Effects of Soluble Ti and Zr Content and Austenite Grain Size on Microstructure of the Simulated Heat Affected Zone in Fe–C–Mn–Si Alloy

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The effect of soluble Ti and Zr contents on the microstructure in a simulated heat affected zone of a Fe-0.05mass%C-1.5mass%Mn-0.20mass%Si alloy was studied. This was done as a function of the austenite grain size as well as the number and size of TiN, Ti₂O₃, MgO(+Ti₂O₃), TiN(+MgO) and ZrO₂(+Ti₂O₃) particles under different peak temperature (1300 and 1400°C), peak holding time (0, 60 and 600 s) and a constant time of cooling (70 s) from 800 to 500°C. The effectiveness of inclusion phases for intragranular ferrite (IGF) formation was studied from the area fraction of IGF for a given austenite grain size and soluble Ti content. For a given austenite grain size, the primary ferrite decreases and the IGF increases with an increased soluble Ti content up to about 100 ppm. After going through a maximum the replacement of IGF by lath bainitic ferrite occurs with an increased soluble Ti content. It is found that the effect of soluble Zr content on the microstructure is much stronger than that of a soluble Ti content. The area fraction of IGF decreases gradually with an increase in the austenite grain size (50–1000 μm) for a given soluble Ti content (50–400 ppm). By using the hardenability parameter based on the non-equilibrium grain-boundary segregation model, it is observed that the IGF formation is encouraged in the following order: TiN>{Ti₂O₃, MgO(+Ti₂O₃)}>ZrO₂(+Ti₂O₃).

KEY WORDS: Ti, Mg and Zr deoxidation; heat affected zone; intragranular ferrite; hardenability; non-equilibrium grain-boundary segregation.

1. Introduction

Non-metallic inclusions inhibit austenite grain growth by pinning and also act as the preferential nucleation site for intragranular ferrite (IGF) such as intragranular polygonal ferrite or intragranular acicular ferrite. The IGF formation improves the toughness of the weld metal and the heat affected zone (HAZ) of a steel weld metal. Thewlis¹) studied the relationship between microstructure constituents and the austenite grain size. He found that at a fine austenite grain size primary ferrite is a predominant constituent, whereas at coarse austenite grain size ferrite sideplates tend to predominate. At an intermediate range of austenite grain size the optimum acicular ferrite content is obtained. In addition, the cooling rate and alloying elements also influence the IGF formation in addition to austenite grain size and inclusion characteristics and these variables are inter-dependent.

In order to produce fine oxide particles, deoxidant elements are added in excess amount instead of increasing the initial oxygen level²) due to high degree of the supersaturation of inclusion formation. Consequently, the residual soluble deoxidant elements segregate at austenite grain-boundaries. This significantly influences the allotriomorphic ferrite formation, through the changes in grain-boundary energy and degree of supercooling, and the precipitation of carbide and nitrides. It has been reported that with an increase in alloying elements such as Cr and Mo,³) the amount of primary ferrite decreases and that of acicular ferrite increases. This increase goes through a maximum and thereafter the acicular ferrite is progressively replaced by lath bainitic ferrite.

It has been reported that the length of grain-boundary ferrite and ferrite sideplates decreases with a decrease in austenite grain size to about 100 μm, whereby causing an increase in the Charpy impact energy.⁴,⁵) However, in order to obtain a fine microstructure consisting of a large amount of acicular ferrite, it is necessary to have an adequate austenite grain size and optimum inclusion density, as was found experimentally by Thewlis.¹) In the present study, the effect of the soluble Ti and Zr contents on microstructure in a simulated HAZ was studied as a function of austenite grain size and inclusion characteristics in a Fe-0.05mass%C-1.5mass%Mn-0.20mass%Si alloy. As cast samples containing deoxidation particles were heat-treated at different peak temperatures and peak holding times by using a simulated HAZ thermal cycle. In most of the experiments the effects of the soluble Ti content and the austenite grain size on the microstructure were studied as a function of...
the inclusion composition (TiN, Ti₂O₃, MgO(+Ti₂O₃), TiN(+MgO) and ZrO₂(+Ti₂O₃)). On the basis of these results, the effectiveness of the inclusion phases for IGF (such as intragranular polygonal ferrite) formation was studied by plotting the area fraction of IGF against a hardenability parameter. This, in turn, is defined as the product of the solute Ti concentration at grain-boundaries and the mean austenite grain diameter at a given simulated HAZ thermal cycle.

2. Experimental

2.1. Sample Preparation

An Fe-0.05mass%C-1.5mass%Mn-0.20mass%Si alloy (200 g) was melted at 1600°C in an alumina crucible using an induction furnace (100 kHz) under a dehydrated Ar atmosphere (% and ppm represent mass% and mass ppm, respectively, hereinafter). After holding for 30 min at 1600°C for homogenization of initial metal composition, the initial oxygen in the melt was about 80–100 ppm. Then, an alloy was deoxidized by the addition of an appropriate amount of various deoxidants. In the blank experiments with Al₂O₃+Ti₂O₃ particles (BL-1~BL-4), the initial melt was deoxidized with an Fe-10%Al alloy, followed by the addition of an Fe-10%Ti alloy. In the experiments with pure Ti₂O₃ (TI-1~TI-5), ZrO₂ (ZR-1~ZR-3) and MgO (MG-1 and MG-2) particles, the initial melt was deoxidized with an Fe-10%Ti, Fe-10%Zr or Ni-15%Mg alloy, respectively. In the experiments with complex MgO(+Ti₂O₃) particles (TM-1~TM-9) and ZrO₂(+Ti₂O₃) particles (TZ-1~TZ-5), the melt was deoxidized with an Fe-10%Ti alloy, followed by an addition of Ni-15%Mg or Fe-10%Zr alloy, respectively. In the experiments with TiN particles (TN-1~TN-5) and complex TiN(+MgO) particles (TNM-1~TNM-4), an Fe-C-Mn-Si alloy was melted and held for one hour under a 0.1 atm partial pressure of N₂. Thereafter, it was deoxidized by an Fe-10%Ti alloy. In the TiN experiments, a melt was kept for 30 min to remove Ti₂O₃ particles, followed by cooling to 1200°C. In the TiN/Mg experiments, after holding for 30 min at 1600°C to remove Ti₂O₃ particles, a Ni-15%Mg alloy was added.

