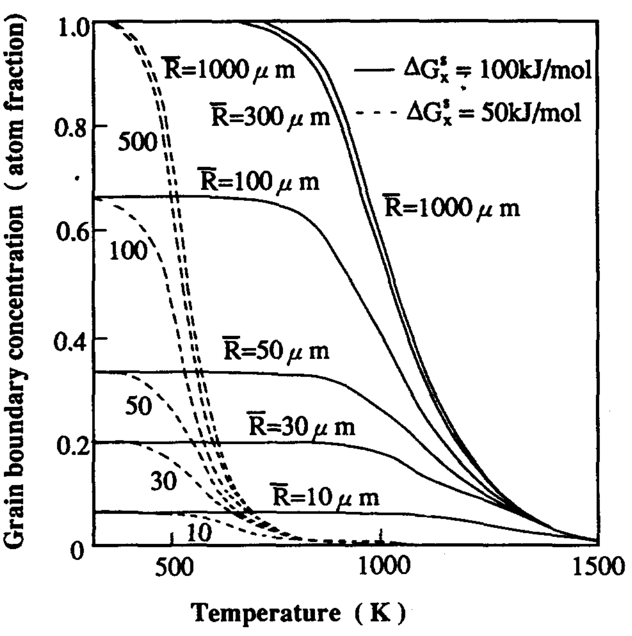

Fig. 2. Solute concentration at grain boundary calculated from Eq. (4), for $\Delta G_{\mathrm{x}}^{\mathrm{s}} = 50$ kJ mol^{-1}, $\Delta G_{\mathrm{x}}^{\mathrm{s}} = 100$ kJ mol^{-1} and ${}^{\mathrm{o}}x = 10^{-5}$.

temperatures and small grain sizes, grain boundary concentration x^b yields the following value.

$$^*x^b = \frac{2\bar{R}}{3t}\,{}^\circ x \tag{5}$$

The critical concentration of $^*x^b$ is the value where all the solute atoms segregate to the grain boundary. Fig. 3 shows the grain size dependence of intergranular solute content as a function of the bulk composition at 1000 K. It is seen that the grain boundary composition is strongly dependent on the grain size at lower bulk concentrations for $\Delta G_x^s = 100$ kJ mol^{-1}, while the grain size effect is small for $\Delta G_x^s = 50$ kJ mol^{-1}. Thus, the effect of grain size on the intergranular segregation is more pronounced at lower bulk concentrations and at higher temperatures for higher segregation free energy. For the high bulk concentrations, however, the effect of the segregation free energy on the deviations from the McLean equation is small. Defining the bulk concentration $^\circ x$ corresponding to a boundary concentration of solute $x^b = 0.2$ as the critical concentration $^\circ x^*$, grain radii $\bar{R}$ vs. $^\circ x^*$ at different temperatures have been calculated using a value of 100 kJ mol^{-1} for the segregation energy ΔG_x^s. The results are plotted in Fig. 4. It is seen that the critical concentration $^\circ x^*$ decreases with decreasing temperature and increasing grain radius. The solid line shown in Fig. 4 is the critical limit of $^\circ x$ given by Eq. (5) and separates the regions between solute concentrations above and below $x^b = 0.2$ at the grain boundary. When the bulk concentration is in the upper area of the shaded lines in Fig. 4, the grain boundary concentration x^b exceeds 20 at.%. In other words, the intergranular segregation of $x^b < 0.2$ is easily controlled at 1500 K for $^\circ x < 10^{-4} = 0.2$ where grain size has no influence on the boundary segregation, while the reduction of solute atom and grain size refinement is necessary for $x^b < 0.2$ at lower temperatures.

