The Effect of Non-Metallic Particles on As-Cast Austenitic Structure of Low Carbon Steel

By

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We accept this thesis as conforming
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Date July 8, 1993
Abstract

The effect of second-phase particles and cooling rate on the as-cast austenite grain size of peritectic plain-carbon steel has been examined. Remelting tests followed by continuous cooling and helium quenching were performed on a Gleeble 1500 Thermomechanical Simulator. Two low alloy types of steel were used; both had basically the same basic chemical composition, but contained different amounts of titanium and calcium. The as-cast austenite grain size was characterized in terms of both the cooling rate, which was obtained by the Gleeble measuring system through the thermocouples welded on the sample surface, and the volume fraction and size distribution of second-phase particles which were obtained by electron metallography. The classical Zener equation and Gladman model were applied to explain the experimental results relating to the pinning effect of second-phase particle against as-cast austenitic grain growth.

It was found that at relatively high cooling rates (4.5 °C/s ~ 17.5 °C/s), the effect of cooling rate was dominant in austenite grain growth behavior, while at slower cooling rates (0.4 °C/s ~ 1.2 °C/s), the effect of second-phase particles in grain boundary pinning could be observed. Regarding the effect of second-phase particles, it was found that the titanium nitride, which is an effective precipitate for inhibiting austenite grain growth in the conventional continuous casting and reheating process, was not effective for pinning the coarse as-cast austenite grain growth. This was due to both the small volume fraction and the small size of titanium nitrides. On the other hand, oxides, which mainly were Ca-aluminates, were effective for pinning the as-cast austenite grain boundaries due to the large volume fraction and the relatively large particle size of oxides. The results were explained using the Gladman model.
Table of Contents

Abstract.................................................................................................................................................. ii
Table of Contents ................................................................................................................................... iii
List of Tables ........................................................................................................................................ vii
List of Figures ........................................................................................................................................ vi
List of Symbols ....................................................................................................................................... xi
Acknowledgment ................................................................................................................................... xiv

1. Introduction ..................................................................................................................................... 1

2. Literature Search ............................................................................................................................. 3
   2.1. Austenite Grain Growth Behavior in the High Temperature Region ........................................... 3
   2.2. Effect of Second Phase Particles on Austenite Grain Growth .................................................. 8
   2.3. Effective Particle Size for Pinning Austenite Grain Boundary .................................................... 19

3. Scope and Objectives ....................................................................................................................... 21

4. Experimental Procedure ................................................................................................................ 23
   4.1. Test Apparatus ........................................................................................................................... 23
   4.2. Sample Preparation ................................................................................................................... 24
   4.3. Remelting and Continuous Cooling Tests .................................................................................. 27
   4.4. Metallographic Tests ................................................................................................................ 28
      4.4.1. Sample Preparation............................................................................................................... 28
      4.4.2. Secondary Dendrite Arm Spacing ..................................................................................... 30
      4.4.3. Austenite Grain Size .......................................................................................................... 30
      4.4.4. Electron Microscopy ......................................................................................................... 31

5. Results and Discussion .................................................................................................................... 33
   5.1. Remelting and Continuous Cooling Tests ................................................................................ 33
      5.1.1. Thermocouple Output ......................................................................................................... 33
      5.1.2. Thermal History ................................................................................................................ 36
   5.2. Dendritic Structure .................................................................................................................... 39
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3. Austenitic Structure</td>
<td>48</td>
</tr>
<tr>
<td>5.4. Particle Size Measurement</td>
<td>57</td>
</tr>
<tr>
<td>5.5. Reproducibility Test</td>
<td>70</td>
</tr>
<tr>
<td>5.6. Volume Fraction of Second Phase Particles</td>
<td>77</td>
</tr>
<tr>
<td>5.7. Application of Gladman's Model</td>
<td>99</td>
</tr>
<tr>
<td>6. Conclusions</td>
<td>109</td>
</tr>
<tr>
<td>References</td>
<td>111</td>
</tr>
<tr>
<td>Appendix (The Program for Gladman Model)</td>
<td>114</td>
</tr>
<tr>
<td>A.1 Flowchart</td>
<td>114</td>
</tr>
<tr>
<td>A.2 Source Code</td>
<td>115</td>
</tr>
</tbody>
</table>
List of Tables

Table 2.1 Chemical compositions of steels used (wt%) [5]. .............................................. 4
Table 4.1 Chemical compositions of steels tested (wt %). .................................................... 25
Table 5.1 Results of thermocouple calibration. ..................................................................... 34
Table 5.2 Actual cooling rates for each test. .......................................................................... 36
Table 5.3 The number of austenite grains counted (N) and the standard deviation (σ). 48
Table 5.3 Calculation for particle forming. .......................................................................... 63
Table 5.4 Calculation of volume fraction of second phase particles on the replicas..... 78
Table 5.5 Summary of the relationship between $\bar{f}/f$ and $R$. ........................................ 79
Table 5.7 The values of $r^*$ (μm) for various $R_0$ and $Z$. ............................................... 107
List of Figures

Fig. 2.1 The effect of carbon content on γ grain size [5]................................. 3

Fig. 2.2 Grain growth of γ phase during continuous cooling. The specimens were remelted at 1580 °C, cooled to a given temperature at a rate of 0.28 °C/s, and quenched in water [5]. .................................................3

Fig. 2.3 The delta ferrite field of a carbon-iron phase diagram [6]..........................4

Fig. 2.4 Effects of Mn and Ni on the C dipendence of Tγ [7].................................5

Fig. 2.5 Relationship between Δγ and Tγ in various steels [7].............................6

Fig. 2.6 Austenite grain growth during continuous cooling at rates of v, 2v, 0.5v, between Tγ and 1000°C [7]..................................................................................7

Fig. 2.7 The relationship between austenite grain size and cooling rate based on the data from previously published literature [5, 7, 8].........................................................8

Fig. 2.8 Schematic presentation of interaction between TiN particle and austenite grain boundary [16]. ............................................................................................10

Fig. 2.9 Relationship between contact angle and interaction energy [16]...............12

Fig. 2.10 Relationship between contact angle and particle size of TiN [16].........12

Fig. 2.11 Schematic diagram illustrating a model for unpinning [17]. ..................15

Fig. 2.12 Model for grain growth. Grain A, R=R₀; grain B, R>R₀ [17]. .............16

Fig. 2.13 Energy changes during unpinning for f=0.0005, R₀=14μm; r=0.0350μm; Z=1.5; γ=800 erg/cm² [17]. ..................................................................................18

Fig. 2.14 Effect of particle size on the barrier to growth for R₀=14μm; Z=1.5; γ=800 erg/cm² [17]. ..................................................................................19

Fig. 2.15 Effect of particles on the inhibition of grain growth [20]. ......................20

Fig. 4.1 Schematic diagram of specimen mounting. .............................................24

Fig. 4.2 Cylindrical steel specimen for Gleeble melting test...............................26

Fig. 4.3 Schematic diagram for sectioning of specimen......................................29

Fig. 5.1 A thermal history of a remelting and continuous cooling test..............36
Fig. 5.2 Cooling curves for air cooling.................................................................37
Fig. 5.3 Cooling curves for cooling rate of 4.5°C/s.............................................37
Fig. 5.4 Cooling curves for cooling rate of 1.2°C/s.............................................38
Fig. 5.5 Cooling curves for cooling rate of 0.4°C/s.............................................38
Fig. 5.6 Plot of measured secondary dendrite arm spacing against cooling rate........39
Fig. 5.7 The dendritic structure of Steel A cooled in air .....................................40
Fig. 5.8 The dendritic structure of Steel B cooled in air.....................................41
Fig. 5.9 The dendritic structure of Steel A cooled at 4.5°C/s...............................42
Fig. 5.10 The dendritic structure of Steel B cooled at 4.5°C/s.............................43
Fig. 5.11 The dendritic structure of Steel A cooled at 1.2°C/s.............................44
Fig. 5.12 The dendritic structure of Steel B cooled at 1.2°C/s.............................45
Fig. 5.13 The dendritic structure of Steel A cooled at 0.4°C/s.............................46
Fig. 5.14 The dendritic structure of Steel B cooled at 0.4°C/s.............................47
Fig. 5.15 The austenitic structure of Steel A cooled in air..................................49
Fig. 5.16 The austenitic structure of Steel B cooled in air..................................50
Fig. 5.17 The austenitic structure of Steel A cooled at 4.5°C/s............................51
Fig. 5.18 The austenitic structure of Steel B cooled at 4.5°C/s............................52
Fig. 5.19 The austenitic structure of Steel A cooled at 1.2°C/s............................53
Fig. 5.20 The austenitic structure of Steel B cooled at 1.2°C/s............................54
Fig. 5.21 The austenitic structure of Steel A cooled at 0.4°C/s............................55
Fig. 5.22 The austenitic structure of Steel B cooled at 0.4°C/s............................56
Fig. 5.23 Plot of measured austenite grain size against cooling rate....................57
Fig. 5.24 The second phase particle size distribution for the samples air cooled......58
Fig. 5.25 The second phase particle size distribution for the samples cooled at 4.5°C/s. .................................................................59
Fig. 5.26 The second phase particle size distribution for the samples cooled at 1.2°C/s. ................................................................. 60