Finally, the melt in all experiments was cooled to 1200°C at 50°C/min, followed by quenching in water.

2.2. Simulated HAZ Thermal Cycle

Specimens (15–25×20–30×2–3 mm) for a simulated HAZ thermal cycle test were prepared from a vertical central slice of an as-cast ingot. This test denotes WHT (Welding Heat Treatment), hereinafter. Each specimen was heated to the peak temperature of 1300 or 1400°C at 10°C/s heating rate in an induction furnace under a surplus Ar atmosphere. Thereafter, it was held for 0 s (1300°C), 60 s (1400°C) or 600 s (1400°C). Each specimen was cooled from respective peak temperatures to about 1000°C at 7–10°C/s. The time of cooling from 800 to 500°C, Δt₈₅, was fixed as 70 s (4.3°C/s on average).

2.3. Observation of Particles and Austenite Grains

The planar size distribution of particles on a polished cross section of each sample was observed by using a SEM at a 1000 times magnification. Total observed area of one sample was 0.25–1.00 mm². The particles greater than 0.3 μm were measured. More specifically, the cross sectional area of each particle was measured by a semi-automatic image analyzer. The diameter of each particle section, dₐ, was estimated as the equivalent diameter of a circle with the same area as a sectioned inclusion particle. Total volume fraction of particles, fᵥ, was estimated from the content of insoluble elements obtained from the chemical analysis. The composition of particles on the polished metal surface was analyzed by using SEM with EPMA.

A polished cross-section of the vertical slice from the centre of the ingot was etched with a 3% nital (3v/v% HNO₃ - amylalcohol) or with a hot 10% picric acid (10w/v% picric acid – H₂O, 50–70°C) solution. A revealed grain structure and microstructure were observed by using an optical microscope at magnification of 25 to 1000 times. The area of each grain section was measured by using a semi-automatic image analyzer. The grain diameter, D, was estimated as the equivalent diameter of a circle with the same area as a sectioned grain. Total observation area for one specimen was 180 to 280 mm². In addition, the austenite grain size was measured by the thermal etching technique. The measured grain size distributions obtained by the chemical etching and thermal etching methods agreed well with each other.

2.4. Chemical Analysis

The concentrations of soluble and insoluble M (M=Ti, Zr and Mg) elements in metals were analyzed after potential-static electrolytic extraction of metal specimens. The used electrolyte solution was 2%TEA (1w/v% tetramethylammonium chloride – 2v/v% triethanolamine – methanol). After extraction, the solution with inclusions was filtered using a PTFE membrane film filter with an open-pore size of 0.1 μm. The dissolved amount of each metal specimen was about 0.4 g. The solute concentration in solution corresponds to the content of soluble element in metal. The residue on a membrane filter corresponds to the insoluble element in metal as inclusions. Both the soluble and insoluble element contents were analyzed by using inductively coupled plasma-emission spectrometry (ICP-AES). In addition, the total oxygen and nitrogen contents in metal were analyzed by inert gas fusion-infrared absorptiometry.

3. Results and Discussion

3.1. Effects of Austenite Grain Size, Soluble Ti and Zr and Inclusion Composition on the Microstructure

3.1.1. Austenite Grain Size

The chemical compositions of the metal sample (contents of total O and N, and soluble and insoluble Ti and M (M=Mg and Zr) element) and the inclusion characteristics (such as number of particles per unit area, Nₐ, and mean size of particles, dₐ , on a cross section of metal sample and volume fraction of particles, fᵥ , calculated from chemical analysis) are given in Table 1. It should be noted that the initial oxygen content (80–100 ppm) is lower in comparison with the equilibrium oxygen content in the melt of Fe-0.05mass%C-1.5mass%Mn-0.20mass%Si alloy. It was assumed that the concentrations of C, Mn and Si are changed insignificantly in all experiments. Therefore, the contents of these elements were not analysed in obtained metal samples. The mean grain size, Dₐ(WHT), was determined after WHT in which an as-cast metal specimens were
heat-treated at 1 300 °C (0 s), 1 400 °C (60 s) and 1 400 °C (600 s).

The austenite grain size measured by thermal etching technique is represented by a parenthesis. Other values in Table 1 were determined after chemical etching by using a 3%-nital solution.

The inclusion composition and the dispersion of particles observed in the present deoxidation experiments are summarized as follows: In the BL-1~BL-4 samples (denoted as Blank-experiments), the inclusions consist of large Al2O3+Ti2O3 complex oxides, but their number is very small. In the TI-1~TI-5 samples (denoted as Ti-experiments), the Ti2O3 particles are present as primary deoxidation product in addition to the precipitated secondary Ti2O3 particles which are located at interdendritic region. In this study Ti-oxide is considered as Ti2O3. The MnO content in Ti2O3 particles is small. In the TN-1~TN-5 samples (denoted as TiN-experiments), most of the TiN particles are present at the interdendritic region6) and the total oxygen content almost corresponds to the dissolved O content, except for TN-1 (174 ppm) and TN-3 (119 ppm) samples. In the samples of MG-1 and MG-2 (denoted as Mg-experiments), the MgO particles are dispersed uniformly and the total O content almost corresponds to the oxygen as MgO particles. In the TM-1~TM-9 samples (denoted as Ti/Mg-experiments), only pure uniformly dispersed MgO particles are observed. However, it is considered that fine Ti2O3 and/or MgO(+Ti2O3) particles seem to be present, judging from the values of insoluble Ti content given in Table 1. Also, titanium nitrides are precipitated on uniformly dispersed MgO particles. In the TNM-1~TNM-4 samples (denoted as TiN/Mg-experiments), no Ti2O3 particles are observed. Most of inclusions in the TiN-experiments are titanium nitrides, except for TN-1 and TN-3 samples. This is because a melt was held for 30 min after Ti addition at 1 600 °C to remove Ti2O3 particles by flotation. However, some amount of small size Ti oxides is formed during solidification of melt in these experiments. Most of these oxide inclusions are covered by heterogeneously precipitated titanium nitrides. Therefore, in this study, the Ti particles in the TN1~TN5 and TNM-1~TNM-4 samples are considered to be TiN.