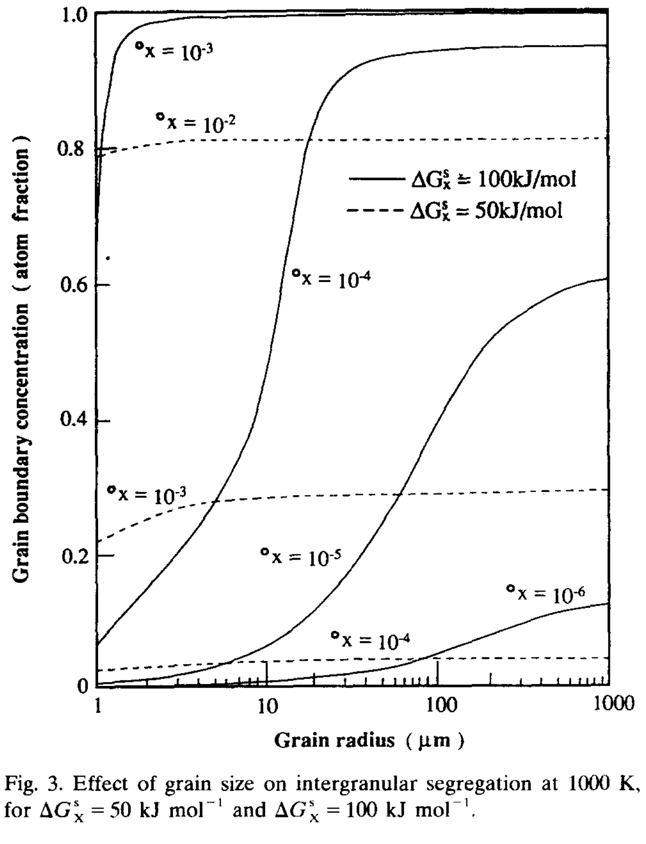

Fig. 3. Effect of grain size on intergranular segregation at 1000 K, for $\Delta G_x^s = 50$ kJ mol^{-1} and $\Delta G_x^s = 100$ kJ mol^{-1}.

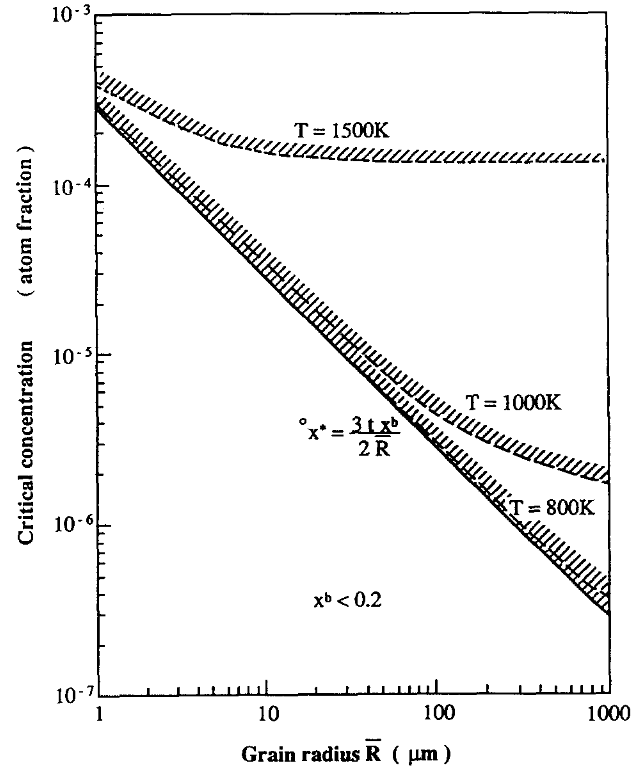

Fig. 4. Effect of grain size on critical concentration of solute where $x^b = 0.2$ and $\Delta G_x^s = 100$ kJ mol^{-1}.

2.2. Ternary and multi-component systems

In ternary and multi-component systems, the segregation concentrations can be expressed by

$$\frac{x_i^b}{1 - \sum_i x_i^b} \approx \frac{{}^\circ x_i - \frac{3t}{2\bar{R}} x_i^b}{1 - \sum_i {}^\circ x_i} \exp\left(\frac{\Delta G_i^s}{RT}\right) \tag{6}$$

where x_i^b and $^\circ x_i$ are respectively the grain boundary and bulk concentrations of component i, and G_i^s is the segregation free energy for the ith component. The effect of grain size on grain boundary segregation in the A–X–Y ternary system is calculated using the above equation with the following parameter values: $\Delta G_x^s = 100$ kJ mol^{-1}, $\Delta G_y^s = 50$ kJ mol^{-1}, $^\circ x = 10^{-5}$

and $^{o}y = 10^{-2}$. The results are shown in Fig. 5. It is seen that when $\Delta G_x^s > \Delta G_y^s$, the intergranular concentration of component X always increases with decreasing temperature and decreases with decreasing grain size, while the grain size dependence of grain boundary segregation of Y atoms is rather complex depending on temperature. Fig. 6 shows the influence of bulk concentration ^{o}y on the grain size dependence of intergranular segregation at 800 K, for the chosen values of $^{o}x = 10^{-5}$, $\Delta G_x^s = 100$ kJ mol^{-1}, $\Delta G_y^s = 50$ kJ mol^{-1}. It is to be noted that the grain size influence is quite marked even when the bulk content of Y solute is large.

