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Non-equilbrium grain-boundary segregation kinetics

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A new model is proposed in this article concerning non-equilibrium grain-boundary segregation kinetics. The model not only includes the isothermal non-equilibrium grain-boundary segregation kinetics but also provides a formula for calculating the non-equilibrium segregation level under continuous cooling. Results calculated from the non-equilibrium grain-boundary segregation model for boron in steel grade Type 316 and chromium in steel grade $2\frac{1}{4}$% Cr–1% Mo are in satisfactory agreement with the observed data for experimental measurements.

1. Introduction

The segregation of solute atoms in grain-boundaries of austenite is classified into equilibrium and non-equilibrium segregation. The findings of McLean [1] on the thermodynamics and isothermal kinetics of equilibrium segregation are still in wide application [1, 2]. Ogura [3] furthered McLean's work and succeeded in advancing his results to handle the calculation of the equilbrium segregation level under continuous cooling.

In the late 1960s a non-equilibrium grain-boundary segregation theory with respect to the solute atoms was proposed by Aust *et al.* [4] and Anthony [5]. It is suggested that the mechanism of segregation be based on an equilibrium in which a sufficient quantity recombined solute atoms and vancancies exists. These three parts: solute atom, vacancy and their recombined complex, are in equilibrium with each other. A sample properly maintained at a solid dissolution treatment temperature will, when cooled to a certain lower temperature, exhibit a loss of vacancies along the grain-boundaries, whereby it attains the equilibrium vacancy concentrations at low temperatures. The decrease in the vacancy concentration causes the dissociation of the recombination complexes into vacancies and solute atoms. This in turn gives rise to the decrease in the recombined complex concentration near the grain-boundary. Meanwhile, in regions remote from the grain-boundary, where no other vacancy traps are present, vacancies would recombine with solute atoms and reduce the vacancy concentration. This makes the recombination complex concentration increase in regions remote from the grain-boundary. Consequently, a concentration gradient appears between the grain-boundary and regions beyond it. The gradient drives the recombination complexes to diffuse from regions remote from the grain-boundary to the grain-boundary. This diffusion causes excessive solute atoms to concentrate in the vicinity of the grain-boundary and results in non-equilibrium grain-boundary segregation. Faulkner [6] evaluated the maximum non-equilibrium segregation level and took for granted that this maximum level was equal to the segregation level found in the process of segregation. Such a postulate is obviously a coarse one. Doig and Flewitt [7] give a kinetic analysis for the non-equilibrium grain-boundary segregation of solute atoms. The analysis, however, makes a number of assumptions which differ from the actual diffusion process in non-equilibrium segregation and their experimental conditions. In the present work, the author proposes an isothermal kinetic model for non-equilibrium segregation of the solute atoms at the grain-boundary, on the basis of a non-equilibrium segregation mechanism resulted from the diffusion of complexes toward the grain-boundary. This model is also applied to the study of the effect of continuous cooling. A comparison is made between the author's theoretical treatment and that of Faulkner and Doig. Finally, data calculated by the author's model show agreement with the observed experimental data.

2. The kinetic model for non-equilibrium segregation

For austenite which contains solute atoms, it is postulated that there is an equilibrium between solute atom I, vacancy V and recombined complex C formed by the former two components:

$$\mathrm{I} + \mathrm{V} \rightleftharpoons \mathrm{C}$$

where it is assumed that one recombined complex is made up of one solute atom and one vacancy. When the forward and reverse reactions proceed to an equilibrium, the following relation holds for the three components as regards their combined concentration C_c:

$$C_c = K_c C_v C_I \exp(E_b/kT) \tag{1}$$

where E_b is the energy of formation of the recombined complex, k is Boltzmann's constant and K_c is a

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geometric factor. The equilibrium concentration for vacancy can be expressed as

$$C_v = K_v \exp(-E_f/kT) \qquad (2)$$

where E_f is the energy of formation of vacancy and E_b is, in general, smaller than E_f while K_v is also a geometric factor. From Equations 1 and 2, the concentration of the recombined complexes in equilibrium, C_c, is

$$C_c = K_c K_v C_I \exp[(E_b - E_f)/kT] \qquad (3)$$

and

$$C_c/C_I = K_c K_v \exp[(E_b - E)kT] \qquad (4)$$

As has been discussed in [6], the recombined complex will diffuse in the direction of its concentration gradient from within the grain towards the grain-boundary when cooled from T_0, the solid dissolution treatment temperature, to room temperature, so as to maintain a uniform concentration throughout the specimen. An assumption is made here that there should be localized and temporary equilibria in the grain and at the grain-boundary, respectively. Thus, an equilibrium at temperature $T_{0.5T_m}$ is attained at the grain-boundary while the components within the grain remain in a state of equilibrium at T_0. It is also assumed that the concentration of the recombined complex within the grain and at the grain-boundary are identical, or $[C_c]^{g}_{T_0} = [C_c]^{gb}_{T}$. Thereupon,

$$C_{gb}/C_g = \exp\{[(E_b - E_f)/kT_0] - [(E_b - E_f)/kT_{0.5T_m}]\}\ E_b E_f \qquad (5)$$

where C_{gb} is the maximum concentration of solute atom at the grain-boundary, and C_g is the concentration of solute atoms within the grain. Faulkner [6] assumes that C_{gb} is the non-equilibrium segregation concentration of solute atom in a specimen which undergoes cooling from T_0 down to room temperature when segregation alone proceeds, without the occurrance of de-segregation.