### Table 1. Chemical compositions of metal samples, characteristics of particles and austenite grain size.

| Experiment | Sample | [T.O] ppm | [T.N] ppm | [sol. Ti] ppm | [insol. Ti] ppm | [sol. M] ppm | [insol. M] ppm | N_A mm⁻² | f_c x10⁻⁴ | S_(WHT), μm |
|------------|--------|-----------|-----------|--------------|---------------|-------------|--------------|---------|-----------|-------------|
| Blank      | BL-1   | 7         | –         | –            | –             | –           | –            | nm      | nm        | (150)       |
|            | BL-2   | 27        | 70        | 59           | –             | –           | nm          | nm      | nm        | (600)       |
|            | BL-3   | 33        | 268       | 3            | –             | nm          | –           | nm      | nm        | (1 520)     |
|            | BL-4   | 8         | 471       | 30           | –             | nm          | –           | nm      | nm        | (1 200)     |
| Ti         | TI-1   | 66        | 17        | 31           | –             | 2 087       | 0.82        | 0.79    | 617       | 626         |
|            | TI-2   | 16        | 187       | 97           | –             | 297         | 0.45        | 0.25    | nm        | (360)       |
|            | TI-3   | 9         | 191       | 9            | –             | 165         | 1.47        | 0.22    | nm        | nm          |
|            | TI-4   | 8         | 240       | 4            | –             | 237         | 0.99        | 0.1     | nm        | (850)       |
|            | TI-5   | 8         | 1 085     | 38           | –             | 62          | 1.2         | 0.97    | 264       | 391         |
| TiN        | TN-1   | 174       | 111       | 54           | 32            | 223         | 1.59        | 0.6     | (25)      | (1 500)     |
|            | TN-2   | 23        | 130       | 71           | 3             | 298         | 1.51        | 0.6     | (65)      | (250)       |
|            | TN-3   | 119       | 126       | 873          | 358           | 159         | 2.02        | 6.68    | 145       | 146         |
|            | TN-4   | 12        | 122       | 869          | 379           | 117         | 2.35        | 7.07    | 182       | 363         |
|            | TN-5   | 9         | 130       | 766          | 402           | 130         | 2.39        | 7.5     | 150       | nm          |
| Mg         | MG-1   | 57        | –         | –            | 10            | 51          | 298         | 1.65    | 1.8       | 360         |
|            | MG-2   | 50        | –         | –            | 33            | 73          | 577         | 0.31    | 2.59      | 514         |
| Ti/Mg      | TM-1   | 77        | 19        | 7            | 2             | 118         | 370         | 1.73    | 4.18      | 420         |
|            | TM-2   | 74        | 54        | 35           | 0.4           | 166         | nm          | nm      | 0.59      | (50)        |
|            | TM-3   | 81        | 58        | 17           | 1             | 48          | nm          | nm      | 0.17      | (150)       |
|            | TM-4   | 64        | 94        | 28           | ns            | 683         | nm          | nm      | 2.42      | (50)        |
|            | TM-5   | 63        | 99        | 26           | ns            | 62          | nm          | nm      | 2.18      | (50)        |
|            | TM-6   | 106       | 105       | 53           | 3             | 94          | 494         | 1.06    | 3.33      | (50)        |
|            | TM-7   | 45        | 148       | 4            | 4             | 88          | 565         | 1.12    | 3.12      | (50)        |
|            | TM-8   | 37        | 386       | 29           | 6             | 81          | 640         | 1.04    | 2.86      | (50)        |
|            | TM-9   | 50        | 147       | 48           | 0.1           | 115         | 1263        | 1.44    | 4.08      | 100         |
| TiN/Mg     | TNM-1  | 62        | 149       | 50           | 17            | 103         | 625         | 1.21    | 3.96      | (50)        |
|            | TNM-2  | 63        | 149       | 60           | 33            | 103         | 699         | 1.27    | 4.27      | (25)        |
|            | TNM-3  | 45        | 119       | 874          | 329           | 67          | 298         | 1.63    | 8.53      | 138         |
|            | TNM-4  | 53        | 112       | 884          | 318           | 1           | 68          | 286     | 1.73      | 8.35        |
| Zr         | ZR-1   | 148       | –         | –            | 28            | 242         | 1 115       | 0.29    | nm        | 327         |
|            | ZR-2   | 68        | –         | –            | 7             | 215         | nm          | nm      | nm        | 330         |
|            | ZR-3   | 77        | –         | –            | 4             | 55          | 623         | 0.17    | nm        | 186         |
| Ti/Zr      | TZ-1   | 33        | 1 164     | 50           | 6             | 25          | nm          | nm      | nm        | 329         |
|            | TZ-2   | 88        | 85        | 38           | 6             | 123         | nm          | nm      | nm        | 302         |
|            | TZ-3   | 38        | 271       | 6            | 31            | 348         | nm          | nm      | nm        | 168         |
|            | TZ-4   | 46        | 182       | 34           | 42            | 126         | nm          | nm      | nm        | 225         |
|            | TZ-5   | 128       | 144       | 4            | 70            | 453         | nm          | nm      | nm        | nm          |

nm: not measured, ns: negligibly small, ( ) : thermal etching.
the ZR-1~ZR-3 and TZ-1~TZ-5 samples (denoted as Zr- and Ti/Zr-experiments, respectively), the ZrO₂ and ZrO₂+TiO₂ particles are uniformly dispersed.