Fig. 5.27 The second phase particle size distribution for the samples cooled at 0.4°C/s. ............................................................................. 61

Fig. 5.28 The log-normal probability plot of the second phase particle size distribution for the samples cooled in air. ................................................................. 65

Fig. 5.29 The log-normal probability plot of the second phase particle size distribution for the samples cooled at 4.5°C/s. ................................................................. 66

Fig. 5.30 The log-normal probability plot of the second phase particle size distribution for the samples cooled at 1.2°C/s. ................................................................. 67

Fig. 5.31 The log-normal probability plot of the second phase particle size distribution for the samples cooled at 0.4°C/s. ................................................................. 68

Fig. 5.32 The cooling curve for the reproducibility test plotted with the curves for the earlier tests (cooling rate: 1.2°C/s). ................................................................. 70

Fig. 5.33 The dendritic structure for the repeated test (Steel B, C.R.=1.2°C/s). .......... 71

Fig. 5.34 The austenitic structure for the repeated test (Steel B, C.R.=1.2°C/s). .......... 72

Fig. 5.35 The relationship between secondary arm spacing and cooling rate. .......... 73

Fig. 5.36 The relationship between austenite grain size and cooling rate. .......... 74

Fig. 5.37 The second phase particle size distribution for the sample of the Steel B cooled at 1.2°C/s. ................................................................. 75

Fig. 5.38 The log-normal probability plot of the second phase particle size distribution for the samples cooled at 1.2°C/s. ................................................................. 76

Fig. 5.39 The relationship between $R$ and $\tilde{f}/f$ . ......................................................... 80

Fig. 5.40 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-1) ................................................................. 83

Fig. 5.41 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-2) ................................................................. 84

Fig. 5.42 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-3) ................................................................. 85

Fig. 5.43 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-4) ................................................................. 86
Fig. 5.44 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-5) ................................................................................................................................. 87

Fig. 5.45 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-6) ................................................................................................................................. 88

Fig. 5.46 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-7) ................................................................................................................................. 89

Fig. 5.47 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-8) ................................................................................................................................. 90

Fig. 5.48 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-9) ................................................................................................................................. 91

Fig. 5.49 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-10) ............................................................................................................................... 92

Fig. 5.50 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-11) ............................................................................................................................... 93

Fig. 5.51 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-12) ............................................................................................................................... 94

Fig. 5.52 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-1) ................................................................................................................................. 95

Fig. 5.53 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-2) ................................................................................................................................. 96

Fig. 5.54 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-3) ................................................................................................................................. 97

Fig. 5.55 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-4) ................................................................................................................................. 98

Fig. 5.56 Effect of particle size on the barrier to grain growth. The average austenite grain radius = 0.4 mm, the volume fraction of particles = 0.001, and the surface energy per unit area of boundary of austenite = 0.8 J/m². .................................................................................................................. 101

Fig. 5.57 Effect of particle size on the barrier to grain growth. The average austenite grain radius = 0.8 mm, the volume fraction of particles = 0.001, and the surface energy per unit area of boundary of austenite = 0.8 J/m². .................................................................................................................. 103

Fig. 5.58 Effect of particle size on the barrier to grain growth. The average austenite grain radius = 1.4 mm, the volume fraction of particles = 0.001, and the surface energy per unit area of boundary of austenite = 0.8 J/m². .................................................................................................................. 105
Fig. 5.59 Effect of austenite grain size and heterogeneity on $r^*$
List of Symbols

The Relationship between Cooling Rate and Slab Thickness

\( d \)  Slab thickness (mm)
\( G \)  Cooling rate (°C/s)

Austenite Grain Growth at High Temperature

\( C \)  A constant which describes grain growth behavior \((m^3/s^2)\)
\( D \)  Austenite grain diameter at 1000 °C (mm)
\( D_0 \)  Initial austenite grain diameter during continuous cooling (mm)
\( D_T \)  Austenite grain diameter at 1300 °C (mm)
\( Q \)  Activation energy for grain boundary movement (J/mol)
\( R \)  Gas constant (J/K-mol)
\( t \)  Time (s)
\( T \)  Absolute temperature (K)
\( T_Y \)  The temperature at which steels become single phase austenite (K)
\( \nu \)  Cooling rate (°C/s)

Okumura-Matsuda Model

\( f \)  Volume fraction of TiN
\( \Delta F(r, \omega) \)  Increment of the interfacial energy per TiN particle (J)
\( \Gamma \)  Grain boundary energy per unit area (J/m²)
\( \delta \)  The interaction parameter between the austenite grain and the TiN particle (dimensionless)
\( K \)  A dimensionless factor, which depends on the nature of the precipitate particles
\( r \)  Mean particle radius of TiN (μm)
\( R \)  Austenite grain radius (μm)
\( s \)  Contact arc length between a TiN particle and an austenite grain boundary (μm)
ω  Contact angle between a TiN particle and an austenite grain boundary (rad)

Y  Axis which shows the direction of boundary movement

**Gladman Model**

\[ a = s \left[ r^2 - \left( \frac{1}{2} s \right)^2 \right]^{\frac{1}{2}} (\mu m^2) \]

A  Area of the distorted planar boundary (\( \mu m^2 \))

\( A_c \)  Increase in boundary area per unit area of interface (dimensionless)

\( A_e \)  Area of grain boundaries which is eliminated by growth of the grain per unit area of interface (dimensionless)

\( A_n \)  Net change in area of grain boundary per unit area of growing interface (dimensionless)

\( \Delta A \)  Change in area of the distorted boundary (\( \mu m^2 \))

\( E_1 \)  Net energy change per pinning particle due to grain growth (J)

\( E_n \)  Net energy change per unit area of interface due to grain growth (J/\( \mu m^2 \))

\( E_p \)  Pinning energy per pinning particle due to the distortion of grain boundary (J)

\( E_T \)  Total energy change associated with the unpinning of a single particle (J)

f  Volume fraction of particle (dimensionless)

\( \phi, \theta \)  Interfacial angles between a particle and a grain boundary (rad)

\( \gamma \)  Grain boundary energy per unit area (J/m^2)

H  Energy barrier against grain boundary movement exerted by pinning particles (J)

k  A constant described by the equation, \( y(s - x) = k \) (\( \mu m^2 \))

\( L_1 \)  Junction between a grain boundary and a pinning particle (\( \mu m \))

\( L_2 \)  Upper limit of the integration for deriving the area of the distorted grain boundary (\( \mu m \))

\( n \)  A dimensionless constant which gives the upper limit \( L_2 \) \( (L_2 = nr) \)
\( n_v \) Number of particles per unit volume (\( \mu m^3 \))

\( r \) Radius of a pinning particle (\( \mu m \))

\( r' \) Critical particle radius above which grain coarsening can occur (\( \mu m \))

\( R_0 \) Matrix grain radius (\( \mu m \))

\( s \) Displacement of a boundary (\( \mu m \))

\( x \) Axis which shows the direction of grain boundary movement

\( y \) Axis which is perpendicular to the direction of grain boundary movement

\( Z \) Ratio of radii of growing grains to matrix grains (dimensionless)

**Temperature Correction**

\( T_{LL} \) Liquidus temperature of steels (°C)

\( T_{cor.} \) Corrected temperature (°C)

\( T_{meas.} \) Output temperature from Gleeble (°C)

**Particle Size Distribution**

\( \alpha \) Fraction of the number of particles extracted on a replica (dimensionless)

\( f \) Volume fraction of second phase particles (dimensionless)

\( N \) Number of particles in examined area on a replica (\( \mu m^2 \))

\( N_S \) Total number of particles intersecting a unit area of a sample (\( \mu m^2 \))

\( N'S \) Number of particles per unit area of a replica (\( \mu m^2 \))

\( \bar{r} \) Arithmetical mean of a particle radius distribution (\( \mu m \))

\( \sigma_G \) Geometric standard deviation of a particle diameter distribution (\( \mu m \))

\( \bar{x}_G \) Geometric mean of a particle diameter distribution (\( \mu m \))
Acknowledgment

I would like to thank professor J.K. Brimacombe, who supervised the work described herein, and professor E.B. Hawbolt, for their advice and guidance during the course of this work. The assistance of Binh Chau, who operated the Gleeble 1500, is also appreciated.

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1. Introduction

In the manufacturing process of steel products, as in the Continuous Casting - Direct Rolling process or in Near Net Shape Casting, the linkage between casting and rolling (or even the elimination of rolling) is receiving increasing attention because of energy savings and reduction of production costs. With respect to energy savings, the consumption of fossil fuel is reduced with less emission of CO₂ due to the elimination of reheating furnaces, which is of great importance for solving the global environmental problem. The reduction of production cost is achieved because the building and maintenance costs for reheating furnaces are not needed.

In these operations, there are fewer transformations than that of conventional processes and smaller reductions in the thickness of the material between casting and the finished product such that the as-cast structure has a larger influence on the final microstructure, which determines the mechanical properties of the final products, than that of conventional processes: Consequently, the mechanical properties of the products by Near Net Shape Casting are poorer compared to those by the conventional processes due to the coarse as-cast structure; this hinders the commercialization of the new process. Therefore, it is essential to make the cast structure as fine as possible in order to exploit Near Net Shape Casting.