The discussion by Faulkner [6] when applied to samples being cooled from solid dissolution treatment temperature T_0 down to an arbitrary temperature T ($T_0 > T$), gives

$$C_b^M(T)/C_g = \exp\{[(E_b - E_f)/kT_0] - [(E_b - E_f)/kT]\}\ E_b/E_f \qquad (6)$$

where $C_b^M(T)$ is the maximum concentration of solute atoms at the grain-boundary cooled down from T_0 to T.

Although here a slight modification is made in Faulkner's formula, Equation 6 is quite different in meaning from Equation 5. In Equation 6, $C_b^M(T)$ depends on temperature T and the equation relates the maximum non-equilibrium segregation concentration to the temperature T when the sample is cooled down from T_0 to T. Equation 6 is an important thermodynamic equation describing the non-equilibrium grain-boundary segregation level. It can be seen in the following discussion that only after Equation 5 is modified in this way can one establish the basis for isothermal kinetic relationship of non-equilibrium segregation.

Suppose that the sample is cooled at such an extremely rapid rate from T_i down to T_{i+1} ($T_i > T_{i+1}$) that no mass transfer occurs in the specimen during cooling. Then the temperature is maintained at T_{i+1} for a period of time, during which time the recombined complexes will diffuse from within the grain toward the grain-boundary, and the solute atoms are concentrated at the grain-boundary. Let $T_{i+1} < T_i < T_0$ and denote $C_b^M(T_i)/C_g$ by α_i, and $C_b^M(T_{i+1})/C_g$ by α_{i+1}. Obviously $\alpha_{i+1} > \alpha_i$. As width d is relatively small as compared with the grain size, and $\alpha_{i+1} \times d$ is very small as compared with the grain diameter, the solute atoms concentrated at the grain boundary will be almost entirely furnished from the very narrow region in the vicinity of the grain-boundary, and the concentration of solute atoms within the grain remains a constant one, C_g. With the above conditions being met, the diffusion of recombined complexes towards the grain-boundary can be simplified into a steady linear flow of recombined complexes into the grain-boundary, in a semi-infinite medium.

The corresponding diffusion equation for combined complexes is, therefore,

$$D_c \partial^2 C_c/\partial x^2 = \partial C_c/\partial t \qquad (7)$$

where D_c is the coefficient of diffusion of the recombined complex in the matrix and C_c is the concentration of the recombined complexes. Substituting Equation 3 into Equation 7 gives

$$D_c \partial^2 C_I/\partial x^2 = \partial C_I/\partial t \qquad (8)$$

where C_I is the concentration of solute atoms and D_c remains the coefficient of diffusion of the recombined complexes.

In the substitution of Equation 3 into Equation 7, there is an implied assumption that, in any of the localized regions, the recombination can be considered in equilibrium even though it is not necessary for the whole system to be in a system of equilibrium. This assumption is justified because this reaction is concerned with short range diffusion in small regions [9].

Equation 8 is an equation of diffusion of a special form. There the coefficient of diffusion is concerned with the recombined complexes while the concentration is concerned with the solute atoms. This properly depicts the diffusion of solute atoms under the drag of recombined complexes toward the grain-boundary, causing the difference in concentration of solute atoms in different parts of the crystal.

In view of the extremely small thickness of the layer at the grain-boundary where the concentration gradient can be neglected, one can imagine an interface between the grain interior and boundary where the concentration is

$$C = C_b(t)/\alpha_{i+1}$$

where $C_b(t)$ is the concentration of the concentrated layer at a constant temperature T_{i+1} and changes with the time at constant temperature. For simplicity in computation, the interface between the grain interior and boundary at $x = 0$ is chosen. According to the First Law of Diffusion and the Principle of Mass Conservation, the interface should suffice the following conditions:

$$(C)_{x=0} = C_b(t)/\alpha_{i+1}$$

$$D_c(\partial C/\partial x)_{x=0} = (d/2)(\partial C_b(t)/\partial t) = \tfrac{1}{2}\alpha_{i+1} d(\partial C/\partial t)_{x=0} \quad (9)$$

where d is the width of the concentrated layer and the factor 1/2 is related to the fact that at both sides of grain-boundaries the solute atoms diffuse towards the grain-boundaries. Assuming Equation 9 to be the boundary condition, the solution to Equation 8 gives [1]

$$C_b(t) = C_b^M(T_{i+1}) - C_g(\alpha_{i+1} - \alpha_i) \times \exp\left[\frac{4Dt}{d_{i+1}^2 d^2}\right] \operatorname{erfc}\left[\frac{2(Dt)^{1/2}}{\alpha_{i+1} d}\right]$$

Rearranging, we obtain

$$[C_b(t) - C_b^M(T_i)]/[C_b^M(T_{i+1}) - C_b^M(T_i)] = 1 - \exp\left(\frac{4Dt}{\alpha_{i+1}^2 d^2}\right) \operatorname{erfc}\left[\frac{2(Dt)^{1/2}}{\alpha_{i+1} d}\right] \quad (10)$$

where

$$\operatorname{erfc}\left[\frac{2(Dt)^{1/2}}{\alpha_{i+1} d}\right] = 1 - \operatorname{erf}\left[\frac{2(Dt)^{1/2}}{\alpha_{i+1} d}\right] = 1 - \frac{2}{\sqrt{\pi}} \int_0^{2(Dt)^{1/2}/\alpha_{i+1} d} \exp(-y^2)\,dy$$

where $D = D_c$.

