Thermodynamics of Microstructure Control by Particle Dispersion

Taiji NISHIZAWA

Formerly of the Department of Materials Science, Tohoku University and the Research & Development Center, Sumitomo Metal Industries. Now Mogasaki, Taihaku-ku, Sendai 982-0843 Japan.

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Even though microalloying was the most striking advance in the progress of steel technology in the later half of the 20th century, there are still uncertainties as to how each individual microalloying element functions in steel. In the present work, microstructure control by the fine dispersion of TiO and AlN particles has been analyzed from a thermodynamic viewpoint. TiO particles, which act as effective inoculants for the formation of an equiaxed fine grain structure during solidification are categorized as a metallic oxides from the Ti–TiO phase diagram. On the other hand, AlN particles which precipitate anisotropically in the Fe matrix and induce a texture or abnormal grain growth due to their inverse-pinning effect on specified boundaries, are characterized as ionic nitrides. Particle dispersion and the ultra-refinement of grain structure are examined from this viewpoint and a simple model for grain-boundary thickening in Fe alloys due to ultra-refinement is presented.

KEY WORDS: grain size; grain boundary; nucleation; microalloying; phase diagram.

1. Introduction

Thermodynamics of microstructure, the late 19th century brain-child of J. W. Gibbs, has grown up to occupy an important position as a master of microstructure control study in the 20th century. The construction of alloy phase diagrams and the formulation of the nucleation theory are among the notable achievements from his 1st stage outputs, and his work on pinning of grain-boundaries is one of the most outstanding pieces of scientific analysis from his 2nd stage developments as listed in Fig. 1.

The main subject of the present paper is the thermodynamic analysis of particle-dispersion in metallic structures on the basis of phase diagram, nucleation and boundary pinning phenomena. Before discussing this subject, some of the considerations from the same viewpoint will be given on the ultra-fine grained structure, which is the central theme of this conference.

2. Thermodynamics of Ultra-refinement of Grain Structure

2.1. Critical Grain Size

There is a critical size criterion which governs the nucleation phenomena in metallic structures. Similarly, it stands to reason to expect that there may be similar controlling factors that may impose limitations on the ultra-refinement of grains. The following rough analysis is one such attempt based on the assumptions that; (i) every grain is a polyhedron of size $d$ with 14 faces as illustrated in Fig. 2, (ii) the grain-boundary thickness $\delta$ and interfacial energy $\sigma$ are constant, and (iii) only the grain boundary energy is the significant energy contribution that needs to be taken into account neglecting the energies due to imperfections.

The volume and the surface area of the polyhedron are given by $V_{14}=0.5d^3$ and $A_{14}=3.35d^2$, respectively. The energy increase in the “grain phase” due to the boundary en-

Fig. 1. Ten topics in thermodynamics of microstructure.
energy is obtained using the Gibbs–Thomson equation as follows;

\[ \Delta G^a = \frac{2A_4}{3V_4} \sigma_b V = 4.47 \frac{\sigma_b V}{d} \] ...................(1)

where \( V \) is the molar volume of the “grain phase”.

The energy of the “boundary phase” denoted as \( \Delta G^{b/a} \) (= \( \sigma_b d \)), on the other hand, is unaffected by the grain refinement, because the total area \( A_{b,\infty} = V/\delta_b \) is kept constant. Therefore, the critical grain size in pure Fe can be estimated from the condition; \( \Delta G^a = \Delta G^{b/a} \), as follows;

\[ d_c = 4.47 \delta_b = 3.3 \text{ nm} \] ................................(2)

where the boundary thickness \( \delta_b \) is assumed to be 0.744 nm, which is 3 times the atomic diameter of Fe.

The volume fraction of the “boundary phase” is expressed by the next equation.

\[ f_b = \frac{A_4 \cdot \delta^2}{V_4 + A_4 \cdot \delta^2} = \frac{2.5}{V + 2.5} \] ...................(3)

The boundary fraction reaches a value of 0.43 at the critical grain size.

If the grain size becomes smaller than \( d_c \), then the “grain phase” becomes less stable than the “boundary phase”, and the transformation from the grain structure to the amorphous state occurs. It should be noted, however, that the grain refinement in pure Fe is actually counteracted by the grain growth phenomenon, which renders the refinement to the critical grain size unattainable in pure bulk Fe.

### 2.2. Thickening of Boundaries

It was assumed in the foregoing section that the boundary thickness would remain constant and not be allowed to increase, because the “boundary phase” was less stable than the “grain phase”. However, this restraint is relaxable in alloy systems where grain-boundary segregation is a possibility.

