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Thermodynamics of Micro-Alloying*1
Tajii Nishizawa*2

The functional role of micro-alloying elements in grain boundary migration, especially their influence on solute drag and particle pinning, are reexamined using very simple models. The solute drag phenomenon is analyzed in terms of the grain boundary dwell time and drag length of the solute, assuming a state of equilibrium boundary segregation. Effect of particle pinning is analyzed using a slightly modified Zener's relation. The role of inverse pinning resulting from the anisotropy of AlN, first proposed by Taguchi and Sakakura in 1966 and utilized in the production of grain oriented Si-steel, is emphasized.

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1. Introduction

Looking back on the development of materials in the 20th century, it can be stated that the first half of the century was marked by the advent of new metals such as duralumin, stainless steel, magnetic alloys, etc., while the latter half was a witness to both the refinement and maturing of metallurgical production techniques of these metallic materials and the successive, parallel introduction of, semiconductors, fine ceramics, functional polymers and other advanced materials.

It is worthwhile mentioning at this point that the developmental directions that the key metallurgical technologies took in the maturing period were fairly different from those in the initial introduction period. For instance, the stabilization of austenite by alloying additions of Mn and Ni was the important concept to be pursued for steel engineers in the first half, whereas the pinning of grain boundaries by micro-alloying additions of Nb and Ti was the dominant concept for producing high strength steel in the latter half of the 20th century. It is the intention of the author in this lecture to examine some theoretical aspects of micro-alloying from a thermodynamic viewpoint.

Typical examples of micro-alloying technologies are listed in Table 1. Even though the principles underlying these technologies have been analyzed precisely from theoretical viewpoints, there remain still some unanswered questions on the actual mechanisms that control micro-alloying behavior, which is generally complicated and variable depending on conditions and circumstances. In the present paper, the effect of solute drag and particle pinning on grain boundary migration will be discussed in a simplified manner to elucidate the connection between micro-alloying theory and practice.

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2. Analysis of Solute Drag

Rigorous theories of the solute drag effect were presented by Lücke et al., Cahn, Hillert and others during 1955–75. The following is a simplified version, assuming equilibrium grain boundary segregation at all times.

2.1 Drag length and transfer frequency

The migration of a grain boundary proceeds by a succession of backward transfers of solvent atoms (A) across the boundary as illustrated in Fig. 1(a), where the boundary is assumed to be composed of 3 atom layers. The length of travel of an atom during a single transfer is considered to be the same as the boundary thickness δ by analogy to the motion of a ball in a series of billiard balls. Thus, the migration rate, v, of solvent atoms can be expressed by the following equation,

\[ v = \delta \cdot \nu_A \]  (1)

where \( \nu_A \) is the transfer frequency of solvent atoms.

Solute atoms (B), on the other hand, move forward as shown in Fig. 1(b). In this case, B atoms in the grain II are taken into the boundary, where they stay for a period of time...
τ_B, and then left behind in the grain I as the boundary moves forward. Assuming the atom fractions of B in the grain interiors and boundaries to be \( x_B \) and \( X_B \) respectively, the following relation is arrived at when the balance of molar fluxes is maintained.

\[
x_B \cdot v = X_B \cdot \delta / \tau_B
\]  

(2)

Since the drag length \( \lambda_B \) is equal to \( v \cdot \tau_B \) and the transfer frequency \( v_B \) is equal to \( 1 / \tau_B \), these are related to each other as follows;

\[
\lambda_B = v \cdot \tau_B = (X_B / x_B) \cdot \delta
\]  

(3)

\[
v_B = 1 / \tau_B = v / \lambda_B
\]  

(4)

According to McLean’s segregation equation, six \( X_B \) is approximated as

\[
X_B = \frac{k_{gb} x_B}{1 + k_{gb} x_B},
\]  

(5)

where \( k_{gb} \) is the segregation coefficient of B atoms, which is evaluated from the segregation energy \( \Delta E_{gb} \) and the relation, \( k_{gb} = \exp(\Delta E_{gb} / RT) \).