Equation 10 is an isothermal kinetic relationship for non-equilibrium segregation. It describes the non-equilibrium segregation concentration $C_b(t)$ of the solute atoms at the grain-boundary as function of time t at constant temperature.

Despite the similarity in appearance of Equation 10 to the equilibrium segregation isothermal kinetic relationship obtained by McLean [1], there is an essential difference in the physical processes they depict. It is shown in Equation 10 that a specimen subjected to rapid cooling from T_i down to T_{i+1} and then kept at a constant temperature will have a non-equilibrium grain-boundary segregation concentration $C_b(t)$ related both to the magnitude of the difference between T_i and T_{i+1} and to the duration of time for which the temperature of the specimen is held constant.

As discussed in [6], a non-equilibrium segregation includes both the processes of segregation and de-segregation. The duration of the segregation process is designated t_c (critical time) and

$$t_c = \frac{R^2 \ln(D_c/D_I)}{4\delta(D_c - D_I)} \quad (11)$$

where R is the grain size and δ is a constant.

Evidently, Equation 10 as obtained above is only concerned with segregation and not de-segregation. This necessitates the condition $t < t_c$ to obtain Equation 10, i.e.

$$\left\{\begin{array}{l} [C_b(t) - C_b^M(T_i)]/[C_b^M(T_{i+1}) - C_b^M(T_i)] \\ \quad = 1 - \exp(4Dt/\alpha_{i+1}^2 d^2) \operatorname{erfc}[2(Dt)^{1/2}/\alpha_{i+1} d] \\ t \leqslant t_c = \dfrac{R^2 \ln(D_c/D_I)}{4\delta(D_c - D_I)} \end{array}\right. \quad (12)$$

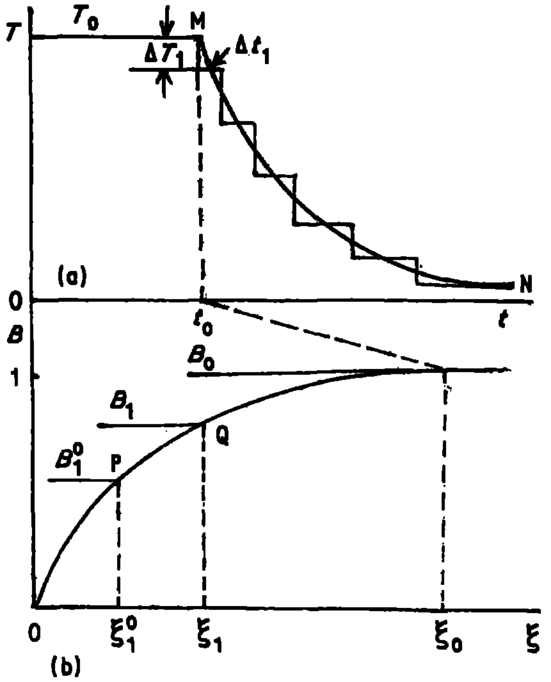

Figure 1 (a) Actual cooling curve MN and its approximate stepped curve. (b) B (ξ) graph representing Equation 13, the non-equilibrium segregation kinetic relationship, showing the change in B during the segregation process occurring in time interval Δt_1 in the first step.

It should be mentioned here that the t_c as obtained in [6] should have arrived at the same expression as Equation 11 in the present work; however a mistake led to the wrong expression, $t_c = \delta R^2 \ln(D_c/D_I)/4(D_c - D_I)$, which led to the erroneous interpretation of specimens which only undergo segregation as being the same as those undergoing de-segregation.

This work presents the boundary conditions in Equation 9 directly from Equation 6, whereby the non-equilibrium isothermal segregation kinetics relationship (Equation 10) is obtained; these equations form the basis for the calculation of non-equilibrium segregation grain-boundary concentration under continuous cooling.

Suppose the specimen attains equilibrium at a solid dissolution treatment temperature T_0, and then cools down to room temperature along the curve MN (Fig. 1). To find the non-equilibrium segregation concentration of solute atoms at the grain-boundary, we make the following assumptions.

1. The isothermal kinetics of non-equilibrium segregation and the maximum concentration at grain-boundary will be governed by Equations 6 and 12. Since $C_b^M(T_{i+1}) > C_b(t) \gg C_b^M(T_i)$ always holds unless $t = 0$, Equation 12 can be simplified to

$$B = \frac{C_b(t)}{C_b^M(T)} = 1 - \exp\left(\frac{4Dt}{\alpha^2 d^2}\right) \times \operatorname{erfc}\left[\frac{2(Dt)^{1/2}}{\alpha d}\right] = f(\xi) \quad (13)$$

where $\xi = 2(Dt)^{1/2}/\alpha d$, and B is degree of saturation which increases with the time when held at a certain constant temperature. Differentiation of Equation 6

TABLE I Ultimate composition of the alloy

Alloy	Composition (wt %)											
	C	Si	Mn	Ni	Cr	Mo	Co	N	B	S	P	Fe
Type 316 steel	0.039	0.32	1.54	11.4	17.3	2.5	0.037	0.023	0.0018	–	–	balance
$2\frac{1}{4}$% Cr–1% Mo steel	0.07	–	0.53	0.10	2.10	1.00	–	–	–	0.02	0.02	balance

yields

$$\Delta C_b^M / C_b^M(T) \;=\; \Delta T (E_b - E_f)/kT^2 \;=\; A(T)\,\Delta T \tag{14}$$

where $A(T) = (E_b - E_f)/kT^2$.