Various techniques, such as single roll, twin roll, or twin belt, have been developed for Near Net Shape Casting [1]. According to Itoh [2], the cooling rate of the casting processes at the mid-thickness of material during casting is a function of thickness of the material to be cast, regardless of the type of caster, as can be seen in the following equation:

\[ G = 803d^{-1.76} \]  

(1.1)

where, \( G \) is cooling rate in °C/s and \( d \) is the casting thickness in mm.

In the case of strip casting with thicknesses in the order of 1 mm, very high cooling rates can be achieved resulting in fine cast structures. Consequently, the most serious technical impediment to reach this goal has been surface quality [3]. For stainless steel strip production,
Chapter 1. Introduction

the twin-roll strip casting technique enables the Near Net Shape Casting processes to be commercialized to some extent [4]. Near Net Shape Casting processes for plates, whose thicknesses are of the order of 10–100 mm, are still far from commercialization because of the relatively slow cooling rate in the interior of the section which causes too coarse a structure in the mid-thickness region to obtain proper mechanical properties. Therefore, a method for grain refining the as-cast austenitic structure is needed in order to commercialize the near-net-shape casting process for plates.

For a given cooling rate, in which the primary cast structure is considered to be fixed, one of the effective ways to obtain a fine microstructure is to utilize second-phase particles for pinning the grain boundaries of austenite which grow rapidly after solidification is completed. As a first step of this project, the as-cast austenite grain growth behavior in the high temperature region and the effect of second-phase particles on austenite grain growth will be discussed based on previously published papers. Following this, the effect of second-phase particles on the as-cast austenite grain size of low carbon steels will be examined in the light of both experimental and theoretical results. The major aim of this project has been to examine the particle size which is effective for inhibiting the grain growth of coarse austenite grains.
2. Literature Search

2.1. Austenite Grain Growth Behavior in the High Temperature Region

Sumitomo Metal Industry Co. [5] has reported that the austenite grain size of as-cast steels was found to depend largely on carbon content; the maximum grain size appeared in the 0.10-0.15% carbon region (See Fig. 2.1). This phenomenon was explained by the higher austenite formation temperature in this carbon region. This explanation was supported by other experimental results which are shown in Fig. 2.2.

![Figure 2.1](image1.png)

**Fig. 2.1** The effect of carbon content on $\gamma$ grain size [5].

![Figure 2.2](image2.png)

**Fig. 2.2** Grain growth of $\gamma$ phase during continuous cooling. The specimens were remelted at 1580 °C, cooled to a given temperature at a rate of 0.28 °C/s, and quenched in water [5].
Chapter 2. Literature Search

The chemical composition of these steels are listed in Table 2.1.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.029</td>
<td>-</td>
<td>0.84</td>
<td>0.020</td>
<td>0.006</td>
<td>0.025</td>
<td>0.0047</td>
</tr>
<tr>
<td>C5</td>
<td>0.16</td>
<td>-</td>
<td>0.68</td>
<td>0.022</td>
<td>0.006</td>
<td>0.010</td>
<td>0.0043</td>
</tr>
<tr>
<td>C9</td>
<td>0.28</td>
<td>-</td>
<td>0.89</td>
<td>0.022</td>
<td>0.007</td>
<td>0.031</td>
<td>0.0066</td>
</tr>
</tbody>
</table>

Figure 2.2 shows that the growth of austenite grains occurs rapidly below some temperature. In the case of steel C5 (0.16%), the temperature was about 1450 °C, while in the other cases it was relatively lower. A separate thermal analysis confirmed that these temperatures were almost equal to the temperatures at which the steels become single austenite phase ($T_Y$). This suggests that the existence of a second-phase, such as liquid phase and δ ferrite, suppresses the austenite grain growth considerably. Therefore, the grain growth of the austenite phase is primarily affected by the temperature of complete transformation to austenite ($T_Y$). The highest $T_Y$ for the steels with the peritectic carbon content can qualitatively be understood by the carbon-iron binary phase diagram in Fig 2.3 [6]. The effect of Mn, which is usually added to steel plates, on the dependence of $T_Y$ on carbon content is shown in Fig. 2.4 [7]. This figure

![Fig. 2.3 The delta ferrite field of a carbon-iron phase diagram [6].](image-url)
Chapter 2. Literature Search

shows that the carbon content which gives maximum $T_\gamma$ decreases slightly due to a 2 wt% Mn addition.

![Fig. 2.4 Effects of Mn and Ni on the C dependence of $T_\gamma$ [7].](image)

This research [7] also showed the grain growth of austenite after the $\delta \rightarrow \gamma$ transformation more quantitatively. As was shown in the previous work, grain growth of the $\gamma$ phase occurred rapidly below the completion temperature of transformation into $\gamma$ phase ($T_\gamma$). As a result of that the strong inhibiting effect of a second phase, such as $\delta$ ferrite and/or liquid phase, on $\gamma$ grain boundary migration disappeared. Thus, the grain size of as-cast steels can be determined mainly by $T_\gamma$. Figure 2.5 shows the relation between $D_\gamma$ and $T_\gamma$, where $D_\gamma$ is the $\gamma$ grain size of specimens which were cooled to 1300 °C at a constant cooling rate, followed by water quenching. This figure shows that the increased cooling rate also reduces the temperature of attaining the single phase field, $T_\gamma$, and thereby reduces the resulting $\gamma$ grain size.
Chapter 2. Literature Search

Fig. 2.5 Relation between $D_\gamma$ and $T_\gamma$ in various steels [7],
(Open: Cooled at 0.5 °C/s, Filled: Cooled at 1.5 °C/s).

The authors proposed the following equation concerning $\gamma$ grain growth based on their experimental observation that the austenite grain growth started at $T_\gamma$,

$$D^3 - D_0^3 = C \int_{0}^{t} t \exp\left(-\frac{Q}{RT}\right) dt$$  \hspace{1cm} (2.1)

where

$D_0$: initial $\gamma$ grain diameter

$D$: $\gamma$ grain diameter at 1000°C

$C$: a constant

$t$: time

$t_1$: time at which temperature is 1000°C

$Q$: activation energy for grain boundary movement

$R$: gas constant

$T$: absolute temperature.

In the case of continuous cooling at a rate of $v$,

$$T = T_\gamma - vt$$  \hspace{1cm} (2.2)
Equations (2.1) and (2.2) indicate that the relative $\gamma$ grain size depends only on the cooling rate, $v$, and the temperature, $T$, as is schematically shown in Fig. 2.6, in which the ordinate axis denotes the relative grain size shown in arbitrary units. If $T_\gamma$ decreases from 1450°C to 1400 °C, at the same cooling rate, the $\gamma$ grain size is halved as can be seen at CD in Fig. 2.6; that is in good agreement with the experimental results shown in Fig. 2.5.

Matsuura et al. [8] studied the effects of carbon content and cooling rate on the development of columnar austenitic grains in as-cast steel. They melted steels containing 0.01 to 0.49 wt% carbon, and cooled them at rates of 0.3 to 40 °C/s down to 1000 °C followed by quenching. Their results are summarized as follows;

1) large columnar grains were developed in the 0.1-0.3 wt% C region,
2) the region of the carbon content favorable for the development of columnar grains extended with increasing cooling rate.

From these experiments and the simulations, they concluded that the formation of columnar grains was attributable to the steep temperature gradient at the $\delta \rightarrow \gamma$ transformation front.

Some of their data on austenite grain size are plotted as a function of cooling rate in Fig. 2.7 [8] and compared with results obtained by researchers at Sumitomo Metal [5, 7]. Since
Chapter 2. Literature Search

Matsuura et al. [8] studied the formation of columnar austenite, both the width (the minor dimension of a columnar grain) and the length (the major dimension of a columnar grain) were distinguished in this paper, as shown in Fig. 2.7.

Data description:
Matsuura 1 : 0.18%C-0.25%Mn, quenched from 1000 °C, width, [8]
Matsuura 2 : 0.18%C-0.25%Mn, quenched from 1000 °C, length, [8]
Matsuura 3 : 0.23%C-0.25%Mn, quenched from 1000 °C, width, [8]
Sumitomo 1 : 0.20%C-2%Mn, quenched from 1300 °C, [7]
Sumitomo 2 : 0.14%C-2%Mn, quenched from 1300 °C, [7]
Sumitomo 3 : 0.16%C-2%Mn, quenched from 1300 °C, [5]

Fig. 2.7 The relationship between austenite grain size and cooling rate based on the data from previously published literature [5, 7, 8].

From this figure, in which the cooling rate dependence of as-cast austenite grain size can be seen, it is apparent that the as-cast austenite grain size is very coarse, in the order of mm, even at relatively high cooling rates.

2.2. Effect of Second Phase Particles on Austenite Grain Growth

As Leslie wrote [9], it is well recognized that grain refinement can be achieved by the addition of Al, Nb [10, 11], or Ti [12], with the reason being that these elements form carbides,
Chapter 2. Literature Search

nitrides, or carbonitrides which inhibit austenite grain growth. This effect, known as Zener pinning, is named after C. Zener [13] who quantified the phenomenon for the first time. Although there have been many studies concerning Zener pinning [e.g. 11-13] in steels, most of the research was concerned with grain coarsening temperatures up to 1350°C obtained during the reheating and soaking process.

