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LETTER TO THE EDITOR

A new kinetic model for non-equilibrium grain boundary segregation

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Abstract. We propose a new kinetic model for non-equilibrium grain boundary segregation. The model is based on three assumptions: that non-equilibrium grain boundary segregation is caused by diffusion of solute–vacancy complexes to the grain boundary; that the grain boundary is a sink for the complexes; and that the grain boundary and grain dimensions are sufficiently large.

Non-equilibrium segregation to grain boundaries and its quantification have been investigated previously [1–5]. Here, a new kinetic model for non-equilibrium grain boundary segregation is advanced, which is based on the following assumptions:

- (i) non-equilibrium grain boundary segregation is caused by the diffusion of solute–vacancy complexes to the grain boundary;
- (ii) the grain boundary is the sink of the complexes;
- (iii) the grain boundary is of a certain thickness and grains are large enough.

When an alloy is subjected to solid solution treatment at the temperature T_0 , the solute equilibrium concentration C_{gb} in the grain boundary can be expressed as [6]

$$C_{gb}(T_0) = C_g \exp(\Delta H/kT_0) \quad (1)$$

where C_g is the solute concentration in the lattice, ΔH is the free energy difference between a solute atom in the lattice and in the grain boundary and k is Boltzmann's constant. In the lattice the equilibrium concentration of the complexes C_{c0} is given by

$$C_{c0}(T_0) = K_c K_v C_g \exp((E_b - E_f)/kT_0) \quad (2)$$

in which K_c is a geometrical constant related to complexes, K_v is another geometrical constant related to vacancies, and E_b and E_f are the thermodynamic free energies of vacancy–solute binding and of vacancy formation, respectively. If the alloy cools from T_0 to T_1 instantaneously and is held at T_1 , the diffusion of the complexes in the grain–grain boundary will take place (see figure 1). The diffusion equation of the complexes

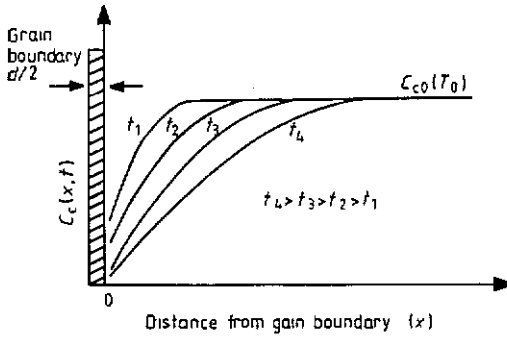


Figure 1. Schematic diagram of the complex concentration change with distance from the grain boundary after different holding times because of the diffusion to the grain boundary. d is the thickness of the grain boundary.

can be written [7]

$$D_c \partial^2 C_c(x, t) / \partial x^2 = \partial C_c(x, t) / \partial t \tag{3}$$

with the restrictions:

$$C_c(x = 0, t) = 0$$

$$C_c(x, t = 0) = C_{c0}(T_0)$$

where D_c is the diffusion coefficient of the complexes, $C_c(x, t)$ the complex concentration in lattice and t the holding time at T_1 . Equation (3) is the classic diffusion equation. We have the solution

$$C_c(x, t) = C_{c0}(T_0) \operatorname{erf}(x / 2\sqrt{D_c t}). \tag{4}$$

When the alloy is held at T_1 for the time t_1 , we have

$$\Delta C_{gb}(t_1) = (2/d)N(t_1) \tag{5}$$

in which $\Delta C_{gb}(t_1)$ is the increment of the solute concentration in the grain boundary due to non-equilibrium segregation after holding time t_1 ; d is the grain boundary thickness and $N(t_1)$ is the number of complexes diffusing into unit grain boundary area within a holding time t_1 . According to the Fick diffusion equation, equation (5) is changed into

$$\Delta C_{gb}(t_1) = (2D_c/d) \int_0^{t_1} \partial C_c(x, t) / \partial x |_{x=0} dt. \tag{6}$$