2. As shown in Fig. 1, when the steps formed by horizontal and vertical segments are chosen small enough, the non-equilibrium grain-boundary segregation level along the cooling curve MN will be practically equal to that along the stepped curve.

3. Since equilibrium is observed at the solid dissolution treatment temperature T_0, it is justified to assume that $B_0 = 1$ in such a case. Moving downward along the stepped curve; in the first step, as T_0 drops by ΔT_1 (see Fig. 1) and $C_b^M(T_0)$ drops to $C_b^M(T_0 - \Delta T_1)$ and B_0 becomes $B_0^1 < 1$. The ξ value corresponding to B_1^0 is the ξ_1^0 value corresponding to P. Segregation occurs at P in the first step and ξ_1^0 increases to ξ_1 and makes B reach B_1 during Δt in the first step on the B–ξ curve from P to Q. This also applies to the subsequent steps.

Let ΔC_b^Q be the non-equilibrium segregation amount produced in the cooling process represented by the curve MN. A correction factor γ is introduced and defined as

$$\gamma \;=\; \Delta C_b^Q / C_b^M(T_0) \tag{15}$$

The concentration of solute atom at the grain-boundary following the cooling process along curve MN is denoted by

$$C_b^* \;=\; (1 + \gamma)\, C_b^M(T_0) \tag{16}$$

where $C_b^M(T_0) = C_g$, and C_b^* can be calculated from Equation 16 when γ is known.

It can be seen from Assumption 2 above that the value of γ on the stepped curve is equal to that on the MN curve. The value of γ on the stepped curve, which can be calculated from Equations 13 and 14, is (see Appendix):

$$\begin{aligned}\gamma \;&=\; \sum_{i=1}^{n} \Delta C_b(T_i, \Delta t_i)/C_b^M(T_0)\\ &=\; \sum_{i=1}^{n} \Delta B_i\,[1 + A(T_{i-1})\,\Delta T_i] \Big/ \prod_{j=1}^{i-1} [1 - A(T_j)\,\Delta T_j]\end{aligned} \tag{17}$$

Here ΔT_i is the decrease in temperature at the ith step on the stepped curve; and $\Delta B_i = B_i - B_i^0 B_1^0$ is the value of B at the beginning of the horizontal segment at the ith step, and B_i is the value of$B$ when the horizontal segment terminates at the ith step.

Calculation of C_b^* by means of Equation 16 only applies to cases where only the segregation process occurs in the whole continuous cooling process, and does not apply to cases where the de-segregation process also occurs. Making use of the concept of effective time as introduced in [6], one can evaluate the effective time $t_e(T_0)$ at T_0 for n steps:

$$t_e(T_0) \;=\; \sum_{i=1}^{n} t_i \exp\,[-E_A(T_0 - T_i)/kT_0 T_i]$$

Since Equation 16 is true only when $t_e(T_0) \leqslant t_c(T_0) = R \ln\,[D_I(T_0)/D_c(T_0)]/4\delta[D_I(T_0) - D_c(T_0)]$ we have

$$\begin{cases} C_b^* \;=\; (1 + \gamma)\, C_b^M(T_0) \\ t_e(T_0) \leqslant t_c(T_0) \end{cases} \tag{18}$$

Equation 18 is a formula for calculating the non-equilibrium segregation level for continuous cooling.

3. A comparison of calculated results and observed data

It is seen in [8] that a boron-bearing steel (Type 316) exhibits observed data for the segregation of B at the grain-boundary of austenite under the specific laboratory conditions. These laboratory conditions are used in the following calculations in this article using Equation 18 to find the amount of non-equilibrium grain-boundary segregation under cooling conditions for the sets of specimens mentioned in [8]. The chemical analysis of steel Type 316 is shown in Table I, and the parameters used in this paper are given in Table II. Experimental conditions, calculated results and observed data quoted from [8] are listed in Table III. The fact that the calculated results agree qualitatively with the experimental data is obvious. Different rates of cooling for the six sets of specimens include 500° C sec^{-1} and 50° C sec^{-1}. Equations relating cooling temperature to time are $T = T_0 - 500t$ and $T = T_0 - 50t$, respectively, which on differentiating yield the relations $\Delta T = -500\Delta t$ and

TABLE II Data used in theoretical calculations

Parameter	B in Type 316 steel		Cr in $2\frac{1}{4}$% Cr–1% Mo steel	
D_I(m^2 sec^{-1})	$2(10^{-7}) \exp(-0.91/kT)$	[10]	$1.5 \times 10^{-5} \exp(-2.6/kT)$	[12]
D_V(m^2 sec^{-1})	$5(10^{-7}) \exp(-0.91/kT)$	[11]	$5 \times 10^{-5} \exp(-2.6/kT)$	[11]
E_f(eV)	1.4	[8]	1.4	[7]
E_A(eV)	0.91	[8]	2.6	[7]
E_b(eV)	0.5	[8]	0.87	[7]
C_g(wt %)	0.0018	[8]	2.1	[7]
d(μm)	1.5	[8]	1×10^{-3}–20×10^{-3}	[7]