There have been very few works which studied the effect of second phase particles on as-cast austenite grain growth. Zhang et al. [14] studied the effect of niobium on the continuous casting solidification structure of HSLA (High Strength Low Alloayed) steels. They simulated continuous casting conditions of several steels in the laboratory by unidirectional solidification, in which a water-cooled copper chill, an exothermic mold, and a hot top were used. The temperature of the ingots at the time of quenching averaged 1000°C. From the experimental results, they concluded that the effect of Nb on cast structures was as follows:

- Small additions of Nb (<0.08 wt%) to the low alloy steels resulted in no significant changes in primary dendrite arm spacing.
- Small additions of Nb (<0.08 wt%) distinctly refined the columnar austenite grain size.

They explained the refinement of the austenite grains in the Nb bearing steel as the result of a reduced austenite grain boundary mobility due to the pinning force exerted by the niobium carbonitride particles precipitated at the boundary. Ueshima et al. [15] studied the effect of MnS on grain boundary migration in a low carbon Al-killed steel using a laboratory-scale twin-roll caster. They reported that MnS played an important role in pinning migrating grain boundaries at high temperatures.

Matsuda and Okumura [16] studied the effects of TiN precipitate particles on the austenite grain size of low carbon, low alloy steels. Although they studied the microstructures of steels which were heat treated simulating the conventional continuous casting and reheating process, some of their fundamental discussion is considered to be applicable to as-cast microstructures.
Chapter 2. Literature Search

They considered the interaction between an austenite grain boundary and a TiN particle from the standpoint of a balance of forces. The driving force for grain growth would be provided through equilibration of two forces: the first is the force due to the increase in the grain boundary energy tending to contract the austenite grain surface, and the second is related to a change in the energy of that part of the grain boundary which contacted the TiN particles. They proposed that the magnitude of this second force, which Gladman [17] did not take into account, depended on the type of precipitation in terms of, for example, chemical composition.

Their schematic illustration of the interaction between an austenite grain boundary and TiN particles is shown in Fig. 2.8. For simplicity, they assumed that a TiN particle was a sphere of radius $r$.

![Fig. 2.8 Schematic representation of interaction between TiN particle and austenite grain boundary [16].](image-url)
Chapter 2. Literature Search

They obtained the following equation both empirically and theoretically;

\[ R = K(r/f^2) \]  \hspace{1cm} (2.3)

where,

- \( R \) : the austenite grain size
- \( f \) : the volume fraction of TiN
- \( r \) : the mean particle size of TiN
- \( K \) : a dimensionless factor, which depends on the nature of the precipitate particles.

When the grain \( A \) grows in the direction of the \( Y \) axis, it meets a resistive force originating from the TiN particle until finally a steady state is attained. They defined the contact angle \((2\omega)\) as follows;

\[ 2\omega = \frac{s}{r} \]  \hspace{1cm} (2.4)

where \( s \) is the contact length of the arc. The increase in the free energy \((\Delta F)\) of the system, which gives rise to a resistive force against the austenite grain growth, is given by the following equation;

\[ \Delta F(r,\omega) = \Gamma(1+\delta)\int_{0}^{\pi/2}2\pi r \sin \omega \cdot r d\omega - \Gamma\pi(r \sin \omega)^2 \]  \hspace{1cm} (2.5)

where,

- \( \Delta F(r,\omega) \) : the increment of the interfacial energy per TiN particle
- \( \Gamma \) : the grain boundary energy per unit area (=800 erg/cm\(^2\) according to Kazenec and Kamenska [18])
- \( \delta \) : the interaction parameter between the austenite grain and the TiN particle.

It is evident that Eq. (2.5) holds for any kind of precipitate particles, with the parameter \( \delta \) denoting the nature of the particular particle.

From Eq. (2.5), the resistive force is obtained as follows;
Chapter 2. Literature Search

\[ \tau(\omega, r) = d(\Delta F) / dY = 2\pi\Gamma(1 + \delta - \cos \omega) \]  
(2.6)

\[ Y = r - r \cos \omega \]  
(2.7)

where \( \tau(\omega, r) \) is the resistive force per TiN particle in the direction of the \( Y \) axis. In this case it is sufficient to examine the balance of forces only in the direction of the \( Y \) axis, since both the driving force for grain growth and the resistive force are symmetric with respect to the \( Y \) axis.

The driving force for grain growth per unit area of grain boundary is given as

\[ 2\Gamma / R \]  
(2.8)

where \( R \) is the radius of the grain \( A \) which is assumed to be a sphere. In an equilibrium state, this driving force is in balance with the resistive force originating from the TiN particle, whereby,

\[ 2\Gamma / R = N \cdot \tau(r, \omega) \]  
(2.9)

where \( N \) is the number of TiN particles per unit area of grain boundary. By substituting Eq. (2.6) into Eq. (2.9), the following equation can be obtained:

\[ R = \frac{4}{3(1 + \delta - \cos \omega)} (r / f) \]  
(2.10)

where the volume fraction of TiN particles \( f \) is equal to \( 4 / 3\pi r^3 / (r / N) \), and \( r / f \) gives the

Fig. 2.9 Relationship between contact angle and interaction energy [16].

Fig. 2.10 Relationship between contact angle and particle size of TiN [16].
Chapter 2. Literature Search

mean distance of the particles.

Equation (2.3), which initially was obtained empirically, is identical to Eq. (2.10), where the dimensionless factor $K$ is defined as,

$$K = \frac{4}{3(1 + \delta - \cos \omega)}$$  (2.11)

It will be noted that $K$ depends on the nature of the precipitate particles through $\delta$ and $\omega$; it was 1.5 in the case of TiN according to their experimental results. They showed the relationship between $\delta$ and $\omega$ for $K=1.5$, as in Fig. 2.9 and also the relationship between contact angle ($\omega$) and the size of TiN particles (See Fig. 2.10). Thus they found that the term $\delta$ was much less than unity, as can be seen in Fig. 2.9. From the analysis above, they concluded that the increase in the interfacial energy of the grain boundary was the main factor controlling the austenite grain growth in the presence of TiN precipitate particles.

Although Matsuda and Okumura [16] pointed out that Gladman's theory [17] did not take into account the kind of pinning particles, they concluded that the parameter $\delta$ denoting the nature of a particular particle was much less than unity and did not inhibit the austenite grain growth very much; therefore it is meaningful to refer to the Gladman theory.

Gladman [17] considered the balance of the energy changes between those accompanying the unpinning process and those accompanying grain growth. He presented a schematic diagram modeling the pinning of a planar boundary by a spherical particle, as shown in Fig. 2.11. The pinning mechanism between a grain boundary and a particle is largely due to the reduction in grain boundary area when a grain boundary intersects a particle. The lowest energy position of the boundary when it contacts a single spherical particle will occur when the boundary intersects the particle across a diametrical plane. As the planar boundary moves away from the particle, the boundary will distort locally to a position of lower energy for a given displacement of the planar boundary, as shown in Fig. 2.11. The change in surface area at the boundary will thus depend on two factors. First, the curvature of the boundary will increase the area, and second, because the particle still occupies a position on the boundary, it tends to reduce the grain boundary area. The
actual change in grain boundary area, thus, depends on the shape of the boundary in the region of the particle and on the circle of contact between the boundary and the particle. He assumed that the distortion from a planar boundary varied inversely as the distance from the particle,

\[ y(s - x) = k, \]  

(2.12)

and that the interfacial angles between the particle and grain A and the particle and grain B were equal,

\[ \theta = \phi. \]  

(2.13)

The equation for the grain boundary profile is derived from Eqs. (2.12) and (2.13) for a given displacement of the boundary, \( s \), as follows;

\[ y = s \left[ r^2 - \left( \frac{1}{2} s \right)^2 \right]^{1/2} / 2(s - x). \]  

(2.14)

Having obtained the grain boundary profile, the grain boundary area may be obtained by evaluating the area of revolution of the profile. The surface area, \( A \), is obtained from,

\[ A = 2\pi \int_{L_1}^{L_2} y \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right]^{1/2} dx. \]  

(2.15)

The solution to this integral for the geometry in Fig. 2.11 is,

\[ A = -\frac{1}{2} \pi a \left[ \sinh^{-1} \left( \frac{2(s - x)^2}{a} \right) - \left\{ 1 + \left( \frac{a}{2(s - x)^2} \right)^{1/2} \right\} \right]^{L_2}_{L_1} \]  

(2.16)

where

\[ a = s \left[ r^2 - \left( \frac{1}{2} s \right)^2 \right]^{1/2} \]  

(2.17)

This equation describes the area of the distorted boundary between the limits \( L_1 \) and \( L_2 \). The lower limit will occur at the junction between the grain boundary and the precipitate particle; that
is, $L_1 = \frac{1}{2} s$. The upper limit of $x$ is $s$, but this involves an infinite area of grain boundary;

Gladman assumed the upper limit $L_2$ by the condition $y = nr$. Although he did not mention the value of $n$ in his paper clearly, it is estimated at 4 by Fig. 2.11. Then the general equation for the area of the distorted planar boundary is given by

$$A = -\frac{1}{2} \pi a \left[ \sinh^{-1}\left( \frac{a}{2n^2 r^2} \right) - \sinh^{-1}\left( \frac{s^2}{2a} \right) - \left\{ 1 + \left( \frac{2n^2 r^2}{a} \right)^2 \right\}^{\frac{1}{2}} + \left\{ 1 + \left( \frac{2a}{s^2} \right)^2 \right\}^{\frac{1}{2}} \right]$$ (2.18)

The change in area from the fully pinned condition may be obtained by subtracting the area of the boundary when in the diametrical plane of the particle, that is,

$$\Delta A = A - \left\{ \pi(nr)^2 - \pi r^2 \right\}.$$ (2.19)

As the second step, Gladman examined the energy change accompanying the grain
growth. When a grain grows and absorbs neighboring grains, there are two principal sources of energy change. Firstly, the energy of the system is increased by the expansion of the interface of the growing grain, and, secondly, the energy of the system is decreased by the elimination of the grain interfaces of the grains which are absorbed by the growing one. He showed a two-dimensional representation of his model, as in Fig. 2.12. The area of grain boundaries per unit area of interface which is eliminated by growth of the grain from a radius $R$ to a radius $(R+s)$, is,

$$A_e = 3s/2R_0,$$  \hspace{1cm} (2.20)

where $R_0$ is the average grain size of the matrix.