Three main types of microstructure, which were observed in different samples after WHT test, are shown in Fig. 1. The microstructure of Type A consists of grain boundary ferrite (GBF), ferrite sideplate (FSP) and small amount of intragranular polygonal ferrite (IPF). The microstructures of Types B and C consists mostly of IPF and lath bainitic ferrite \( \text{Bu}(\alpha_{B}) \), respectively. The effect of the austenite grain size on the microstructure after a WHT test has been studied for the samples obtained in the Ti/Mg deoxidation experiments (TM-2, TM-4 and TM-8). The microstructures are plotted against the mean austenite grain size for soluble Ti contents of 54, 94 and 386 ppm in the top, middle and bottom diagrams of Fig. 2, respectively. It is seen that the area fraction of intragranular polygonal ferrite (IPF) decreases gradually with an increased austenite grain size in all experiments. This is valid for a given oxide inclusion (MgO+TiO₂), a soluble Ti content and \( \Delta t_{8/5} \). Furthermore, the area fraction of IPF at a given austenite grain size is significantly higher at a soluble Ti content of 94 ppm in comparison to contents of 54 and 386 ppm. Therefore, in order to have a high area fraction of IPF, the control of a soluble Ti content in a certain range is more important than that of the austenite grain size (50–800 \( \mu \)m). However, the effect of soluble Ti content on %IPF decrease significantly in the range of \( D_{(WHT)}>800 \mu \text{m} \). The effect of soluble Ti and Zr contents on the micro-structural change and other micro-phases are explained in Section 3.1.2.

A similar trend to the result in Fig. 2 was observed by Thewlis\(^\text{1)}\) who studied the effect of austenite grain size (20–200 \( \mu \)m) on microstructure in B–Ti weld metals with low (6 ppm) and high (15 ppm) contents of boron. In the case of a low B–Ti content, the fraction of acicular ferrite (AF) increases, reaches a maximum and thereafter decreases with an increasing austenite grain size. The area fraction of AF for a given grain size at high B–Ti contents is much larger than that at low B–Ti contents. It also has been reported\(^\text{15)}\) that the area fraction of grain boundary ferrite (GBF) decreases while the intragranular ferrite (IGF) increases with an increased austenite grain size in the range below 100–150 \( \mu \text{m} \). This is due to that the surface area of grain per unit volume, \( A_{GB} \), decreases drastically in this range.\(^\text{1,9,10)}\)

The effect of austenite grain size on the area fraction of IGF (as %IPF) in the Ti, Ti/Mg, Zr and Ti/Zr deoxidation experiments has also been studied. The results of Ti and Ti/Mg deoxidations are shown in Fig. 3. It was found that the IGF formation becomes less favorable with an increased austenite grain size for given soluble Ti content, oxide composition and \( \Delta t_{8/5} \) value. A similar tendency was obtained for Zr and Ti/Zr deoxidation experiments. These results are not consistent with those in previous study,\(^\text{7,8)}\) in which the IGF area fraction was found to increase with an increased grain size.

The effect of the austenite grain size on the microstructure

![Fig. 1. Three types of microstructure A, B and C in Fe-0.05%C-1.5%Mn-0.2%Si alloy after WHT test. A: GBF, FSP and IPF (intragranular polygonal ferrite), B: IPF, C: Bu(\alpha_{B}) (lath bainitic ferrite).](image)

![Fig. 2. Effect of austenite grain size on microstructure as a function of soluble Ti content in Ti/Mg deoxidation experiments (TM-2, 4 and 8).](image)

![Fig. 3. Effects of austenite grain size on area fraction of intragranular ferrite in Ti (TI-1, 2, 3 and 5) and Ti/Mg (TM-1, 3, 5 and 6) deoxidation experiments.](image)
should be considered as a function of soluble elements, which segregate at grain-boundaries. The degree of segregation which corresponds to the concentration of these elements on grain boundaries increases with an increased grain sizes due to the decreasing $A_{GB}$ value. Therefore, the lath bainitic ferrite {$Bu(α_B°)$} formation becomes favorable with an increasing grain size and soluble Ti content (>90 ppm), as shown in Fig. 2. For this reason, the austenite grain size should be lowered to an optimum size in order to have IGF formation. This also depends on the solute content and the nucleation potency of oxide phases, which is defined as an ability of inclusions as IGF nucleation sites for a given $Δt^{8/5}$.

In this study, it is not certain whether solute Ti segregates to the oxide/matrix interface surface and retard the nucleation of IGF formation.

### 3.1.2. Soluble Ti and Zr Contents

An as-cast specimen containing inclusion particles was heated to 1 300°C (0 s), 1 400°C (60 s) or 1 400°C (600 s) and then cooled with fixed $Δt^{8/5}$=70 s. The effect of the soluble Ti and Zr contents on the microstructure was studied as a function of the austenite grain size. The area fractions of IGF are plotted against the soluble Ti content at three thermal cycles in Fig. 4. For the present experimental conditions, no TiC particles were observed in an as-cast sample. Therefore, it is considered that the $[Ti]_{sol.}$ in as-cast sample corresponds to that present just above 800°C during a thermal cycle. The $B_{(WHT)}$ values at different thermal cycles are given in Table 1.

It can be seen from Fig. 4 that the area fraction of IGF has a maximum value at certain soluble Ti content. In the case of a small austenite grain size (50–150 μm) in the top diagram, a high area fraction of IGF is obtained in a wide range of soluble Ti content (50–270 ppm). In addition, it is almost independent of particle composition. However, as shown in the middle ($B_{(WHT)}=250–750$ μm) and bottom ($B_{(WHT)}=550–1 150$ μm) diagrams, a high %IGF is observed only in a limited range of soluble Ti contents. Moreover, it is obtained at 1 400°C for 600 s only in the Ti/Mg experiments with MgO or MgO(+TiO$_2$) particles.

It should be pointed out that the TiN particles in TN-1~TN-5 and TNM-1~TNM-4 samples, which correspond to the open triangles in Fig. 4, are observed before a WHT test. These TiN particles were dissolved and re-precipitated during thermal cycle depending on the peak temperature (particularly at 1 400°C) and holding time. Therefore, in this study it is assumed that the soluble Ti content analyzed before a WHT test corresponds to that obtained during cooling from 1 400 to 800°C.