TABLE III Observed and theoretically calculated results for Type 316 steel

Solid dissolution treatment temperature, T_0 (°C)	Cooling rate (°C sec^{-1})	Grain size, R (μm)	Critical time, t_c (sec) ($\delta = 0.05$)	Effective time, t_e (sec)		Segregation concentration (at %)			
				$\lvert\Delta T\Delta t\rvert = 5$	$\lvert\Delta T\Delta t\rvert = 3.2$	Calculated results			Observed segregation
						$\Delta T\Delta t = 5$	$\Delta T\Delta t = 3.2$	$\Delta T\Delta t = 0$	
1350	500	60	5.0	0.27	0.26	0.56	0.49	0.37	none
1200	500	45	7.5	0.21	0.22	0.35	0.30	0.21	none
1050	500	30	10	0.16	0.16	0.16	0.15	0.13	none
1350	50	60	5.0	2.6	2.6	0.61	0.59	0.55	high
1200	50	45	7.5	2.2	2.2	0.41	0.39	0.35	medium
1050	50	30	10	1.7	1.7	0.18	0.17	0.16	low

TABLE IV Experimentally observed and theoretically calculated results for water-quenched 2¼ % Cr–1 % Mo steel

Position of measurement (distance from grain boundary in nm)	Observed chromium (%)	Calculated prior γ grain-boundary composition (%)			
		1 nm wide profile	5 nm wide profile	10 nm wide profile	20 nm wide profile
grain-boundary 1/1423 K					
0	3.01(3.27)*	6.04	3.46	3.29	2.63
20	2.20				
50	2.11				
100	2.21				
grain-boundary 1/1323 K					
0	3.10(2.94)*	4.83	3.01	2.52	–
20	2.09				
50	2.11				
100	2.20				
150	2.10				

*Figures in parenthesis are those quoted from [7] in which they represent statistical averages from several regions where measurements are made in their grain-boundary segregation layers.

$\Delta T = -50\Delta t$. Taking $|\Delta T \Delta t| = 5$ and $|\Delta T \Delta t| = 3.2$, one finds that for specimens undergoing cooling at a cooling rate of 500° C sec^{-1}

$$|\Delta T \Delta t| = 5, \quad \Delta T = -50^\circ\,\mathrm{C} \quad \text{and } \Delta t = 0.1\,\mathrm{sec};$$

$$|\Delta T \Delta t| = 3.2, \ \Delta T = -40^\circ\,\mathrm{C} \text{ and } \Delta t = 0.08\,\mathrm{sec}.$$

For specimens undergoing cooling at 50° C sec^{-1}, one has

$$|\Delta T \Delta t| = 5, \quad \Delta T = -15.81^\circ\,\mathrm{C}$$

$$\text{and } \Delta t = 0.3162\,\mathrm{sec};$$

$$|\Delta T \Delta t| = 3.2, \quad \Delta T = -12.58^\circ\,\mathrm{C}$$

$$\text{and } \Delta t = 0.2530\,\mathrm{sec}.$$

Calculations in the present article make use of the above mentioned ΔT and Δt, forming a step curve which replaces the *T–t* curve for the respective specimens. The calculated results indicate that the calculated segregation concentration reduces monotonously with the reduction in the product $|\Delta T \Delta t|$. Therefore, the segregation concentration obtained by extrapolation to $|\Delta T \Delta t| = 0$ should be most accurate in theory.

In [7] a microanalysis of the grain-boundary regions of a 2¼ % Cr–1 % Mo steel is made using a scanning transmission electron microscope (STEM) in connection with an energy dispersive spectrometer (EDS). The analysis shows the non-equilibrium segregation of chromium in prior austenite grain-boundaries. Here the same steel specimen is studied with the help of the model proposed in Section 2, and the anticipated calculated results are in agreement with the observed laboratory data, as shown in Table IV. Data used in the calculation are listed in Table II; ultimate composition of the 2¼ % Cr–1 % Mo specimen is listed in Table I. The *T–t* cooling curve is replaced approximately by the function $T_n = T_0 \exp(-\phi n \Delta t)$ as proposed in [7], and is treated as such, taking $\phi = 1$, $\Delta t = 0.05$ sec; ΔT is found by the foregoing equation.

Related calculations as regards the specimen at $T_0 = 1423$ K show that $t_e = 0.024$ sec and $t_c = 1128$ sec, i.e. $t_e(1423) < t_c(1423)$. The calculations as regards the specimen at $T_0 = 1323$ K show that $t_e = 0.20$ sec and $t_c = 5610$ sec. Evidently what happens in both specimens is simple segregation without desegregation. This justifies the application of the model proposed in Section 2 to this part of the present article (grain size $R = 2\,\mu$m, $\delta = 0.05$).

4. Discussion

A number of authors have recently reported their findings on non-equilibrium grain-boundary segregations on the basis of the mechanism of the formation of recombined complexes of vacancies and solute atoms, and the diffusion toward the grain-boundary during cooling. Also, many different analyses have been introduced [6, 7]. Here a new kinetic model of non-equilibrium segregation is proposed. This new kinetic model describes an entirely different physical process from that of McLean [1] although it takes a similar form. The similarity and dissimilarity between the two models appropriately reflects the similarity and dissimilarity in nature between the equilibrium segregation of solute atoms toward grain-boundary and the non-equilibrium segregation. This paper provides a generalized relation for the behaviour of non-equilibrium grain-boundary segregation in a kinetic manner, just as McLean's model does in the case of equilibrium grain-boundary segregation.