In a particular case for which \( \Delta E_{gb} = 50 \text{ kJ mol}^{-1} \), \( x_B = 10^{-3} \), \( v = 1 \mu \text{m s}^{-1} \) and \( \delta = 0.75 \mu \text{m} \), the values of the parameters in eq. (5) turn out to be \( k_{gb} \approx 410 \) and \( X_B = 0.3 \) at 1000 K. The drag length, the dwell time and the transfer frequency of B atoms are obtained from eqs. (3) and (4) as \( \lambda_B \approx 0.2 \mu \text{m} \), \( \tau_B \approx 0.2 \text{s} \) and \( v_B \approx 5 \text{s}^{-1} \), while the transfer frequency of A atoms is evaluated as \( v_A \approx 1330 \text{s}^{-1} \).

2.2 Micro-alloying and decrease in boundary mobility

The effect of micro-alloying on grain boundary mobility is easily analyzed by analogy to current flow in a wire made up of two components connected in series (Ohm’s law);

\[
i = \left( \frac{1}{X_1 \rho_1 + X_2 \rho_2} \right) \cdot \Delta V,
\]  

(6)

where \( \rho_1 \) and \( \rho_2 \) are resistances of each wire per unit length, \( X_1 \) and \( X_2 \) the length fractions, and \( i \) and \( \Delta V \) the electric current and potential, respectively.

Since both the flow of electric current and atom transfer are essentially transport phenomena, the rate equations governing both the flows should be analogous to each other. Thus, the equation for boundary migration in the A-B system (eq. (7)) is obtained by substitution of each electrical parameter in eq. (6) by its mass equivalent, as shown below.

\[
v = \left( \frac{1}{X_A/M_A + X_B/M_B} \right) \cdot \Delta G,
\]  

(7)

where \( M_A \) is the boundary mobility in pure A, and \( M_B \) is the boundary mobility when the boundary is wholly occupied by segregated B atoms only. \( X_A \) and \( X_B \) are the atom fractions of A and B in the boundary, respectively.

Since the boundary mobility is proportional to the frequency of atom transfer across the boundary, the next relation is obtained from eqs. (1)–(5).

\[
\frac{M_A}{M_B} = \frac{v_A}{v_B} = \frac{X_B}{x_B} = \frac{k_{gb} x_B}{1 + k_{gb} x_B}
\]  

(8)

Consequently, the mobility of the boundary in an A-B solid solution can be approximated as follows;

\[
M_{A:B} = \frac{1}{X_A/M_A + X_B/M_B} \approx M_A \left[ \frac{1 + k_{gb} x_B}{1 + (k_{gb} x_B)^2} \right]
\]  

(9)

The calculated mobility results using eq. (9) are given in Fig. 2(b), which show that boundary mobilities are markedly reduced by micro-alloying at a level of 0.01 at% if the solute segregation energy is larger than 40 kJ mol\(^{-1}\).

2.3 Role of interstitial-substitutional (I-S) bonding

The experimental results\(^5\) on the mobility of \( \alpha / \gamma \) interface in Fe–C–M system are given in Fig. 3. The relative extents of the reduction in the mobility of the iron boundary on addition of alloying elements Nb, Mo and Cr agree well with the expected effect of decreasing atomic diameter of these elements, which is a fundamental factor influencing boundary segregation.\(^6\)

The other factor that needs to be considered is the interaction between interstitial (I) and substitutional (S) atoms.\(^4\)

The bond energy of an I-S pair in Fe is estimated from the following relation\(^,8,9\)

\[
\Delta E_{I:S} = RT \cdot \ln (1 - W_{SI}/zRT),
\]  

(10)

where \( W_{SI} = (\partial \mu_I / \partial x_S)_{I,S \rightarrow 0} \) is the interaction parameter rep-
representing the effect of S on the chemical potential of I and Z the number of interstitial sites affected by the presence of an S atom. Figure 4 is a summary of the bond energies estimated from the data on Fe–C (or N)-M systems,10,11 which shows that the bond energy for Nb, Mo, Cr and Mn with C in Fe ranges from 5 to 25 kJ·mol⁻¹. However, it is still unclear as to how the I-S bonding energy could be taken into account in the model. Results of recent studies from Stockholm12,13 using the software DICTRA are encouraging in that they have been able to address some of these difficulties.

3. Particle Pinning—Simplified Analysis

3.1 Zener model

In an alloy with a microstructure containing finely dispersed particles, the matrix grain growth generally stops when it reaches a certain grain size. Zener14 proposed the following concise relation for the grain growth and pinning by particles based upon the balance of forces.

\[ \tilde{R}_p = \frac{4}{3} \frac{\tilde{r}}{f_N}, \]  

(11)

where \( \tilde{R}_p \) is the attainable radius of grains, and \( \tilde{r} \) and \( f_N \) are the mean radius and volume fraction of particles.