The segregation of solute atoms to the grain-boundary is readily understood by recourse to the parallel tangent law as illustrated in Fig. 3, where \( \Delta^o G_{Fe}^{b/a} \) and \( \Delta \mu_{Fe}^{b/a} \) are the boundary energies in pure Fe and Fe–X solution, respectively.

In the alloy system shown in Fig. 3(a), the solute X has complete solid solubility in Fe, and hence the segregation to the grain-boundary is not so pronounced. As a consequence, the limitation on grain refinement is not so different from that in the case of pure Fe.

In the alloy system shown in Fig. 3(b), the interaction between the solute atom X and Fe is repulsive in the “grain phase” and attractive in the “boundary phase”, thus forcing the solute atoms strongly to segregate to the boundaries, reducing the boundary energy rather steeply. Grain refining raises the energy of the “grain phase” as shown by the dotted line in Fig. 3(b), where the parallel tangents merge to constitute the common tangent. In this situation where \( d = d'_c \), the boundary energy \( \Delta \mu_{Fe}^{b/a} \) is equal to zero, and boundary thickening proceeds as shown in Fig. 4. It is also predicted that the amorphous phase may be possibly produced by continuing the grain refinement below \( d''_c \) because grain growth is not expected to occur when the boundary...
energy is equal to zero.

2.3. Ultra-fine Mixing

Recent results from mechanical alloying and rapid quenching studies have led to substantial revisions to our understanding of microstructures. For instance, it has been conclusively proved that Y$_2$O$_3$ can be dissolved in Fe to a certain degree by mechanical alloying, although such a possibility had been ruled out earlier.

According to the boundary thickening model presented above, it seems reasonable to expect that ceramic materials can be dissolved in the ultra-fine grained Fe to some extent. Details on the mixing possibilities in ceramics/metal systems will be presented elsewhere.

Figure 5 shows a summary of experimental results on ultra-fine mixing in metal/metal systems, in a plot with $Y$-axis as the interaction energy in the liquid state and the $X$-axis the Hume–Rothery’s size factor. The microstructures resultant on ultra-fine mixing are classified under the headings nanodispersion, solid solution and amorphous, depending upon the type of the phase diagram of each system.

3. Microstructure Control by Particle Dispersion

3.1. Inclusion Utilization Technology

In 1990, Takamura and Mizoguchi proposed a new concept for producing fine grained steel using Ti as a deoxidizer. Since then, many studies from various angles have been attempted to establish the mechanisms underlying the inclusion utilization technology (IUT). As a result of such work, it has become obvious that the principal process mechanism in IUT is mainly operative in the nucleation stage. However, as there are always difficulties in identifying the key factors in such nucleation problems, a trial attempt at providing a thermodynamic basis of IUT has been made as follows.

3.2. Classification of Dispersed Particles

The way the dispersed particles function in a metal matrix, depend mainly on their chemical compatibility with the Fe matrix. In the present work, this compatibility has been roughly estimated from the phase equilibria in the liquid Fe–M–X systems. The typical ones from among them are illustrated in Fig. 6.

Most of the carbides and nitrides are covalent crystals that are generally soluble in liquid metals in all proportions. On the other hand, the oxides and sulfides are mostly ionic, and hardly soluble in liquid metals, tending to form “slag” or “matte” above liquid metal as shown in Figs. 6(b) and 6(c). However, there are a few exceptions to this rule as typified by AlN and TiO in particular.

TiO is not ionic but metallic, and the Ti–TiO system has a wide range of solubility even in the solid state, as shown in Fig. 6(d). Therefore, it can be said that the Fe–TiO equilibrium in the liquid state is similar to a metallic system with a liquid phase miscibility gap. On the contrary, though it is a nitride AlN is an ionic crystal and the Al–AlN system is a monotectic type, showing extensive immiscibility in the liquid state similar to the Mn–MnS system.

The consequence of such a consideration based on phase diagrams is the classification of the dispersed particles in steel as falling into three groups; (i) the compatible, (ii) the semi-compatible and (iii) the incompatible with Fe, as listed in Fig. 7. More details on the correlation between chemical compatibility and phase diagram in Fe–MX system will be presented elsewhere.8)
3.3. Inoculation by TiO

3.3.1. Driving Force for Nucleation

The solubility of a metallic inclusion MX in liquid Fe is generally described by the next equation.

\[ z = C \exp(-Q/RT), \] ............................(4)

where \( z \) is the composition parameter in the Fe–MX system defined as \( z = 0 \) for Fe, and \( z = 1 \) for MX as shown in Fig. 8. \( Q \) is the free energy of solution which is evaluated by Eq. (5) using the parameter \( A \) in Eq. (6) for the solubility product of MX in Fe.*

\[ Q = \frac{R}{2} \ln 10 \] .............................(5)

\[ \log(\%M)/(\%X) = -A + B \] ........................(6)*

The driving force for the nucleation of MX per mole·atom is approximated as

\[ \Delta G_{MX} = RT \ln(z/z_0) = \frac{Q \Delta T_{MX}}{T} \] ..........................(7)

where \( \Delta T_{MX} \) is the degree of undercooling from the equilibrium temperature.