The growing grain, however, also increases its own boundary area. The increase in boundary area per unit area of interface, $A_e$, is given by

$$A_e = 2s/R.$$  \hspace{1cm} (2.21)

Thus the net change in area, $A_n$, of grain boundary per unit area of growing interface when a grain increases its radius from $R$ to $(r+s)$ is

$$A_n = s(2/R - 3/2R_0).$$  \hspace{1cm} (2.22)

![Fig. 2.12 Model for grain growth. Grain A, $R = R_0$; grain B, $R > R_0$ [17].](image)
Chapter 2. Literature Search

By defining the ratio of the radii of the growing grain and its neighbor as $Z$, the energy change is written as,

$$E_n = \frac{s\gamma}{R_0} \left( \frac{2}{Z} - \frac{3}{2} \right), \quad (2.23)$$

where $\gamma$ is the grain boundary energy per unit area. This is the general equation governing the energy changes during grain growth when the boundary displacement is very small with respect to the grain size.

As the third step, Gladman combined two energy changes: that accompanying the unpinning process and that accompanying grain growth. The unpinning energy was derived for a single particle, whereas the energy change accompanying grain growth was expressed in terms of energy per unit area of the advancing interface. In order to combine these energy changes, it is necessary to determine the area of the moving interface which is occupied by a single particle. The volume fraction of spherical particles, $f$, is expressed by the following equation,

$$f = \frac{4}{3} n_p r^3 \quad (2.24)$$

where $n_p$ is the number of particles per unit volume. The condition that a particle is in contact with an interface is that, before the start of grain growth, the center of the particle must lie within $\pm r$ of the interface. Thus there will be $2n_p$ particles per unit area of the interface. Then energy release per particle due to grain growth, $E_1$, is

$$E_1 = \frac{E_n}{2n_p}$$

or

$$E_1 = \frac{2s\pi r^2 \gamma}{3R_0 f} \left( \frac{2}{Z} - \frac{3}{2} \right). \quad (2.25)$$

Thus the total energy change associated with the unpinning of a single particle, $E_T$, is
Fig. 2.13 Energy changes during unpinning for \( f=0.0005, R_0=14\mu m; r=0.0350\mu m; Z=1.5; \gamma=800\text{ erg/cm}^2 \) [17].

\[
E_T = E_P + E_I
\]

\[
= \gamma \cdot (\Delta A) + \frac{2 \pi r^3 \gamma}{3 R_0 f} \left( \frac{2}{Z} \frac{3}{2} \right)
\]

(2.26)

where \( E_P \) is the pinning energy and \( \Delta A \) is the change in area of the distorted boundary derived before, as in Eq. (2.19). Gladman showed a typical sequence of energy change, occurring when a boundary is unpinning, as in Fig. 2.13, and he mentioned that unless the rate of decrease in energy due to grain growth exceeded the maximum rate of increase in energy due to unpinning, an energy barrier (\( H \)) would occur in the total energy change accompanying grain boundary movement. Such a barrier varies as a function of particle size and volume fraction of precipitate particles, as he showed in Fig. 2.14.

Gladman applied his model only to a relatively small austenite grain size, as shown in Fig. 2.14; however, Eq. (2.23) which gives energy change during grain growth contains the term \( R_0 \), the matrix austenite grain size; therefore his model is useful to study the pinning effect of second phase particles in a coarse as-cast austenitic structure assuming that the model is valid to a coarse grained structure.
**Chapter 2. Literature Search**

![Diagram](image)

**Fig. 2.14** Effect of particle size on the energy barrier to growth for $R_o=14\mu m$; $Z=1.5; \gamma=800$ erg/cm$^2$ [17].

### 2.3. Effective Particle Size for Pinning Austenite Grain Boundary

As mentioned earlier, most of the studies concerning the effect of second phase particles on austenite grain growth concerned the grain coarsening temperatures attained during the reheating and austenitic soaking processes [10-12]. Gladman and Pickering [11] suggested that the main factor controlling grain growth was particle coalescence, showing that there was a critical particle diameter at which the particles lost their pinning effectiveness, and was given by the following equation:

$$r^* = \frac{6R_0f}{\pi} \left( \frac{3}{2} - \frac{2}{Z} \right)^{-1}$$  \hspace{1cm} (2.27)

where

- $r^*$ : critical particle radius above which grain coarsening can occur,
- $R_0$ : matrix grain radius,
- $f$ : volume fraction of particle,
- $Z$ : the ratio of radii of growing grains to matrix grains.
Chapter 2. Literature Search

These researchers have reported a critical diameter of 0.05-0.1 μm for AlN, which meant that only very small particles could inhibit the austenite grain growth.

Another field of study concerning the effect of second phase particles on microstructure is that of the weld fusion zone. Kanazawa et al. [19] studied the improved toughness of the weld fusion zone by fine TiN particles and showed experimentally that TiN particles smaller than 0.05 μm gave rise to a decrease in austenite grain size.

These two studies suggested that the smaller particles were more effective in pinning the austenite grain boundaries. However, this statement may not be applicable for a coarse as-cast austenitic structure because, as can be seen in Eq. (2.27), \( r^* \) is a function of the matrix grain size. Also, as Gladman [20] showed theoretically in another paper, for large grains, large particles, e.g. diameter of the order of 1 μm, possibly inhibit the grain growth (see Fig. 2.15); therefore, oxides, which usually have larger sizes than AlN, Ti(C, N), or Nb(C, N) and are more stable at higher temperatures than these precipitates, may be effective for pinning as-cast austenite grain boundaries.

![Diagram](image-url)

Fig. 2.15 Effect of particles on the inhibition of grain growth [20].
3. Scope and Objectives

The mid-thickness cooling rate of a thin slab whose thickness is 50 mm is estimated at 0.8 °C/s from Eq. (1.1). Judging from Fig. 2.6, this will produce a large as-cast austenite grain structure which may be too coarse to obtain preferred mechanical properties with as-cast material. References [5],[7],[8], also showed that the as-cast austenite grain of carbon steel tends to be coarsest at the peritectic carbon region (0.17wt%C), a carbon level common in steel plates for structural purposes. Therefore, the need for structure refinement is apparent for steels in this carbon region.

To refine as-cast austenitic structures, the pinning action of second phase particles against austenite grain boundary movement should be considered; however, little research has been reported on this subject. Although the effect of niobium on continuous casting solidification structure has been published [14] and the effectiveness of the niobium addition for refining the columnar austenite grain has been experimentally observed, the mechanism of this phenomenon, in particular the size of the precipitates which were responsible for pinning the austenite grain boundary, was not clear.

This thesis was undertaken to:

1. Examine the effect of cooling rate on the precipitation behavior of second phase particles (such as TiN) and their effect on the as-cast austenite grain size of steels in the peritectic region; and
2. Examine the effect of second phase particle size on its pinning effectiveness on as-cast austenite grain boundaries in peritectic steels.

The experimental work was divided into two major phases:

1. Remelting and solidifying tests at four different cooling rates, followed by characterization of the as-cast dendritic and austenitic structure for two kinds of steels, both of which had the same carbon content but had slightly different
Chapter 3. Scope and Objectives

micro-alloying elements; and

2. Optical and electron microscopy characterization of the size and composition of second phase particles resulting from the remelting test.
Chapter 4. Experimental Procedure

4. Experimental Procedure

4.1. Test Apparatus

The remelting tests, which were followed by continuous cooling and helium quenching, were performed on a Gleeble 1500 Thermomechanical Simulator. The Gleeble is equipped with a sealed chamber, inside of which, samples of various shapes and sizes can be resistively heated, gas or water quenched, and hydraulically tested in compression or tension. The machine is controlled by a computer which provides a wide variety of heating and cooling rates, stress and strain rates, and also stores data from each test at a set sampling rate; these conditions are programmed for each test.

The schematic diagram of the specimen mounting procedure for the remelting tests is shown in Fig. 4.1. To control and measure the sample temperature during heating, melting, and cooling followed by helium quenching, a Pt/Pt-10%Rh thermocouple of diameter 0.25 mm was spot welded to the sample surface at the diametrical plane at mid length of the specimen. The two thermocouple wires were separated by two wire diameters. The thermocouple was sheathed with a two-hole alumina tube, which was supported by a glass holder made specifically for this purpose. This holder allowed the thermocouple to move only in the vertical direction after the steel became liquid. Without the holder, stable temperature control could not be obtained because of unexpected movements of the thermocouple after melting of the steel.