As in the case of the binary system, a critical concentration $^{o}y^*$ is defined as the bulk concentration that corresponds to a grain boundary concentration of $y^b = 20$ at.%. The relation between grain size and this critical concentration in the bulk calculated using the parameter values $^{o}x = 10^{-5}$, $\Delta G_x^s = 100$ kJ mol^{-1}, $\Delta G_y^s = 50$ kJ mol^{-1}, is plotted in Fig. 7. At higher temperatures, the critical content $^{o}y^*$ is virtually independent of grain size, but as the temperature is lowered it shows an increasingly strong dependence on grain radius. With decreasing temperature this critical bulk concentration Y converges to the values given by the following equation

$$^{o}y^* = \frac{3t}{2\bar{R}} y^b \qquad (7)$$

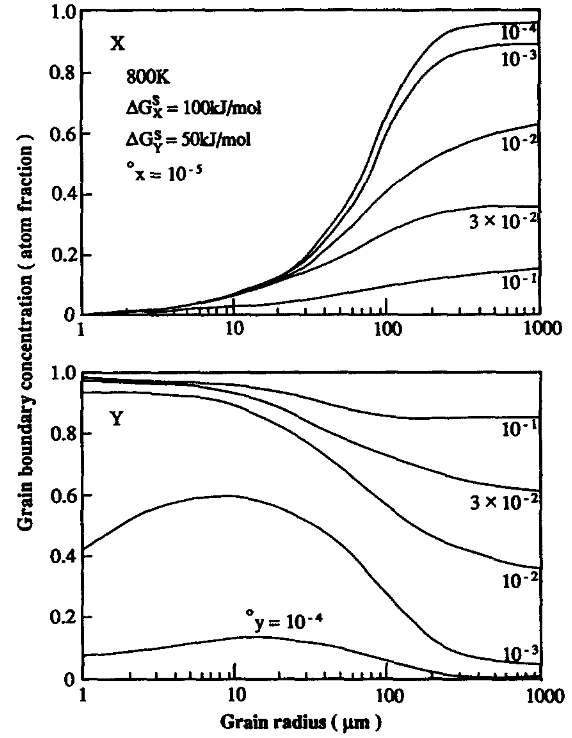

Fig. 6. Effect of grain size on segregation of two solutes at 800 K calculated from Eq. (6), for $\Delta G_X^s = 100$ kJ mol^{-1}, $\Delta G_Y^s = 50$ kJ mol^{-1} and $^{o}x = 10^{-5}$.

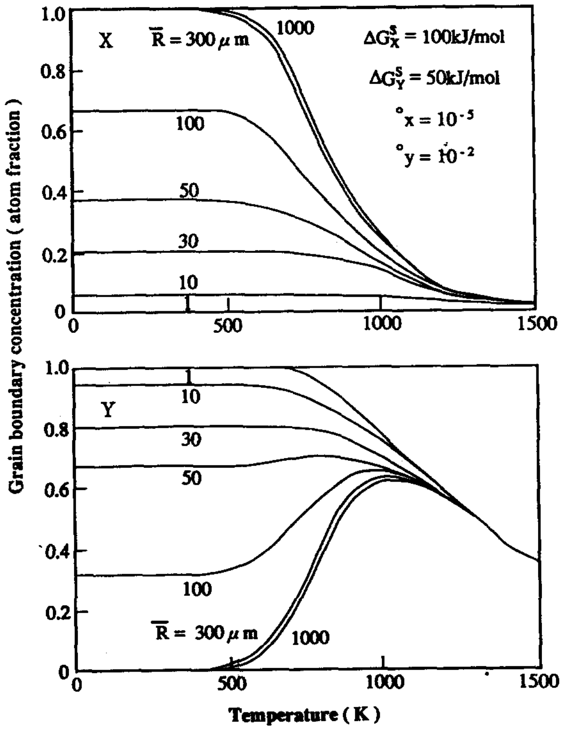

Fig. 5. Grain boundary segregation of two solutes calculated from Eq. (6), for $\Delta G_X^s = 100$ kJ mol^{-1}, $\Delta G_Y^s = 50$ kJ mol^{-1}, $^{o}x = 10^{-5}$ and $^{o}y = 10^{-2}$.