The effect of the soluble Ti content on the microstructure in the presence of only pure MgO particles in TM-1~TM-9 samples is studied as a function of the austenite grain size. The results are shown in Fig. 5. It can be seen that the maximum area fraction of IGF (as IPF) is obtained at $[Ti]_{sol.}$ about 100 ppm for all studied grain sizes. However, the region representing a high area fraction of IGF becomes narrower with an increased austenite grain size.

In the range of soluble Ti content up to 100 ppm, the area fraction of IPF increases. Furthermore, the percentage of primary ferrite such as grain-boundary ferrite (GBF) and primary ferrite sideplates {FSP(pri)} growing from prior austenite grain-boundaries decreases slightly and the secondary ferrite sideplates {FSP(sec)} decreases significantly. Subsequently, with an increased soluble Ti content above 100 ppm, the area fraction of lath bainitic ferrite {$Bu(α_B°)$} increases drastically. Furthermore, the percentage of GBF and FSP(pri) tend to increase for 1 300°C/0s and 1 400°C/60s and to decrease for 1 400°C/600s.

These changes of the microstructure with a soluble Ti

![Fig. 4. Effect of soluble Ti content on area fraction of intragranular ferrite at different simulated HAZ thermal cycles.](image)

![Fig. 5. Effect of soluble Ti content on microstructure as a function of austenite grain size in Ti/Mg deoxidation experiments.](image)
content are consistent with those observed in Cr and Mo-containing weld metals. In this case, the microstructure is classified by primary ferrite, ferrite with second phase (Widmanstatten ferrite and bainite) and acicular ferrite.\(^ {13}\)

Soluble Ti segregated on grain-boundaries retards the formation of allotriomorphic ferrite, which increases hardenability. As a result, the lath bainite is formed at the austenite grain-boundaries. This lath bainitic ferrite formation for a given high soluble Ti content becomes favorable with an increased grain size. This is due to that the degree of grain-boundary segregation increases with a decreased value of the grain-boundary area per unit volume. However, it is pointed out that the degree of grain-boundary segregation depends on time-depending kinetic factors (such as solute micro-segregation during solidification, solute dragging during the austenite grain growth during HAZ thermal cycle and non-equilibrium grain-boundary segregation).\(^ {11,12}\) This is discussed more in detail in Section 3.2.

The effect of the soluble Zr content on the microstructure has been studied in twelve Zr deoxidation experiments. The data for three samples (ZR-1~Zr-3) are given in Table 1. The microstructures were observed after a HAZ thermal cycle (1400°C for 60 s) and the results are shown in the upper diagram of Fig. 6. The soluble Zr content was analyzed in an as-cast sample. In addition, the insoluble Zr contents as ZrC was estimated from the difference between the total insoluble Zr content and the insoluble Zr content as ZrO\(_2\). The value of [Zr]\(_{\text{insol}}\) as ZrO\(_2\) can be calculated from the total oxygen content and the dissolved oxygen content determined from the Zr/ZrO\(_2\) equilibrium. The values of the total insoluble Zr content obtained by chemical analysis are given in parenthesis in Fig. 6 and in Table 1. However, in the present study, it is assumed that the insoluble Zr content as ZrC observed in an as-cast sample dissolves during a HAZ thermal cycle (1400°C for 60 s). Thereafter, ZrC is precipitated during cooling from 1400 to 800°C in the same amount of ZrC obtained in an as-cast sample.

The percentage of intragranular polygonal ferrite and primary ferrite \{GBF+FSP\(_{\text{pri}}\}\) decrease, whereas the area fraction of the lath bainitic ferrite \{Bu\(_{\alpha^\theta}\)\} increases with an increased soluble Zr content. It is considered that the effect of the soluble Zr content on the IPF formation is stronger than that of the soluble Ti content. This is based on the comparison of the middle diagram in Fig. 5 with the upper diagram in Fig. 6. These results suggest that the soluble Zr content more strongly leads to a suppression of the grain-boundary reaction in comparison to the soluble Ti content. Thus, Zr leads to a coarser bainitic ferrite structure. Moreover, it should be noted that the IPF nuclei are MgO particles in the middle diagram of Fig. 5, but they are ZrO\(_2\) particles in the upper diagram of Fig. 6, which are not effective to the IPF nucleation.

In the lower diagram of Fig. 6, the effects of the soluble Ti and Zr contents on the microstructure are shown in the fourteen experiments obtained by Ti/Zr complex deoxidation. Only the data for five experiments (TZ-1~TZ-5 samples) are given in Table 1. The soluble Zr content is 1 to 70 ppm and soluble Ti content is 13 to 271 ppm (except TZ-1 sample). The results in the lower diagram of Fig. 6 for samples with ZrO\(_2\)+Ti\(_2\)O\(_3\) particles are nearly the same as those in the middle diagram of Fig. 5 for Ti/Mg experiments with MgO particles.

The effectiveness of the inclusion phases is influenced by the solute Ti content at grain-boundaries for a given austenite grain size and cooling rate. This is discussed in the following section.

### 3.2. Effects of Non-Equilibrium Grain-Boundary Segregation on Microstructure

The boron segregation on grain-boundaries was firstly discussed by Williams et al.\(^ {13}\) in terms of a non-equilibrium segregation model. Later, Akselsen et al.\(^ {14}\) applied this model to estimate the boron segregation on grain-boundaries and showed the importance of hardenability parameter in explaining the HAZ toughness. In this study the hardenability is considered based on a non-equilibrium solute segregation at grain-boundaries. Only a limited amount of attention has been paid to understand how the hardenability influences the IGF formation. However, the balance of ferrite nucleation between austenite grain-boundaries and the intragranular regions has been discussed.\(^ {19}\) In this section the limit of the hardenability parameter proposed by Akselsen et al.\(^ {14}\) is discussed and a new method for estimation of hardenability parameter is proposed.

When a material at a given solution temperature is rapidly cooled to a lower temperature, a loss of vacancies along grain-boundaries occurs. Thereby, the equilibrium concentration corresponding to the lower temperature is obtained. The decrease in vacancy concentration leads to the dissociation of the vacancy-impurity complexes into vacancies and solute atoms.