The most obvious defect in the kinetic analysis described in [6] is that Equation 5 is improperly used to calculate the non-equilibrium grain-boundary segregation level whereas only segregation and no de-segregation ($t_e < t_c$) is proceeding. Evidently this is unacceptable. As a matter of fact, it has been shown by many experiments that non-equilibrium grain-boundary segregation concentration is closely related to the cooling rate the specimen undergoes. The segregation concentration as calculated from Equation 5, as is done in [6], is actually the maximum non-equilibrium segregation concentration caused by cooling down from the solid dissolution treatment temperature T_0 down to room temperature. The segregation as such is independent of the cooling rate. But the model presented here partly based on the model quoted from [6], correlates the non-equilibrium segregation concentration at $t_e < t_c$, not only to the solid dissolution treatment temperature but also to the cooling rate, which upgrades the findings of Faulkner [6].

Calculations based on the present model for all the six specimens of type 316 steel indicate that the condition $t_e < t_c$ is met throughout all the six specimens. This goes diametrically against what is calculated in [6]. Reasons for such a difference have been described in Section 2. Theoretical calculations made in the present article for all six specimens show that, at a constant solid dissolution treatment temperature, the segregated amount in a specimen cooled at a rate of $500°\text{C}\,\text{sec}^{-1}$ is smaller than that cooled at a rate of $50°\text{C}\,\text{sec}^{-1}$. Furthermore, it demonstrates that, at the same cooling rate, the higher the solid dissolution temperature, the greater the segregated amount. Such a conclusion has been verified in the observed data listed in Table III, adapted from [8].

From the viewpoint based on the calculated results in the present article, segregation at the grain-boundary should have been observed as well for specimens cooled at the rate of $500°\text{C}\,\text{sec}^{-1}$, as compared with specimens which undergo a cooling rate of $50°\text{C}\,\text{sec}^{-1}$. Unfortunately, Williams *et al.* [8] failed to observe such a phenomenon. The author of the present article maintains that when cooled at a lower rate, because the segregation of extremely fine grains of boride is probably induced by grain-boundary segregation, the transition process of which in turn, prompts the concentration of boron toward the grain-boundary. When cooled at a faster rate, however, the process of segregation as mentioned above can hardly occur due to the negligible amount segregated and in the short time. It follows that the quantitative difference in segregation appears larger than would be expected from the calculation. Williams *et al.* [8] observed the distribution of boron with an autoradiograph which adds to the difficulty in identifying the segregation of minute boride particles and boron atoms at the grain-boundary.

A scanning transmission electron microscope (STEM) fitted with a energy dispersive spectrometer (EDS) is used, as reported in [7], to obtain quantitative experimental data for the non-equilibrium segregation of chromium at the grain-boundary of prior austenite for a 2¼ % Cr–1 % Mo alloy steel. The author of the present article evaluates, on the basis of the kinetic model proposed in Section 2, the non-equilibrium segregated chromium at the grain-boundary in accordance with the solid dissolution treatment temperature and the T–t quenching curve $T_n = T_0 \exp(-\phi n \Delta t)$, $\phi = 1$, quoted for the said specimen, where the width of the segregation layers is assumed to be 1, 5, 10 and 20 nm, respectively. It seems that the theoretically calculated results are in satisfactory agreement with the observed data in [7] (see Table II).

The changes in the theoretically calculated segregation levels caused by the change of the assumed width (d) of the segregated layer are shown in Fig. 2a. According to the observed results in [7], a steel specimen subjected to a solid dissolution treatment at $T_0 =$ 1423 K shows that chromium has an average segregation level of 3.27% at the grain-boundary, while a specimen subjected to a solid dissolution treatment at 1323 K an average segregation concentration of 2.94%. As shown in Fig. 2, the segregation widths corresponding to these average concentration values are ~10 and 6 nm, respectively. The results indicate that the widths of both segregated layers do not exceed 20 nm, justifying the observed data in [7]. It can readily be inferred that when comparing the calculated values in this article with the data observed in [7], with a rise in temperature from 1323 to 1423 K, more chromium is segregated in the prior austenite grain-boundaries; but such an increase is chiefly caused by the widening of the segregation layer from ~6 to 10 nm, without a considerable increase in concentration of chromium in the grain-boundary segregation layer.

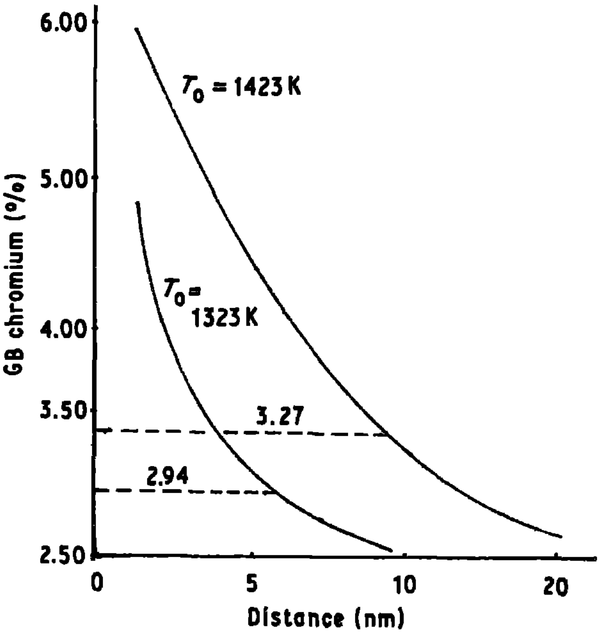

Figure 2 Curves showing the assumed width (d) of the segregated layer plotted against the calculated chromium content in prior austenite grain-boundary. 2¼ % Cr–1 % Mo steel austenized at 1423 and 1323 K.