In order to contain the liquid steel during the melting tests, a quartz tube was used, as is recommended in the Gleeble operational manual [21]. The tube was slipped over the initially solid specimen. The diametral clearance required for steel was approximately 2% [21]; this is required to accommodate the larger linear coefficient of thermal expansion of the steel. As can be seen in Fig. 4.1, a slit was cut on the top of each quartz tube to provide for thermocouple access and an exit for gas.

During each test, the time, programmed temperature, measured temperature, and
Chapter 4. Experimental Procedure

measured stroke were recorded continuously. Tests were run in an atmosphere of pre-purified argon admitted to the test chamber after mechanical and diffusion pumping to a vacuum of approximately $10^{-4}$ torr. When back filling the argon into the chamber after vacuum pumping, the pressure inside the chamber was set slightly below atmospheric pressure to maintain the O-ring seal at the glass lid of the test chamber.

![Diagram of specimen mounting for remelting tests.](image)

**Fig. 4.1 Schematic diagram of specimen mounting for remelting tests.**

4.2. Sample Preparation

The two steels chosen to examine the effect of second phase particles on the as-cast austenitic structure of carbon steel were selected for the following reasons:
Chapter 4. Experimental Procedure

1. The basic chemical compositions, aside from the particle forming elements such as Ti and Ca, were similar, as shown in Table 4.1.

2. The carbon contents were close to the peritectic point, where carbon steels have been reported to have the coarsest as-cast austenite grains; consequently, any effect of second phase particles on the structure was expected to be visible.

3. The quantity of elements which form second phase particles, such as titanium, was different between the two steels.

4. These were common grades, and were easily obtained.

| Table 4.1 Chemical compositions of steels tested (wt %). |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|                | C   | Si  | Mn  | P   | S   | Cu  | Ni  | Cr  | Al  | Ca  | Ti  | N   | O   |
| Steel A        | 0.16| 0.45| 1.46| 0.013| 0.006| 0.02| 0.01| 0.02| 0.023| 0   | 0.003| 0.0020| 0.0010 |
| Steel B        | 0.16| 0.44| 1.43| 0.012| 0.001| 0.01| 0.01| 0.02| 0.028| 0.0017| 0.012| 0.0031| 0.0010 |

These are typical plain low-carbon steels used for structural purposes whose nominal tensile strength is 500 MPa. The main differences between these steels are as follows:

1. Steel A is for general use.

2. Steel B is usually used for specific parts such as the box column of high-rise buildings, which requires good weldability, good toughness in the heat affected zone, and lamella tear resistance; thus Steel B contains less sulphur, more calcium, and more titanium than Steel A.

The test material was obtained from two pieces of plate, 45mm×120mm×450mm for Steel A, and 40mm×140mm×450mm for Steel B, supplied by Nippon Steel Corporation, Kimitsu Works. Test samples, 13mm×13mm×140mm were cut from these plates and then machined into the final cylindrical shape as shown in Fig. 4.2.
Chapter 4. Experimental Procedure

The basic specimen diameter was taken from the recommendations of the Gleeble operational manual [21], in which tests assessing the volume-to-surface area ratio of the specimen were reported for three diameters, viz. 6mm, 10mm, and 12mm. In order to minimize the influence of the quartz tube inner surface on the solidified specimen, a large volume to surface was recommended. However, the specimen with 12mm diameter, which had the largest volume-to-surface ratio, was not recommended because it could not be cooled as fast as specimens with smaller diameters. For these reasons, the diameter of 10mm was chosen.

The outer diameter of the specimen was determined by the inner diameter of the quartz tube which was used to contain the molten steel. If the gap between the specimen and the quartz tube was too narrow, the quartz tube would be broken because of thermal expansion of the steel specimen. If the gap was too large, the molten steel would flow out of the center of the specimen into the gap between the specimen and the quartz tube. For this reason, the diameter of the specimen was machined 2% smaller than the 10.01mm inner diameter of the quartz tube.

The test specimen length was selected to accommodate the 12.5mm thread length and the
30mm length of the copper electrical contact jaws at each end of the specimen, requiring a length of 85mm as shown in Figs. 4.1 and 4.2. The rest of the specimen length, the so-called free span, was limited by the length of the quartz tube which held the molten steel. According to Duffers [21], a suitable melt length should be 1 to 1½ times the diameter. The typical quartz tube length for the 10mm specimen was 30mm to which 2 to 4mm had to be left as clearance on each end of the quartz tube. Thus a total free span of 34 to 38mm was recommended [21]. In preliminary tests, specimens of 60mm free span were attempted; however, the long melting zone, which was about 30mm, was difficult to control, resulting in unstable thermocouple output and molten steel flowing out of the quartz tube. Thus the free span of 40mm was used.

4.3. Remelting and Continuous Cooling Tests

Remelting and controlled continuous cooling tests, followed by helium quenching were performed as follows. (Note: During these tests, errors in thermocouple output were recognized. This detail will be discussed in the "Results and Discussion" section. The temperatures mentioned in this section are corrected values.)

Before heating the specimens, the ram of Gleeble was backed off by 2mm to allow the specimens to thermally expand during heating. The specimens were initially heated up to 1425 °C at the rate of 10 °C/s, and then at a rate of 0.5 °C/s to 1520 °C, this being about 10 °C above the liquidus temperature of the steels tested. A slower heating rate on approaching the melting temperature was chosen to enable the Gleeble to provide the latent heat of melting smoothly without a sudden change of power supply, which would cause unstable experimental conditions.

The peak temperature was held for one minute, followed by continuous cooling at one of four cooling rates down to 1260 °C at which time the steels were expected to be single-phase austenite. The cooling rates ranged from 0.4 °C/s, which approximately corresponds to the cooling rate of conventional continuously cast slabs (210 mm thick) at the quarter thickness [22],
to 17.5 °C/s, which approximately corresponds to the cooling rate at the center of thin slabs (10 mm thick) cast by a belt caster [23]. Between these two cooling rates, two other cooling rates, 1.2 °C/s and 4.5 °C/s, were chosen to divide the interval between minimum and maximum cooling rates into approximately equal portions on a logarithmic scale. The maximum cooling rate was obtained by air cooling of the specimen, which meant that after holding at peak temperature for one minute the electric current through the specimen was shut off and the heat in the specimen was extracted by the atmosphere and copper jaws. The other three cooling rates were obtained by computer controlling the resistive heating power to the specimen.

During melting, stirring of the liquid due to the magnetic field caused by the heating current flow was expected [21]. To reduce this condition, the MODE switch of the 1531 T-SERVO of the Gleeble was set at 1 to reduce the heating frequency, as was recommended by Duffers; this resulted in the heating frequency being reduced to half of the line frequency.

The control of stroke was also important to maintain the full sample cross section in the molten zone and to accommodate the shrinkage of liquid steel during solidification. The compression pattern was decided as follows according to the results of the preliminary tests;

- compressed 0.5 mm during holding at peak temperature to ensure a full sample cross section during melting, and
- compressed another 1.5 mm during cooling from peak temperature down to 1350°C to accommodate sample shrinkage and minimize the thermal stresses during solidification and cooling.

After cooling down to 1260 °C, the specimens were quenched by helium to retain the evidence of the austenite grain size at this temperature.

### 4.4. Metallographic Tests

#### 4.4.1. Sample Preparation

First, the specimens were cut at the cross section where the thermocouples remained
Chapter 4. Experimental Procedure

attached. This location was not necessarily the exact longitudinal center of the specimens because the thermocouples, which had been welded at the center, sometimes moved slightly from the original position during melting. The microstructure at the thermocouple position was considered to represent the thermal history measured during the test. The microstructure was expected to change with increased distance from the controlling thermocouple due to the steep thermal gradients present along the axis of the sample. A 10mm long cylindrical piece of the sample containing the cross section at the thermocouple position at one end was cut and mounted in plastic. The determination of austenite grain boundaries might be difficult at a cross section for some cases; therefore, the longitudinal section was examined as well as the cross section for each specimen. The adjacent 10mm length of each specimen, also containing the cross section at the thermocouple position was used for longitudinal section examination. This section was cut in half along the longitudinal axis, one of the two halves being mounted for longitudinal microstructure examination (See Fig. 4.3). All samples were polished to 1μm diamond prior to examination.

![Fig. 4.3 Schematic diagram for sectioning of specimen.](image)
Chapter 4. Experimental Procedure

4.4.2. Secondary Dendrite Arm Spacing

The secondary dendrite arm spacing was measured for each cooling rate. The dendritic structure was revealed using the following picric acid etch and etching procedure [24]:

1. The composition of the etchant was 5g of picric acid, 100 ml of H₂O, and 2 drops of liquid soap.
2. The etchant was heated up to 80 °C in a water bath.
3. The sample was immersed into the etchant for 2 minutes, then polished lightly with 1μm alumina.
4. The polished surface was examined with an optical microscope.
5. If the dendritic structure was not revealed clearly enough, the sample was immersed into the etchant for an additional 30 seconds followed by polishing with 1μm alumina.
6. Steps 4 and 5 were repeated until the dendritic structure was revealed clearly.