3.3.2. Spontaneous Nucleation

According to the nucleation theory, the critical radius for nucleation, the energy barrier and the number of nuclei are given by the following equations.

\[ r_c = \frac{2 \sigma V}{\Delta G_{MX}} = \frac{2 \sigma V T}{\Delta T_{MX} Q} \] ............................(8)

\[ \Delta g_c = (4/3) \pi \sigma R^3 = (6/3) \pi \sigma V T^2/\Delta T_{MX} Q^2 \] ...........................(9)

\[ n_c = n \exp(-\Delta g_c/k_B T) \] ...........................(10)

where \( \sigma \) is the interfacial energy between MX and liquid Fe, \( V \) is the volume of MX per mole·atom, and \( n \) is the number of embryos in the undercooled liquid Fe.

The total number of atoms in liquid Fe is about \( 10^{29} \text{ m}^{-3} \), and the number of embryos is taken as \( n = 10^{24} \text{ m}^{-3} \). Then, the energy barrier for the spontaneous nucleation of \( n = 10^{15} \text{ m}^{-3} \) of MX nuclei, 10 \( \mu \text{m} \) apart from each other, is roughly estimated to be \( \Delta g_c = 2.1 k_B T = 5.2 \times 10^{-19} \text{ J} \).

The undercooling and driving force necessary for crossing the energy barrier are calculated using Eqs. (7) and (9) as listed in Table 1, where the interfacial energies are chosen from the references.14–20) It can be readily inferred from the results that it would be impossible to finely disperse the Al2O3, MnO and MnS particles, because they would require an extremely large undercooling for spontaneous nucleation to take place. TiN has been known as a good catalyst for the crystallization of Fe.21,22) According to the results in Table 1, however, an undercooling of more than 70 K is needed for the spontaneous nucleation of TiN in liquid Fe.

TiO is the only promising candidate for spontaneous nucleation, because its solubility product in liquid Fe is smaller than TiN, though it melts at a comparatively low temperature as shown in Fig. 9. Moreover, the interfacial energy between liquid TiO and liquid Fe was estimated to be quite small, nearly 0.1 J · m\(^{-2}\). Thus, it can be speculated that the spontaneous nucleation of liquid TiO occurs due to the presence of the metastable miscibility gap illustrated by broken lines in Fig. 8. This gives rise to the formation of micro-emulsion23) of TiO droplets prior to the crystallization of Fe.

3.3.3. From Nuclei to Catalyst

It is also reasonable to expect that these TiO droplets

![Fig. 8. Phase diagram and Gibbs energy curves for the Fe–MX system with a liquid phase miscibility gap.](image)

![Fig. 9. Solubility product and melting temperature of the MX inclusion in steel.](image)

* In the case of Fe–MX system, Eqs. (5) and (6) are altered to

\[ Q = R[b/(a + b)] \ln 10 \] ..........................(5')

\[ \log(\%M)/(\%X) = -A' + B' \] ...........................(6')

Table 1. Undercooling and driving force necessary for spontaneous nucleation.

| MX      | \( \alpha \)/k mol\(^{-1} \) | \( \Delta T_{MX} \)/K | \( \Delta g_c \)/kJ mol\(^{-1} \) |
|---------|-------------------------------|------------------------|-------------------------------|
| Al2O3   | 247                           | 2.3                    | 1030                          |
| MnO     | 122                           | 1.4                    | 970                           |
| MnS     | 88                            | 0.6                    | 380                           |
| TiN     | 76                            | 0.2                    | 90                            |
| TiO     | 144                           | 0.1                    | 20                            |
| Ti2O3   | 157                           | 0.3                    | 70                            |
| CaO     | 88                            | 0.6                    | 380                           |
| CeS     | 144                           | 0.1                    | 20                            |
| ZrO     | 224                           | 0.3                    | 50                            |
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| MnS     | 88                            | 0.6                    | 380                           |
| TiN     | 76                            | 0.2                    | 90                            |
| TiO     | 144                           | 0.1                    | 20                            |
| Ti2O3   | 157                           | 0.3                    | 70                            |
| CaO     | 88                            | 0.6                    | 380                           |
| CeS     | 144                           | 0.1                    | 20                            |
would crystallize just after the nucleation event, because
the residual Gibbs energy estimated to be
\[ \Delta G_{\text{TiO}} = \Delta G_{\text{TiO}}^\text{f} - \Delta G_{\text{TiO}}^\text{l} \approx 5.4 \text{ kJ} \cdot \text{mol}^{-1} \], would be sufficient enough to trigger
spontaneous crystallization. Simultaneously, TiO would
grow to a certain size of TiX crystal by absorbing Ti and N
in the liquid Fe providing TiX crystallites as catalysts for
the solidification of Fe, producing an equiaxed fine-grained
structure, as illustrated in Fig. 10.