Fig. 3 shows a curve representing a change in non-equilibrium grain-boundary segregation concentration, as calculated from Equation 18, with the change in binding energy E_b of the recombined complex. With the increase in E_b, the non-equilibrium grain-boundary segregation concentration decreases. This is doubtless true. Meanwhile, it can be seen from Equation 6 in Section 2 that, within a given temperature interval, C_b^M increases as E_b decreases. The kinetic model proposed in [7], however, gives a calculated result opposite to what is shown in Fig. 3. Evidently, this is unacceptable (see Fig. 7a in [7]). The kinetic model in the present article can apply to the representation of diffusion process of the "drag" action of the recombined complexes on the solute atoms, driving them to segregate at the grain-boundary, whereby the model conforms more correctly with the actual mechanism of non-equilibrium grain-boundary segregation. On the other hand, the suggested model in [7] which depicts the non-equilibrium segregation process as a result of the diffusion of vacancies toward the grain-boundary does not reflect the facts. Perhaps the contrary results

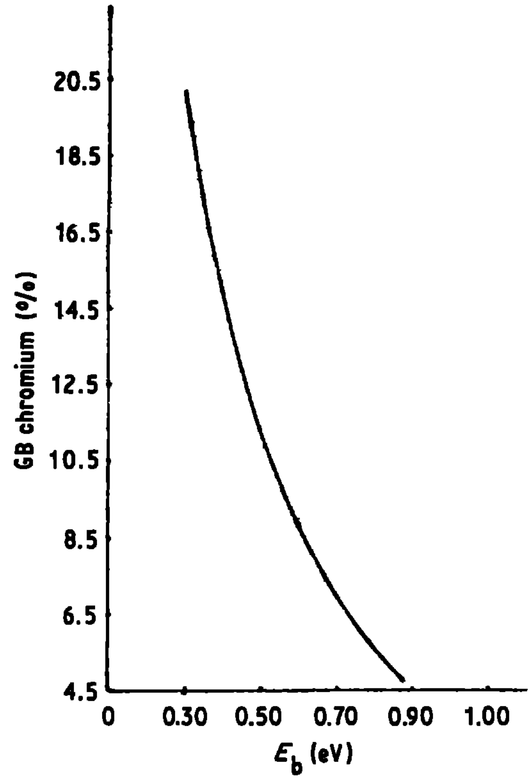

Figure 3 Calculated variation of prior austenite grain-boundary chromium composition with vacancy–solute binding energy, E_b, for austenitizing temperature 1323 K ($\phi = 1$, $\Delta t = 0.05$ sec, $d = 1$ nm).

between the two models arises from the difference in their kinetic models.

The model proposed in the present article has a further advantage over that in [7] in that for the arbitrary shape of the T–t curve the former gives a corresponding step curve which replaces the arbitrary T–t curve. Taking smaller and smaller ΔT and Δt intervals, any desired precision can be attained by such a replacement. In contrast, [7] makes use of taking different values of ϕ with the purpose of representing various T–t curves for the function $T_n = T_0 \exp(-\phi n \Delta t)$.

5. Conclusion

1. A new kinetic model is derived in the present article for the non-equilibrium grain-boundary segregation of solute atoms. The model consists of an isothermal kinetic relationship, Equation 12, and a continuous cooling relationship, Equation 18. Criteria for the range of application of these relationships are also given in this article.

2. Calculated results obtained from the new kinetic model agree satisfactorily with the observed data in [7, 8]. The author's anticipated calculated results and the observed data in [7, 8] indicate that, when effective time t_c is not greater than the critical time t_c for specimens cooled at the same cooling rate, the higher the solid dissolution treatment temperature, the greater the segregation; whereas for specimens treated at the same temperature, the lower the cooling rate, the greater the segregation.

The non-equilibrium segregation level of chromium at prior austenite grain-boundary in a $2\frac{1}{4}$% Cr–1% Mo steel specimen increases with the rise of the solid dissolution treatment temperature. The increase in segregation chiefly depends on the widening of the segregation layer. However, the increase in the concentration of chromium in the grain-boundary segregation layer is insignificant, as compared with the widening of the segregation layer.

3. As calculated with the help of the proposed model in this article, the non-equilibrium grain-boundary segregation amount decreases rapidly with increase in binding energy E_b of the recombined complex.

Appendix: Derivation of correction factor

Fig. A1 shows the ith step on the stepped curve, the ith step corresponding to temperature T_i and time interval $\Delta t_i = t_i - t_{i-1}$; the segregation concentration is $C_b(t_i)$ at time t_i, B at t_{i-1} is B_i^0 and that of B at t_i is B_i. From Equation 13

$$B_{i-1} = C_b(t_i - 1)/C_b^M(T_{i-1}) \qquad \text{(A1)}$$

As B_{i-1} becomes B_i^0 when the temperature drops from T_{i-1} by $\Delta T = T_{i-1} - T_i$, B_i^0 can be expressed by the following equation:

$$\begin{aligned} B_i^0 &= B_{i-1} = C_b(t_{i-1})/C_b^M(T_i) \\ &= \frac{C_b(t_{i-1})}{C_b^M(T_{i-1}) + \Delta C_b^M(T_{i-1})} \\ &= B_{i-1}/(1 + A(T_{i-1})\Delta T_i) \qquad \text{(A2)} \end{aligned}$$