The concentration of the complexes, \([C]\), is given by

\[
[C] = k_c \frac{k_Y [I]}{[E_b - E_i]/(kT)} \tag{1}
\]

where \([I]\) is the total concentration of impurity in the metal, \(E_b\) is the vacancy-impurity binding energy (\(0.5\) eV for boron), \(E_i\) is the vacancy-formation energy (\(1.4\) eV), \(k_c\) is a geometric constant for complex formation (\(12\) for boron).
$k_B$ is a geometric constant for vacancy formation (=4), $k$ is the Boltzmann’s constant (=8.617x$10^{-5}$ eV/K) and $T$ is an absolute temperature in Kelvin degree.

The amount of boron (11 and 26 ppm by weight) which segregated to the austenite grain-boundaries, $[B]_{gb}$, within the temperature range from the peak temperature, $T_b$, to the start temperature of austenite to ferrite transformation, $T_s$, on cooling is approximately given by Akselsen et al.\(^\text{16}\) for $T_b >> T_s$ as

$$[B]_{gb}(\text{ppm}) = [B]_{VT} - [B]_{VT} = 48[B] \exp\left[\left(\frac{E_b - E_i}{kT_b}\right)\right] \quad \quad \quad \quad \quad \quad (2)$$

where $[B]_{VT}$ and $[B]_{VT}$ are the concentrations of boron-vacancy complexes estimated from Eq. (1) at $T_b$ and $T_s$, respectively.

Since the grain-boundary surface area per unit volume, $S_b$, is inversely proportional to the austenite grain diameter, $D$, Akselsen et al.\(^\text{14}\) defined the hardenability parameter as the product of $D[B]_{gb}$, which is taken as a measure of the grain-boundary boron concentration. However, they point out that this hardenability parameter does not express the real concentrations of boron at grain-boundaries. In addition, a conversion to appropriate units (e.g. atoms per $\mu m^3$) requires further assumptions regarding the thickness of the grain-boundaries.

Equation (2) is derived under the following assumptions:
The boron-vacancy complex diffusion to the grain-boundaries occurs sufficiently rapid to keep pace with the falling temperature. More specifically, the equilibrium concentration $[B]_V$ is maintained from the peak temperature, $T_b$, down to the start temperature of the austenite to ferrite transformation, $T_s$. A second assumption is that the solute impurity concentration, $[I]$, in Eq. (1) is equal to the total boron concentration, $[B]$, in Eq. (2). Furthermore, it is assumed that $[B]_{VT}=0$. It should be noted that the total boron concentration in $[B]_V$ if there is one impurity atom per complex. Therefore, this assumption implies that the complex concentration, $[C]$, is negligibly small.

By using a similar equation as Eq. (2), $[M]_{gb}/[T.M]$ ratios ($[M]_{gb}$ and $[T.M]$ are the concentration of $M$ element on grain-boundaries and the total $M$ concentration, respectively) for $M$=B, Ti and Zr can be estimated: The vacancy-impurity binding energy for Ti ($=0.65$ eV) and Zr (=$1.0$ eV) estimated by Faulkner et al.\(^\text{15}\) are used. Furthermore, the $k_c$ values for Ti and Zr are assumed to be the same as for B (=12). It was found that the $[M]_{gb}/[T.M]$ ratios for $M$=B, Ti and Zr are 0.093, 0.264 and 2.994, respectively. This indicates that this ratio increases with an increased vacancy-impurity binding energy. This finding is inconsistent to the fact that the concentration of non-equilibrium grain-boundary segregation decreases with an increased $E_b$ value.

The relationship between the concentration of $M$ within the grain, $c_M$, that at grain-boundaries, $c_b$, and total concentration of $M$, $[T.M]$, is derived as a function of the width of grain-boundaries, $L$, and austenite grain size as follows:

$$c_M/[T.M] = \frac{[1 + 3(l/D)]}{[1 + 3(l/D)]} L_{gb} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \cd
1600 to 1400°C at 50°C/min and then quenched. The measured mean austenite grain diameter is 64 μm. The total Ti content is 0.326 mass%. It was found that the mean \( c_b \) value for Ti is 3.48 mass% and the mean \( L_{gb} \) value is about 28. In this case, the width of grain-boundaries, \( l \), calculated from Eq. (4) is 1.4 μm on average. The \( L_{gb} \) value for Ti agrees satisfactorily well with that estimated from Eq. (5) at 1400°C.

According to the indirect measurement using the microhardness technique, the width of non-equilibrium grain-boundaries was estimated as a few 10 μm to about 100 μm from the hardness-distance profile of a given boundary in sulfur-segregated iron\(^{17}\) and Ni.\(^{18}\) The width of the solute-enriched zone was measured by an autoradiographic technique and a scanning transmission electron microscope equipped with microanalysis facilities. Furthermore, this also estimated from the model of the diffusion rate equation. The measured and estimated width for boron in austenite also estimated from the model of the diffusion rate equation. The non-equilibrium segregation is a process driven by kinetics and which appears during cooling within the high temperature region. The resulting width of segregated layer against the austenite grain diameter as a function of \([T.M]\) is according to Faulkner\(^{16}\) in the range of 0.5 to 4 μm under a given condition. It can be seen that the value of \( l=1.4 \) μm obtained from LA-ICP-MS measurements is in this range.

By using Eq. (4), the \( c_b \) values in atomic ppm are plotted against the austenite grain diameter as a function of \([T.M]\) at the width of segregated layer \( l=1 \) and 10 μm in Fig. 8. As shown in the upper diagram, which corresponds to Ti deoxidation \( (L_{gb}=10) \), it is seen that the \( c_b \) values at \([T.M]=50–200\) atomic ppm increases slowly at \( l=1 \) μm with an increased grain size from 200 to 1000 μm. On the other hand, the \( c_b \) values at \( l=10 \) μm increase continuously with an increasing grain size. These calculated results from Eq. (4) suggest that the \( c_b \) values for a given grain size increase with an increasing \([T.M]\) and a decreasing \( l \). However, the degree of increase in \( c_b \), with respect to grain size in the range above 200 μm, is significantly higher at \( l=10 \) μm compared to that at \( l=1 \) μm. The lower diagram shows the result of \( L_{gb} \), which corresponds to boron.