From equation (4) we have

$$\partial C_c(x, t) / \partial x |_{x=0} = C_{c0}(T_0) / \sqrt{D_c t}. \tag{7}$$

Then

$$\Delta C_{gb}(t_1) = 4\sqrt{D_c/\pi} C_{c0}(T_0) \sqrt{t_1} / d \tag{8}$$

$$C_{gb}(T_1, t) = C_{gb}(T_0) + \Delta C_{gb}(t) \quad (t < t_c) \tag{9}$$

where $C_{gb}(T_1, t)$ is the solute concentration in the grain boundary at T_1 , and t_c is the critical holding time; when $t > t_c$, C_{gb} will be greater than the grain boundary equilibrium concentration and solute atoms in the grain boundary will diffuse back to the grain centre

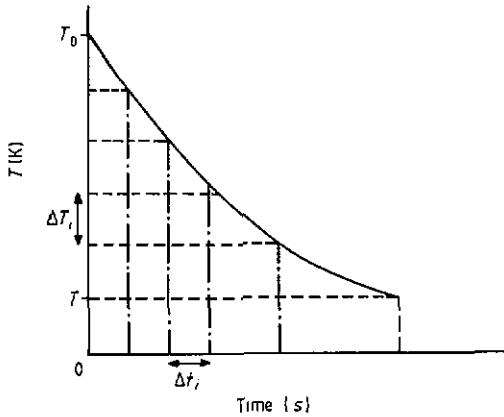


Figure 2. Schematic diagram of continuous cooling from T_0 to T .

during the continuity of complex diffusion to the grain boundary, which means that desegregation occurs.

When the alloy cools continuously from T_0 to T at a rate $V(T)$, we can divide the temperature range and time into N intervals (see figure 2). Each small interval can be considered an isothermal process. For the i th interval

$$\Delta_i C_{gb}(T_0 - i\Delta T) = (2/d) \int_0^{\Delta t_i} \partial C_c(x, t)/\partial x|_{x=0} D_c(T_0 - i\Delta T) dt \quad (10)$$

in which $D_c(T_0 - i\Delta T)$ is the diffusion coefficient of the complexes at the temperature $T_0 - i\Delta T$. So we have the increment of the solute concentration in the grain boundary at the temperature T :

$$\Delta C_{gb}(T) \doteq \sum_{i=1}^N \Delta_i C_{gb}(T_0 - i\Delta T) \quad (11)$$

where $N = (T_0 - T)/\Delta T$. When $\Delta t_i \rightarrow 0$

$$\lim_{\Delta t_i \rightarrow 0} \int_0^{\Delta t_i} \partial C_c(x, t)/\partial x|_{x=0} dt = -\partial C_c(x, t)/\partial x|_{x=0} dT/V$$

in which $dt = -dT/V(T)$. So

$$\begin{aligned} \Delta C_{gb}(T) &= -\lim_{N \rightarrow \infty} \sum_{i=1}^N (2D_c/d) \partial C_c(x, t)/\partial x|_{x=0} dT/V \\ &= -\int_{T_0}^T (2D_c/d) \partial C_c(x, t)/\partial x|_{x=0} dT/V \\ &= -\int_{T_0}^T (2/d) \sqrt{\frac{D_c}{\pi}} (C_{c0}(T_0)/V) dT/\sqrt{t} \end{aligned} \quad (12a)$$

if $V(T)$ is a constant independent of T , $t = (T_0 - T)/V$ and

$$\Delta C_{gb}(T) = -[2C_{c0}(T_0)/(d\sqrt{\pi V})] \int_{T_0}^T \sqrt{D_c/(T_0 - T)} dT \quad (12b)$$

$$C_{gb}(T) = C_{gb}(T_0) + \Delta C_{gb}(T). \quad (13)$$

Combining the investigation of rare earth segregation in Al [8], and the related binding energy and solubility data [9], according to equation (9) for the isothermal process and equation (13) for continuous cooling, reasonable agreement between the experimental data and calculated results has been obtained for the non-equilibrium grain boundary segregation of rare earth atoms in aluminium, which we intend to present, in detail, in a later paper.

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