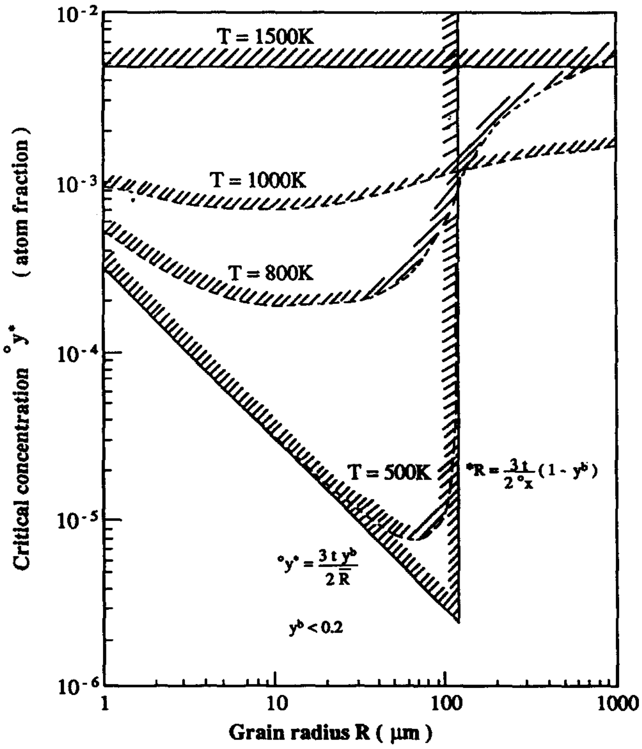

Fig. 7. Effect of grain size on critical concentration of solute of ^{o}y, where $y^b = 0.2$, $^{o}x = 10^{-5}$, $\Delta G_X^s = 100$ kJ mol^{-1} and $\Delta G_Y^s = 50$ kJ mol^{-1}.

When the segregation energy of X is larger than that of Y, Y atoms do not segregate because the boundary is already covered and saturated by X atoms, once the critical grain radius $\bar{R}^*$, given by the following equation, is exceeded

$$\bar{R}^* = \frac{3t}{2^{\circ}x}(1 - y^{\mathrm{b}}) \tag{8}$$

This is illustrated by the sharp discontinuity in the solid line in Fig. 7 which shows the limitation on the value of the critical bulk concentration of Y corresponding to $y^{\mathrm{b}} = 0.2$. In addition, the following interesting feature is also noted; for decreasing grain boundary concentration y^{b} at constant $^{\circ}y$, one has a choice of either decreasing the grain size to less than the value given by the equation $\bar{R} < (3t/2^{\circ}y)y^{\mathrm{b}}$, or increasing the grain size to a value above the one given by Eq. (8) ($\bar{R} > \bar{R}^*$).

It has been reported that the ductile to brittle transition temperature (DBTT) in steel is a linear function of the intergranular concentration of impurities like S and P [12,13]. For example, the DBTT of a low alloy Cr–Mo steel increases with increasing bulk concentration of P. The relationship between the grain size and the critical bulk concentration of P in Fe–C–P alloys with a DBTT of about 20°C, and corresponding to a grain boundary concentration of P = 20 at.% [13] is calculated and shown in Fig. 8. In this calculation, the values of segregation free energies for C and P estimated to be 76 kJ mol^{-1} and 53 kJ mol^{-1} respectively at 873 K [14] have been used. It can be seen that the critical bulk compositions of C and P vary with grain size at very small concentration and finer grain size, while the grain size dependence is negligibly small at larger bulk contents.

The fact that the segregation to the grain boundary is a sensitive function of grain size in metallic systems implies that the grain size effect is likely to be all the more significant in ceramic materials, which generally have finer grains than the metallic alloys. Assuming the grain boundary thickness in ceramic materials to be the same as in metallic alloys, the grain size effect on the intergranular segregation of Ca and Ni in Al_2O_3 at 1600 K has been evaluated and shown in Fig. 9, taking the values for the segregation free energies of Ca and Ni as 117 kJ mol^{-1} and 23 kJ mol^{-1} respectively [15] and the concentration of Ca as $^{\circ}x_{\mathrm{Ca}} = 5 \times 10^{-5}$. The grain size strongly influences the grain boundary segregation, even at higher temperatures in the range of grain radii usually observed in Al_2O_3. It is thus evident that the grain size has an important role in the segregation phenomena in ceramic systems as well.