3.3. Hardenability Parameter and Microstructure

In this section the characteristics of Eqs. (2), (4) and (5) are studied by plotting the area fraction of IGF against the respective hardenability parameters for different heat treatments. Furthermore, the effectiveness of TiO\(_2\), MgO (MgO+TiO\(_2\)), TiN (TiN+MgO) and ZrO\(_2\)+TiO\(_2\) particles for IGF formation is studied by using Eq. (4) at \( l=1 \) and 10 μm.

In Fig. 9 the area fractions of IGF in TI1~TI5 samples are plotted against hardenability parameter, \( HP(Ti) \), which is derived from the product of \( c_b \) from Eq. (4) at \( l=1 \) and 10 μm and austenite grain diameter for three heat treatments. The particle composition obtained by EPMA is Ti-oxide (as TiO\(_2\)) without containing MnO. It is seen that the curve at \( l=10 \) μm is shifted to the left-hand side. This is due to that the \( c_b \) value at \( l=10 \) μm is significantly smaller than that at \( l=1 \) μm for a given \([T.M]\) and austenite grain size, as shown in Fig. 8. These results indicate that for \( HP(Ti) \) values up to 5.2×10\(^5\) ppm μm (l=10 μm), the intergranular ferrite formation is encouraged. Furthermore, that %IGF reaches the maximum, followed by the formation of upper bainite after \( HP(Ti) \) >1.6×10\(^5\) ppm μm.

The area fraction of IGF for the TN1~TN9 samples and for the TN1~TN5 and TNM1~TNM4 samples are plotted against \( HP(Ti) \) from Eqs. (2), (4) \( (l=10 \) μm) and (5) in the upper and lower diagrams of Fig. 10, respectively. Since the application of \( HP(Ti) \) from Eqs. (2) and (5) depends on the validity in the assumption of \( c_b=[T.M] \), the data for 1400°C (600 s) in which the \( l/D \) ratio is small are used, as is clear in Fig. 7.

As shown in the upper and lower diagrams, the curve from Eq. (2) is located at significantly smaller \( HP(Ti) \) values compared to those from Eqs. (4) and (5). The difference between Eq. (2) by Askelsen et al.\(^{19}\) and Eq. (5) by...
Faulkner,\textsuperscript{16}) in which the maximum non-equilibrium segregation level is considered, is due to the $c_b$ values obtained from the different assumption made in these two models, as explained previously. It can be seen that the curve from Eq. (4) at $l=10 \mu m$ is in good agreement with that from Eq. (5) for the data at 1 400°C (600 s). It is to be noted, however, that the ratio of $HP(Ti)$ from Eq. (4) to $HP(Ti)$ from Eq. (5) becomes smaller with a decreasing grain size and increasing $l$ and $L_{gb}$ values.

The results obtained by using Eq. (4) at $l=10 \mu m$ are shown in the upper (TM1~TM9) and lower (TN1~TN5 and TNM1~TNM4) diagrams of Fig. 11 as a function of heat treatment. As shown in the upper diagram, the $HP(Ti)$ values at the maximum %IGF moves to the left-hand side and the width of the curve becomes broader with a decreasing grain size obtained at different WHT tests. This may be explained by the change of $l$ with grain size. If the width of the segregated layer becomes smaller with a decreasing grain size, the $c_b$ value increases for a given value of $[\text{T.M}]$, $L_{gb}$ and $D$, as is clear in Fig. 8. Another reason is that the equilibrium between the solute Ti, a vacancy and a complex is not attained within a short holding time at lower temperatures. This indicates that the concentration of Ti-vacancy complexes within the grain is significantly low. The shape of the curve representing TiN particles is different from that for MgO (MgO+Ti$_2$O$_3$) particles, as shown in the lower diagram. However, a similar trend to MgO particles is observed with respect to the heat treatment, as shown in Fig. 4.

The area fraction of the IGF for the ZR1~ZR3 and TZ1~TZ5 samples are plotted against $HP(Ti)+HP(Zr)$ obtained from Eq. (4) at $l=10 \mu m$ in the upper (1 400°C for 60 s) and lower (1 400°C for 600 s) diagrams of Fig. 12. It is clear that two peaks exist at $HP(Ti)+HP(Zr)=1.3 \times 10^3$ and $2.7 \times 10^3$. The left-side peak corresponds to the solute Zr in the ZR1~ZR3 samples and the right-side peak corresponds to the solute Ti in the TZ1~TZ5 samples. The observed particles in the ZR1~ZR3 and TZ1~TZ5 samples are ZrO$_2$ and ZrO$_2$+Ti$_2$O$_3$, respectively. Although ZrO$_2$ is not an effective nuclei for IGF, a 50% amount of IGF is observed in the ZR1~ZR3 samples and a 45% amount of IGF is observed in the TZ1~TZ5 samples.

On the basis of the plot of %IGF versus $HP(Ti)$ obtained by using Eq. (4) at $l=10 \mu m$, the nucleation potency of inclusion phases, which is defined as an ability of inclusions as IGF nucleation sites, is discussed for the data treated at
1 400°C for 60 s. This is done under the assumption that the particle size and number of nuclei are constant. It can be seen that the curves for Ti2O3 (Fig. 9) and MgO (upper diagram of Fig. 11) for the TM1~TM9 samples with MgO and MgO+Ti2O3 inclusions) are very similar. However, these curves are different from the TiN curve (lower diagram of Fig. 11) and the ZrO2+Ti2O3 or ZrO2 curves (upper diagram of Fig. 12). Based on these results, it can be concluded that the nucleation potency of IGF on particles decreases in the order of TiN>Ti2O3, MgO(+Ti2O3)>ZrO2(+Ti2O3). This result is different from the order of MgO>TiN>Ti2O3 predicted from the plot of %IGF versus the solute Ti content shown in Fig. 4. Moreover, the effectiveness of inclusion phases is influenced by the solute elements on grain-boundaries, but the measurement of the solute concentration at grain-boundaries and the hardenability parameter are difficult to perform.