During the time interval Δt_i when temperature is held at T_i, B_i^0 increases because a certain amount of non-equilibrium segregation is acquired at the grain-boundary. At the end of the ith step, the value of B, which is denoted by B_i, can be written as

$$\begin{aligned} B_i &= \frac{C_b(t_{i-1}) + \Delta C_b(T_i, \Delta t_i)}{C_b^M(T_{i-1}) + \Delta C_b^M(T_{i-1})} \\ &= \frac{B_{i-1} + C_b(T_i, \Delta t_i)/C_b^M(T_{i-1})}{1 + A(T_{i-1})\Delta T_i} \qquad \text{(A3)} \end{aligned}$$

Substituting Equation (A2) into the equation above, one obtains

$$\frac{C_b(T_i, \Delta t_i)}{C_b^M(T_{i-1})} = \Delta B_i(1 + A(T_{i-1})\Delta T_i) \qquad \text{(A4)}$$

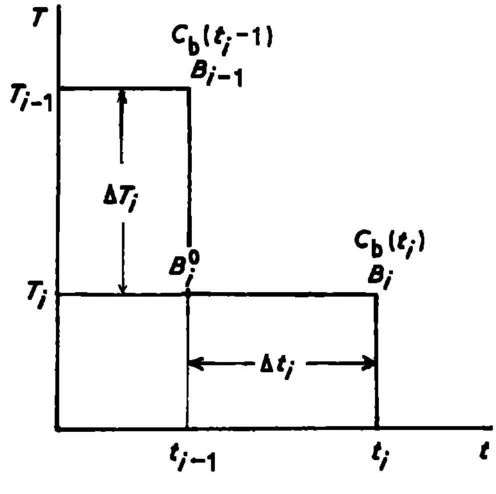

Figure A1 Schematic diagram showing the ith step.

where $\Delta B_i = B_i - B_i^0$. Similarly, the following equations are obtained:

$$\frac{\Delta C_b(T_i, \Delta t_i)}{C_b^M(T_{i-2})} = \frac{\Delta C_b(T_i, \Delta t_i)}{C_b^M(T_{i-1}) - \Delta C_b^M(T_{i-1})} = \frac{\Delta C_b(T_i, \Delta t_i)/C_b^M(T_{i-1})}{1 - \Delta C_b^M(T_{i-1})/C_b^M(T_{i-1})} = \frac{\Delta B_i[1 + A(T_{i-1})\Delta T_i]}{(1 - A(T_{i-1})\Delta T_{i-1})} \qquad \text{(A5)}$$

$$\frac{\Delta C_b(T_i, \Delta t_i)}{C_b^M(T_{i-3})} = \frac{\Delta C_b(T_i, \Delta t_i)/C_b^M(T_{i-1})}{C_b^M(T_{i-3})/C_b^M(T_{i-1})}$$
$$= \frac{B_i(1 + A(T_{i-1})\Delta T_i)}{[C_b^M(T_{i-2})/C_b^M(T_{i-1})]\,[C_b^M(T_{i-3})/C_b^M(T_{i-2})]}$$
$$= \frac{\Delta B_i[1 + A(T_{i-1})\Delta T_i]}{[1 - A(T_{i-1})\Delta T_{i-1}]\,[1 - A(T_{i-2})\Delta T_{i-2}]} \qquad \text{(A6)}$$

$$\frac{C_b(T_i, \Delta t_i)}{C_b^M(T_0)} = \frac{\Delta B_i[1 + A(T_{i-1})\Delta T_i]}{\prod_{j=1}^{i-1}[1 - A(T_j)\Delta T_j]} \qquad \text{(A7)}$$

Equation A6 gives the ratio of the non-equilibrium segregation concentration attained at the ith step, to the grain-boundary equilibrium concentration attained at solid dissolution treatment temperature T_0. Correction factor is the ratio of the total amount of non-equilibrium grain-boundary concentration attained in the cooling process along the step curve from T_0 down to t_n, to the grain-boundary equilibrium concentration at T_0. The expression for γ is readily obtained as follows:

$$\gamma = \sum_{i=1}^{n} \Delta C_b(T_i, \Delta t_i)/C_b^M(T_0)$$
$$= \sum_{i=1}^{n} \left\{\Delta B_i[1 + A(T_{i-1})\Delta T_i] \middle/ \prod_{j=1}^{i-1}[1 - A(T_j)\Delta T_j]\right\} \qquad \text{(A8)}$$

The value of $\Delta B_i = B_i - B_i^0$ must be found before evaluating γ. Given $B_{i-1}(B_0 = 1)$, B_i^0 can be found from Equation A2 and the value of ξ_i^0 corresponding to B_i^0 is found from Equation 13:

$$\xi_i^0 = f^{-1}(B_i^0) \qquad \text{(A9)}$$

Again from Equation 13

$$\Delta\xi_i = (\beta/\xi_i^0)\Delta t_i, \; \beta = 2D/\alpha^2 d^2 \qquad \text{(A10)}$$

Using Equation A10, $\Delta\xi_i$ can be found for given Δt_i, β and ξ_i^0. With $\Delta\xi_i$ being found, ΔB_i is readily found from Equation 13:

$$\Delta B_i = f(\xi_i) - f(\xi_i^0), \quad \xi_i = \xi_i^0 + \Delta\xi_i \qquad \text{(A11)}$$

Because $B_0 = 1$, ΔB_1 and B_1 are found by Equations A2, A9, A10 and A11 successively; ΔB_2 and B_2 are found in a similar way from B_1, and so on.

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