3.4. Inverse Pinning by AlN

It is well-known that abnormal grain growth often occurs
during austenitizing of Al-killed steels, even though the dis-
persion of AlN particles is almost uniform. In addition, it is
also recognized that the formation of (111) texture in low
carbon steel sheets strongly relates to the mode of AlN pre-
cipitation.\(^\text{24}\) The explanation for such phenomena are as yet
not available, and the following is an attempt to explain
them on the basis of arguments developed above.

Dispersed particles generally retard the migration of the
grain-boundaries by pinning.\(^\text{25,26}\) In the case of anisotrop-
ic particles, however, there is a fair chance for the occur-
rence of “inverse pinning”, as illustrated in Fig. 11(b). The
driving force arising from inverse pinning is approximated by
\[ \Delta G_{\text{inv-p}} = \left( f_p \lambda / \delta_p \right) \left( \sigma^{\text{dp}} - \sigma^{\text{ip}} \right) \] .................(11)
where \( f_p \) and \( \delta_p \) are the volume fraction and the thickness of
dispersed platelet particles, \( \lambda \) is the molar volume of steel,
and \( \sigma^{\text{dp}} \) and \( \sigma^{\text{ip}} \) are the interfacial energies of the platelets
in grains I and II, respectively.

Taking \( f_p = 10^{-3}, \quad \delta_p = 10^{-8} \text{ m}, \quad \lambda = 7 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1} \) and
\( (\sigma^{\text{dp}} - \sigma^{\text{ip}}) = 1 \text{ J} \cdot \text{m}^{-2} \), the driving force is calculated to be
\( \Delta G_{\text{inv-p}} = 1.4 \text{ J} \cdot \text{mol}^{-1} \), which is nearly the same as that for
grain growth in a matrix with grains of 10 \( \mu \text{m} \) in radius.

AlN has a hexagonal, B\(_4\) type of structure, and tends to
precipitate anisotropically on the (111) plane along [110]
axes of bcc Fe. During annealing after rolling (or austenitiz-
ing after normalizing), AlN platelets may assist the selec-
tive growth of their parent \( \alpha \) grain (or the \( \gamma \) phase grain
prior to the formation of the \( \alpha \) phase), promoting the for-
mation of a (111)[110] texture (or the abnormal grain
growth).

Figure 12 shows a computer simulation of the abnormal
grain growth in the presence of AlN particles, where the
particles \((f_p = 0.01)\) retard the growth of normal grains by
pinning, while they assist the growth of specified grains
(shaded) by inverse pinning. The fraction of the shaded
specified grains was also 10\%, the same as the others at
start, but the shaded grains grew abnormally and occupied
more than 60\% of the whole area after 2000 Monte Carlo
steps.\(^\text{27}\)

4. Conclusion

(1) Roles of TiO and AlN in the formation of mi-
crostructure in steel have been discussed on the basis of
thermodynamics. These compounds are unusual substances
in the sense that TiO is metallic while AlN is ionic contrary
to the general rule that the oxides are ionic and the nitrides
are covalent. Due to these special characteristics, TiO plays
a key role in the formation of equiaxed fine grain structure
in solidification, while AlN induces inequalities in the grain
structure, forming textures and abnormal grains during an-
nealing.

(2) The ultra-refinement of grain structure has been
studied according to a simple model of grain-boundaries. It
is predicted that in pure Fe, the degree of grain refinement
is limited by the counteraction due to grain growth. In Fe-
alloys, however, segregation of solute to the grain-bound-
aries, which reduces the boundary energy and retards the
grain growth, is predicted to assist ultra-refinement by pro-
moting the thickening of boundaries. This may also possi-
ably lead to the formation of the amorphous phase.

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