4. Conclusions

The effect of the soluble Ti and Zr contents on the microstructure in simulated HAZ was studied in an Fe-0.05%C+1.5%Mn-0.2%Si alloy as a function of the austenite grain size. Furthermore, the number and size of Ti2O3, MgO(+Ti2O3), TiN(+MgO) and ZrO2(+Ti2O3) particles and the heat treatment for a HAZ thermal cycle. The following conclusions were obtained:

(1) For a given solute Ti content, the area fraction of IGF decreases with an increased austenite grain size. This trend was found to depend significantly on the composition of inclusion particles.

(2) For a given austenite grain size, the primary ferrite decreases and the IGF increases with an increased solute Ti content up to a value of about 100 ppm. After going through a maximum the replacement of IGF by lath bainitic ferrite occurs.

(3) A non-equilibrium grain-boundary segregation model was applied to estimate the solute Ti content at grain-boundaries, assuming that c{sub g}[T.M] = c{sub g}[T.M]. It was found that the hardenability parameter is valid at lower grain-boundary width of grain-boundaries, assuming that g=M-T is the total mass of soluble M within the grain and on grain-boundaries, respectively. The 1/2 coefficient in this expression arises from the reason that the two neighboring grains have a single grain-boundary layer.

By using the density, ρ, and the volume, V, for the metal (M), within the grain (g) and at grain-boundaries (b), the following expression may be derived:

V{sub Me} ρ{sub Me} [T.M] = V{sub g} ρ{sub g} c{sub g} + 1/2 V{sub b} ρ{sub cb}................. [A-2]

where c{sub g} and cb are the concentrations of soluble M within the grain and at grain-boundaries, respectively. If we assume that ρ{sub Me}=ρ{sub g}=ρ{sub b}, Eq. [A-2] may be rewritten as:

V{sub Me} [T.M] = V{sub g} c{sub g} + 1/2 V{sub b} c{sub b}................. [A-3]

Also, the total volume of one grain with half thickness of the grain-boundary layer can be expressed as

V{sub v} = V{sub b} + 1/2 V{sub b}................. [A-4]

The combination of Eqs. [A-3] and [A-4] yields the following relationship:

V{sub v} [T.M] = ([V{sub g} + 1/2 V{sub b}]/[V{sub b} + 1/2(V{sub b} L{sub gb})]................. [A-5]

where L{sub gb}=c{sub b}/c{sub g}.

In addition, since V{sub b}=S{sub b}/l (S{sub b} is the surface area of a grain and l is the width of grain-boundary) and S{sub b}/V{sub b}=6l/D for spherical grains (S{sub sh}=V{sub sh}/(π/6·D{sub sh})), the following relationship may be derived:

V{sub v}/V{sub g} = S{sub v}/l V{sub g} = 6l/D................. [A-6]

It is pointed out that the surface area of a grain-boundary per unit volume is equal to 3/D. It is not 6/D, since the two neighboring grains have a single grain-boundary layer. However, we have already used a 1/2 coefficient for one grain in Eq. [A-1]. Thus, by substituting Eq. [A-6] into Eq. [A-5], we can obtain the following expressions:

V{sub v} [T.M] = 1 + 3(l/D)] / [1 + 3(l/D) L{sub gb}]................. [A-7]

and

c{sub g} [T.M] = [1 + 3(l/D)] / [1/L{sub gb} + 3(l/D)]................. [A-8]

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Appendix:

The mass balance relation for soluble M is written as

m{sub Mt,M} = m{sub g,M} + 1/2 m{sub Gb,M}................. [A-1]

where m{sub Mt,M} is the total mass of soluble M in metal. m{sub g,M} and m{sub Gb,M} are the mass of soluble M within the grain and on grain-boundaries, respectively. The 1/2 coefficient in this equation arises from the reason that the two neighboring grains have a single grain-boundary layer.

By using the density, ρ, and the volume, V, for the metal (Me), within the grain (g) and at grain-boundaries (b), the following expression may be derived:

V{sub Me} ρ{sub Me} [T.M] = V{sub g} ρ{sub g} c{sub g} + 1/2 V{sub b} ρ{sub cb}................. [A-2]

where c{sub g} and cb are the concentrations of soluble M within the grain and at grain-boundaries, respectively.

If we assume that ρ{sub Me}=ρ{sub g}=ρ{sub b}, Eq. [A-2] may be rewritten as:

V{sub Me} [T.M] = V{sub g} c{sub g} + 1/2 V{sub b} cb................. [A-3]

Also, the total volume of one grain with half thickness of the grain-boundary layer can be expressed as

V{sub v} = V{sub g} + 1/2 V{sub b}................. [A-4]

The combination of Eqs. [A-3] and [A-4] yields the following relationship:

V{sub v} [T.M] = ([V{sub g} + 1/2 V{sub b}]/[V{sub b} + 1/2(V{sub b} L{sub gb})]................. [A-5]

where L{sub gb}=c{sub b}/c{sub g}.

In addition, since V{sub b}=S{sub b}/l (S{sub b} is the surface area of a grain and l is the width of grain-boundary) and S{sub b}/V{sub b}=6l/D for spherical grains (S{sub sh}=V{sub sh}/(π/6·D{sub sh})), the following relationship may be derived:

V{sub v}/V{sub g} = S{sub v}/l V{sub g} = 6l/D................. [A-6]

It is pointed out that the surface area of a grain-boundary per unit volume is equal to 3/D. It is not 6/D, since the two neighboring grains have a single grain-boundary layer. However, we already used a 1/2 coefficient for one grain in Eq. [A-1]. Thus, by substituting Eq. [A-6] into Eq. [A-5], we can obtain the following expressions:

V{sub v} [T.M] = 1 + 3(l/D)] / [1 + 3(l/D) L{sub gb}]................. [A-7]

and

c{sub g} [T.M] = [1 + 3(l/D)] / [1/L{sub gb} + 3(l/D)]................. [A-8]