The pinning force is generated by each particle when the advancing boundary leaves it behind as shown in Fig. 5(b). The maximum value of the force per each particle is estimated as

\[ F_p \approx 2\pi \tilde{r} \sin \theta \cdot \sigma \cos \theta = \pi \tilde{r} \sigma \quad \text{(at } \theta = 45^\circ) \]  

(12)

Since the number of dispersed particles cut by a randomly selected plane is equal to the number of particles in a slice of \( 2\tilde{r} \) in thickness as shown in Fig. 5(c), Zener approximated the number of particles located on unit area of grain boundary as follows;

\[ n_{gb} = n_N \cdot 2\tilde{r} = \frac{3f_N}{2\pi \tilde{r}^2}, \]  

(13)

where \( n_N (= 3f_N/4\pi \tilde{r}^2) \) is the number of particles in a unit volume.

From eqs. (12) and (13), the total amount of pinning force per unit area is estimated as

\[ n_{gb} \cdot F_p = \frac{3f_N}{2\tilde{r}^2} \cdot \sigma \quad [\text{N·m}^{-2}] \]  

(14)

Zener’s relation (eq. (11)) is obtained by equating the excess pressure inside the grain, \( \Delta P = 2\sigma/R \quad [\text{N·m}^{-2}] \), to the pinning force (eq. (14)).

3.2 Number of pinning particles

There is, however, a considerable difference between the actual value of grain radius in a dispersion matrix and that predicted by Zener’s approximation. For instance, the actual matrix grain radius is about 30 μm when the dispersed particle size \( \tilde{r} = 0.1 \mu m \) and its volume fraction \( f_N = 10^{-3} \). The estimated \( \tilde{R}_p \) for the same particle size and fraction however, is 130 μm using Zener’s relation. Several modifications of the Zener model have been tried in various ways,15-18 to improve the agreement between prediction and experiment which have led to a unified general form of the Zener’s relation as follows;

\[ \tilde{R}_p = \beta \frac{\tilde{r}}{f_N^{1/3}}, \]  

(15)

where \( \beta \) is the pinning coefficient and \( m \) is the fraction index.

One of the modifications18 to the Zener’s model, described below, is concerned with the estimation of the number of effective pinning particles.

In the Zener’s model, the shape of the grain boundary is assumed to be independent of the presence of dispersed particles. However, moving boundaries in the dispersion structure are covered by domes and indents due to pinning as shown in Fig. 6(a). Therefore, one should approximate the number of pinning particles to those in a slice of \( \tilde{r} \) in thickness as shown Fig. 6(b), where \( \tilde{\rho} \) is the mean radius of the effective territory for each particle.

Since \( \tilde{\rho} \) is approximated to \( \tilde{r} / f_N^{1/3} \), the number of pinning
particles per unit area is estimated as

\[ n_{gb}' = n_V \cdot \frac{R_p}{f_V^{2/3}} \]

Zener's relation is modified as follows, assuming that the pinning force per particle is given by eq. (12).

\[ R_p' = \frac{8}{3} \frac{f}{f_V^{2/3}} \]

where \( R_p' \) is estimated as 27 \( \mu \)m for a particle diameter \( R = 0.1 \) \( \mu \)m and particle fraction \( f_V = 10^{-3} \) using the above modified relation, which is in better agreement with reality than that obtained using Zener's original approximation.

### 3.3 Inverse Pinning

Dispersed particles have been generally considered to be the inhibitors for boundary migration. However, it is supposed that, when anisotropic particles are present in the matrix and the interfacial energy of these particles in (say) grain I is smaller than that in the adjacent (say) grain II, as illustrated in Fig. 7, the grain boundary between grains I and II is induced to migrate by these particles.

A typical example of such a phenomenon is observed in steels when AlN precipitates are present. AlN is an anisotropic ionic compound with an hexagonal B4 structure that precipitates in steel in the form of platelets or fine needles along specific planes of the parent metallic crystals. Consequently, the selective growth of favorably oriented grains of type I due to inverse pinning\(^{19}\) occurs, if the grain of type I has the same orientation as the parent crystal of the group of AlN.