In the present study, the boundary thickness in the metallic and ceramic materials has been assumed to be constant and equal to 1 nm for the sake of simplicity. It has been recognized, however, that the thickness of grain boundary interface depends not only on temperature [16] but also on grain boundary orientation

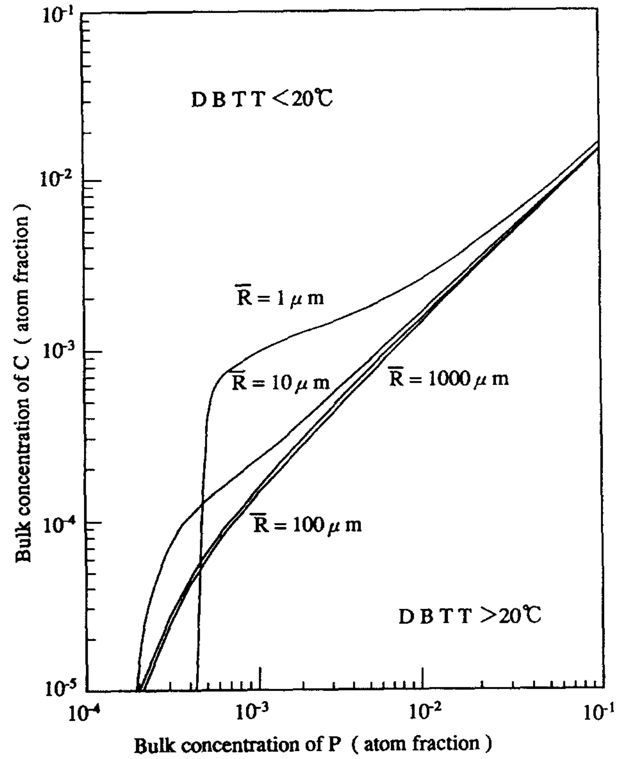

Fig. 8. Effect of grain size on the critical bulk concentrations of Fe–C–P alloys, for the grain boundary concentration of P = 20 at.% at 873 K.

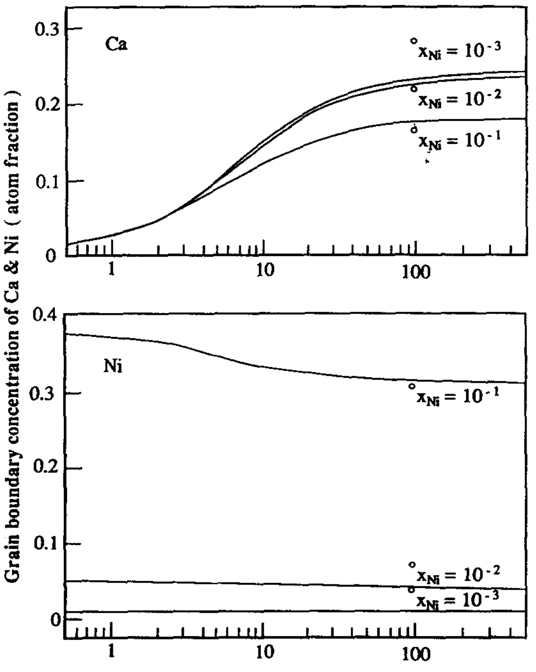

Fig. 9. Effect of grain size on the grain boundary segregation of Ca and Ni in Al_2O_3 at 1600 K, where $^{\circ}x_{\mathrm{Ca}} = 5 \times 10^{-5}$, $\Delta G^{\mathrm{s}}_{\mathrm{Ca}} = 117$ kJ mol^{-1} and $\Delta G^{\mathrm{s}}_{\mathrm{Ni}} = 23$ kJ mol^{-1}.

[17]. Moreover, the segregation free energies for the segregating species also vary with the misorientation angle of the adjacent grains [18] and have complicated temperature dependence in magnetic materials [19,20]. Further studies are required to take these effects explicitly into account. Finally, it should also be noted that the grain size effect is likely to play a significant part in the interphase boundary segregation.

3. Conclusions

Quantitative analysis of the effect of grain size on grain boundary segregation in metallic and ceramic systems has been performed and the results obtained are as follows.

(1) The grain size effect on intergranular segregation of solute is quite marked when the segregation energies are high, bulk solute concentrations are low and the temperature is low.

(2) In ternary systems A–X–Y, when the segregation free energy of X is larger than that of Y the grain boundary concentration of solute X decreases with decreasing grain size, while that of solute Y depends on the bulk concentration of the solute.

(3) It is suggested that grain size has a significant role on grain boundary segregation, not only in metallic but also in ceramic systems.

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