Two or three photographs of dendritic structure were taken for each sample at a magnification of 50 times revealing at least eight secondary dendrite arm spacings for each sample. The number of measurements was determined by the number of clearly revealed secondary dendrite arms. The dendrite arm spacing was not clearly revealed in the slowly cooled samples.

4.4.3. Austenite Grain Size

Prior austenite grain boundaries were revealed by etching with 2% nital, as was done in previous studies [5, 7, 8]. Photographs of the macrostructure at a magnification of 6.5 were taken to measure the austenite grain size. Each sample was also examined at a higher magnification, up to 400 times, to clearly identify the individual austenite grain boundaries. The austenite grain boundaries were revealed by the existence of ferrite plates or feather-like bainite along the boundaries. The boundaries were drawn on transparent sheets placed on the macrophotographs to facilitate the measurement of austenite grain size.

The size of each austenite grain was determined as follows:

1. Each grain was assumed to have an ellipsoidal shape.
Chapter 4. Experimental Procedure

2. The minor axis and the major axis of the ellipse were measured on the transparent sheet which corresponded to the macrostructure at a magnification of 6.5.

3. The arithmetical mean of the minor and major axes was defined to be the size of each grain.

4.4.4. Electron Microscopy

Second phase particles were examined with a Transmission Electron Microscopy (TEM) and a Scanning Electron Microscopy (SEM). The TEM was used mainly to determine the size distribution of the second-phase particles, and the SEM was used to assess the relationship between second-phase particles and austenite grain boundaries. Both the TEM and SEM were attached to an energy dispersive X-ray spectrograph (EDX), which enabled the chemical compositions of particles to be determined.

For the TEM examination, the conventional carbon extraction replica technique was employed. In this technique, non-metallic particles on a etched sample surface can be extracted by a very thin carbon layer, whose thickness is the order of 100 Å, deposited on the sample surface by a carbon evaporator. Replicas were prepared by the following procedure [25],[26]:

1. A polished surface was etched with 2% nital before carbon coating.
2. The etched sample was placed in a carbon evaporator with carbon rods placed 100 mm above the sample, and the carbon was evaporated for about 20 seconds.
3. After the evaporation, the sample was removed from the evaporating unit and the carbon film was scored into several squares with sides of about 3 mm.
4. The sample was immersed in 5% nital to strip the carbon film off. Some pieces of the stripped carbon film were immersed in distilled water where the surface tension forces prevented those pieces of carbon film from rolling up.
5. The pieces of carbon film designated as to location on the sample were picked up with TEM grids, and placed on a piece of filter paper to dry.

The pieces of carbon film were identified as to location in the sample (step 5) because the center of the sample, which was considered to be the last part to solidify, might have a different
distribution of second phase particles because of the segregation of solutes. The examination of the extraction replicas quickly revealed the second phase particles which were usually dark compared to the light carbon of the TEM image. However, it was very difficult to identify austenite grain boundaries in the TEM image of the replicas. Therefore, the SEM, which made it possible to observe the surface of the sample directly, was employed to observe the relationship between austenite grain boundaries and second phase particles. For the SEM examination, the polished surface of a sample was etched with 2% nital.

The size of the second phase particles was determined in a similar way as was done in determining the austenite grain size. Namely, the shape of a particle was assumed to be an ellipsoid and the arithmetical mean of the minor and major axes of the ellipse was defined as the diameter of the particle.

In order to obtain the size distribution of second phase particles, two replicas were examined, one from the center and the other further away from the center. For each replica, three fields were investigated; each field was a square of 110μm×110μm, which corresponded to the grids of the TEM specimen holder.
5. Results and Discussion

5.1. Remelting and Continuous Cooling Tests

5.1.1. Thermocouple Output

In preliminary tests, some error in the thermocouple output was noticed, namely the output temperature of the Gleeble was lower than the expected temperature. The liquidus temperature of the steels used in the experiments was considered to be about 1512–1513°C according to the Kawawa equation [27] which indicates the effect of compositions as shown below:

$$T_{\text{LL}} = 1536 - 78[\text{wt}\%\text{C}] - 7.6[\text{wt}\%\text{Si}] - 4.9[\text{wt}\%\text{Mn}] - 34.4[\text{wt}\%\text{P}] - 38[\text{wt}\%\text{S}]$$  \hspace{1cm} (5.1)

where $T_{\text{LL}}$ is the liquidus temperature of steels in °C.

However, the Gleeble thermocouple showed that the samples melted completely at around 1430°C.

This error was considered to be due to the following two factors:

- the error of the converter installed on the Gleeble to convert the thermocouple output into temperature, and

- the error of the thermocouple output, i.e. the E.M.F. (electromotive force), itself.

Concerning the first factor, the calibration of the Gleeble was carried out and the relationship between input voltage and the temperature output from the converter was examined. The results are shown in Table 5.1. From these results, it can be seen that the error is about 40°C when the output from the converter is around 1400°C; however, the difference between the Gleeble output and the expected temperature when the steels melted was 80°C ($=1510^\circ\text{C} - 1430^\circ\text{C}$), larger than the error caused by the converter, suggesting that the output from the thermocouple, i.e. the E.M.F. itself had some error.
Table 5.1 Results of thermocouple calibration.

<table>
<thead>
<tr>
<th>Input Voltage (mV)</th>
<th>Temperature corresponding to the Input Voltage* (°C)</th>
<th>Output from the converter of Gleeble (°C)</th>
<th>Error (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.26</td>
<td>519</td>
<td>509</td>
<td>-10</td>
</tr>
<tr>
<td>8.46</td>
<td>917</td>
<td>906</td>
<td>-11</td>
</tr>
<tr>
<td>11.96</td>
<td>1217</td>
<td>1196</td>
<td>-21</td>
</tr>
<tr>
<td>14.38</td>
<td>1417</td>
<td>1385</td>
<td>-32</td>
</tr>
<tr>
<td>15.58</td>
<td>1516</td>
<td>1477</td>
<td>-39</td>
</tr>
<tr>
<td>16.77</td>
<td>1616</td>
<td>1569</td>
<td>-47</td>
</tr>
</tbody>
</table>

*)The relationship between the input voltage (E.M.F.) and the corresponding temperature was based on the temperature vs. E.M.F. table for type S thermocouple (Pt/Pt-10%Rh) from ASTM [28]; however, this table was for 0°C reference junction; therefore, the room temperature at the time when the calibration was done (=16°C) was added to the values from the ASTM table.

The error in E.M.F. of the thermocouple, the second factor, was considered to be caused by the thermocouple mounting technique; namely, the thermocouple wires were directly welded onto the surface of the sample (so called intrinsic thermocouple). Although no quantitative data concerning the error of E.M.F. of an intrinsic thermocouple, applicable for this work, were found, it is said that iron affects the E.M.F. of Pt/Pt-Rh thermocouples [29]. Also Walker et al. [30], [31] reported that a small amount of iron in ceramic protection tubes covering Pt/Pt-Rh thermocouples caused a significant error (=5%) in the E.M.F. after long time use such as 120 hours at 1600°C. Although the experimental time was relatively short in the present work, the earlier study suggests that the intrinsic thermocouple which is welded directly onto the steel gives an error due to the iron contamination which is caused by the diffusion of iron from the sample to the thermocouple wires, and due to the diffusion of platinum or rhodium from the thermocouple wires to the sample [32], especially above the liquidus temperature of a steel, where the diffusion rate of solutes is very large. This supposition is supported by the fact that a previously used thermocouple showed a lower steel melting temperature after a few tests than was measured using a new thermocouple, although the 5mm to 10mm tip of the thermocouple was cut after each test.
Chapter 5. Results and Discussion

In order to eliminate the error due to the contamination of iron and the diffusion between the sample and the thermocouple wires, a thermocouple sheath was needed. Alumina tubes were tried; however, the response of the thermocouple output was not fast enough to control the sample temperature properly. One study suggested [33] a ceramic coating method to protect thermocouples from attack of liquid metal without losing a good thermal contact; however, the feasibility of this approach is a subject left for future study, as was the quantification of the E.M.F. error with respect to diffusion.

Although the errors in E.M.F. were not fully understood or minimized, tests were performed nonetheless because of the limited time of Gleeble availability for this project, and because the relative cooling rates were considered to be more important than the absolute values of temperature. The following two measures were taken to correct the temperature data as much as possible and to make the comparison between the tests in this project reasonable;

- new thermocouple wires were used for each test, and
- the measured temperatures were corrected as follows.

\[
T_{\text{cor.}} = T_{\text{meas.}} \left(1 + \frac{1520 - 1440}{1440}\right)
\]  
(5.2)

where \( T_{\text{cor.}} \) is the corrected temperature and \( T_{\text{meas.}} \) is the output temperature from the Gleeble. Eq. (5.2) was determined for the following reasons:

1. the peak temperature programmed on the Gleeble thermocouple response was 1440°C, which was 10°C higher than the melting temperature, and which was actually considered to be 1520°C, and
2. the difference between the output temperature and the actual temperature was considered to increase as the output temperature increased, judging from the calibration results shown in Table 5.1.

All temperatures which appear in this work have been corrected using Eq. (5.2), unless otherwise stated.
Chapter 5. Results and Discussion

5.1.2. **Thermal History**

An example of a thermal history for a remelting and continuous cooling test is shown in Fig. 5.1, for air cooled Steel B.