If one assumes the size of AlN particle to be 0.01 \( \mu \)m in thickness, the volume fraction to be \( 10^{-3} \) and the interfacial energy in grain of type I to be smaller than in grain of type II...
by 1 J-m⁻², the driving force induced by inverse pinning can be estimated as

\[ \Delta G_{\text{inv-p}} = \frac{2 \Delta \sigma_{\text{AIN}} f_{\text{AIN}} V}{\delta_{\text{AIN}}} \approx 1.4 \text{ [J \cdot mol}^{-1}] \]  

(18)

which is as large as the driving force required for grain growth in a matrix with grains of 10 μm radius.¹⁰

4. Role of Phase Diagrams in Micro-alloying

4.1 Calphad techniques and micro-alloying

Calphad (Calculation of phase diagram) programme which owes its origin to the pioneering efforts of Kaufman, Hillert and others in 1973, has made significant contributions to the way in which phase equilibria could be analyzed in multi-component systems.²²²⁶

The phase diagrams, particularly of importance to the investigation of the effects of micro-alloying have been clarified by the Calphad method, providing important information, such as the chemical composition and the solubility of the relevant dispersed phases. In addition, these phase diagrams have been useful in providing a basis for the understanding of the functions of micro-alloying as described below.

4.2 Compatibility of precipitates with matrix

Most of the dispersoids in micro-alloyed steels are carbides, oxides or nitrides. The carbides and nitrides are covalent compounds, and they are soluble in liquid metals in all proportions. Therefore, the phase diagrams of the binary metal-metal carbide or metal nitride M-MC (or MN) systems are generally of the eutectic type.

The phase diagrams of binary metal-metal oxide M-MO systems, on the other hand, are generally of the monotectic type with large liquid phase miscibility gaps, because the oxides are ionic and are hardly soluble in liquid metals. However, AlN and TiO are two of the few exceptions to the rule as shown in Fig. 8.

AIN is not covalent but ionic, and the Al–AIN system is of the monotectic type, showing an extensive immiscibility even in the liquid state. Accordingly, AlN is semi-compatible with Fe matrix, and plays an unique role in recrystallization and grain growth, producing oriented texture in Fe matrix as mentioned in the foregoing section.

TiO, on the contrary, is not ionic but metallic, with a wide range of solubility in the Ti–TiO system even in the solid state. In consequence, TiO is compatible with the Fe matrix, and acts as the nucleation catalyst in solidification, producing equi-axed fine grain structure.¹⁹

Some more results of the compatibility of ceramics with metals analyzed on the basis of phase diagrams will be published in the near future.²⁵

5. Conclusion

The author would like to close the lecture with the following two remarks: One is the quote “what is essential is invisible to the eye” by Saint-Exupéry.²⁶ We used to believe that every aspect of microstructures can ultimately be made visible and understood because of the wonderful strides made in the field of microscopy in the 20th century. In the field of micro-alloying, however, it has turned out that the most fundamental and essential understanding of the components of the microstructure and their sequence of formation has been largely due to the application of thermodynamic principles.

The other remark is to do with the serious caution on “the limit to growth” presented by the Club of Rome²⁷ 30 years ago, which has emphasized the urgent need for economization of world’s natural resources. It is the author’s belief that micro-alloying technology will go a long way towards meeting that caution in the 21st century.

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REFERENCES

20) After the presentation of the paper on inverse pinning, the author noticed that the unique action of AIN in steel had already been reported by Taguchi and Sakakura in 1966. They had termed this phenomenon “preferred orientation inhibition”, and exploited it in producing grain-oriented Si-steel with excellent magnetic permeability as shown in Table 1. Such a marvelous function of AIN in orienting grains resembles the act of a homing pigeon in the sense that both seek stabilization by going “home”, which is concomitant with reduction of energy in the former and settling mentality in the latter.

© Born in Sendai (1930). Graduated from Tohoku Univ. (‘52). Research associate at the Royal Inst. of Tech. in Stockholm (‘64–’66). Prof. in Dept. of Materials Sci., Tohoku Univ. (‘69–’93).

© Studied on microstructure control of steel. Computer calculation of phase diagrams.

© Received an honorary doctor from the Royal Inst. of Tech. (‘89). Gibbs Triangle Award from CALPHAD (‘94). Honda Memorial Award (‘98).