![Steel B, Air Cooling](image)

**Fig. 5.1 A thermal history of a remelting and continuous cooling test.**

The thermal history associated with the heating at two different rates, holding at the peak temperature, air cooling, and helium quenching can be seen in this figure. The thermal histories were the same for all tests up to the start of cooling, which occurred after an elapsed time of approximately 420 seconds.

Figures 5.2 to 5.5 show a comparison of the thermal histories of the A and B steels, the controlled cooling rate of each steel following melting being apparent. The cooling curves for air cooling (Fig. 5.2), were not linear due to the release of the latent heat of solidification. The programmed and measured value of the cooling rate for each test are listed in Table 5.2.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Actual cooling rates for each test. (°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air Cooling</td>
</tr>
<tr>
<td>Steel A</td>
<td>17.5</td>
</tr>
<tr>
<td>Steel B</td>
<td>15.9</td>
</tr>
</tbody>
</table>

*) The average cooling rate was calculated between the start of the cooling and the start of quenching.
Chapter 5. Results and Discussion

Fig. 5.2 Cooling curves for air cooling.

Fig. 5.3 Cooling curves for cooling rate of 4.5°C/s.
Chapter 5. Results and Discussion

Fig. 5.4 Cooling curves for cooling rate of 1.2°C/s.

Fig. 5.5 Cooling curves for cooling rate of 0.4°C/s.
Chapter 5. Results and Discussion

5.2. Dendritic Structure

The dendritic structure of each test sample is shown in Figs. 5.7-5.14. For each sample, two to three regions were observed. From these photographs secondary dendrite arm spacings were measured. The values obtained are plotted in Fig. 5.6 as a function of cooling rate. In this figure, the error bars correspond to ±σ, where σ is the standard deviation around an arithmetic mean, and the lines are taken from studies undertaken at Kawasaki Steel [34] and Sumitomo Metal [35].

![Graph showing relationship between secondary dendrite arm spacing and cooling rate.](image)

**Fig. 5.6** Plot of measured secondary dendrite arm spacing against cooling rate.

The relationship between secondary dendrite arm spacing and cooling rate determined in the current work agrees well with the previous investigations, suggesting that the temperature correction described in the previous section (as well as the measured temperature) is reasonable, at least for obtaining cooling rates.
Fig. 5.7 The dendritic structure of Steel A cooled in air. (×50)
Fig. 5.8 The dendritic structure of Steel B cooled in air. (×50)
Fig. 5.9 The dendritic structure of Steel A cooled at 4.5°C/s. (×50)
Fig. 5.10  The dendritic structure of Steel B cooled at 4.5°C/s. (×50)
Fig. 5.11 The dendritic structure of Steel A cooled at 1.2°C/s. (×50)
Fig. 5.12 The dendritic structure of Steel B cooled at 1.2°C/s. (×50)
Fig. 5.13 The dendritic structure of Steel A cooled at 0.4°C/s. (×50)
Chapter 5. Results and Discussion

Fig. 5.14 The dendritic structure of Steel B cooled at 0.4°C/s. (×50)
Chapter 5. Results and Discussion

The secondary dendrite arm spacings of the samples cooled at the higher cooling rates were clearly revealed as in Figs. 5.7-5.10. However, those obtained at the slower cooling rates were revealed less clearly, as shown in Figs. 5.11-5.14. Consequently, fewer dendrite arm spacing measurements were made for samples cooled at slower cooling rates; at least 20 measurements were obtained for each high cooling rate condition, whereas, only 8 was possible for the lower cooling rates.

5.3. Austenitic Structure

Austenitic macrostructures of the samples are shown in Figs. 5.15-5.22. From these photographs, austenite grain sizes were measured, the values of which are plotted as a function of cooling rate in Fig. 5.23. In this figure, the circles represent the arithmetic mean of the austenite grain size for each sample and an error bar, $\pm \sigma$, the standard deviation around an arithmetic mean is included. In Table 5.3, the number of grains counted and the value of $\sigma$ for each test is listed. The $\sigma$'s are relatively large especially those for the slower cooling rate; this is because only a few grains were observed in the cross sections examined and those grains had a range of sizes, as can be seen in Figs. 5.15-5.22. The grain sizes for the samples, with the exceptions of those that were air cooled were measured by the procedure described in Chapter 4. Measurements for the air cooled samples were made by linear analysis; the photographs of the longitudinal sections (Figs. 5.15 (b), 5.16 (b)) were examined and the diametric line lengths which were intersected by two adjacent grain boundaries at the thermocouple position were measured to obtain the mean grain sizes and the standard deviation. These values are considered to be reasonable because the austenite grains in the air cooled samples were very uniform, as shown in Figs. 5.15 (a), 5.16 (a).

Table 5.3 The number of austenite grains counted (N) and the standard deviation ($\sigma$).

<table>
<thead>
<tr>
<th></th>
<th>Air Cooling</th>
<th>C.R.=4.5°C/s</th>
<th>C.R.=1.2°C/s</th>
<th>C.R.=0.4°C/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N $\sigma$ (mm)</td>
<td>N $\sigma$ (mm)</td>
<td>N $\sigma$ (mm)</td>
<td>N $\sigma$ (mm)</td>
</tr>
<tr>
<td>Steel A</td>
<td>12 0.43</td>
<td>47 0.76</td>
<td>11 1.8</td>
<td>7 2.6</td>
</tr>
<tr>
<td>Steel B</td>
<td>11 0.56</td>
<td>35 0.98</td>
<td>34 0.8</td>
<td>11 1.6</td>
</tr>
</tbody>
</table>
Fig. 5.15 The austenitic structure of Steel A cooled in air. (×6.5)
Chapter 5. Results and Discussion

(a) Cross section at thermocouple position.

(b) Longitudinal section.
(Thermocouple position at top)

Fig. 5.16 The austenitic structure of Steel B cooled in air. (×6.5)
Chapter 5. Results and Discussion

(a) Cross section at thermocouple position.

(b) Longitudinal section.
(Thermocouple position at top)

Fig. 5.17 The austenitic structure of Steel A cooled at 4.5°C/s. (×6.5)
Chapter 5. Results and Discussion

Fig. 5.18 The austenitic structure of Steel B cooled at 4.5°C/s. (×6.5)
Chapter 5. Results and Discussion

Fig. 5.19 The austenitic structure of Steel A cooled at 1.2°C/s. (×6.5)

(a) Cross section at thermocouple position.

(b) Longitudinal section.
(Thermocouple position at top)
Chapter 5. Results and Discussion

(a) Cross section at thermocouple position.

(b) Longitudinal section.
(Thermocouple position at top)

Fig. 5.20 The austenitic structure of Steel B cooled at 1.2°C/s. (x6.5)
Fig. 5.21 The austenitic structure of Steel A cooled at 0.4°C/s. (×6.5)
Chapter 5. Results and Discussion

Fig. 5.22 The austenitic structure of Steel B cooled at 0.4°C/s. (×6.5)

(a) Cross section at thermocouple position.

(b) Longitudinal section.
(Thermocouple position at top)
Figure 5.23 shows a similar tendency of change in austenite grain size as a function of cooling rate as can be seen in Fig. 2.6, which summarizes the results from published works. At a given cooling rate, the austenite grain sizes are almost the same for Steel A and Steel B, except at the cooling rate of 1.2°C/s. The explanation for this observation will be discussed in the following sections.

5.4. Particle Size Measurement

The size distribution of second phase particles, which were obtained by examining carbon extraction replicas with the TEM, are shown in Figs. 5.24-5.27. Normal and log-normal particle size distributions are common in nature [36], [37], and the log-normal distribution seemed to reveal the tendency of these measurements better. For this reason, the particle diameter is plotted on a log scale in these figures.

The maximum magnification of the TEM was 100K in the scanning mode in which the qualitative chemical analysis of particles was carried out with EDX; this resulted in a resolution of 0.05μm in particle diameter.
Chapter 5. Results and Discussion

Fig. 5.24 The second phase particle size distribution for the samples air cooled.
Chapter 5. Results and Discussion

(a) Steel A

(b) Steel B

Fig. 5.25 The second phase particle size distribution for the samples cooled at 4.5°C/s.
Chapter 5. Results and Discussion

(a) Steel A

(b) Steel B

Fig. 5.26 The second phase particle size distribution for the samples cooled at 1.2°C/s.
Chapter 5. Results and Discussion

(a) Steel A

Steel A, C.R.=0.4 °C/s

(b) Steel B

Steel B, C.R.=0.4 °C/s

Fig. 5.27 The second phase particle size distribution for the samples cooled at 0.4°C/s.
Chapter 5. Results and Discussion

Although, light elements, such as carbon, nitrogen, and oxygen, could not be detected with the EDX attached to the TEM, most of the particles were considered to be oxides which contained Al, Si, and/or Ca, judging from both the shape and the chemical composition of the particles. Also some Ti bearing particles, some of which were identified as titanium-sulphides, and the rest of which were considered to be titanium-carbonitrides (or titanium-nitrides, titanium-carbides), were found. In Steel A, which contained more sulphur than Steel B, some manganese sulphides were also found.

In the foregoing figures, the size distribution of titanium bearing particles and manganese sulphides is plotted with different notations from that of the total (thick solid line for total, thin solid line for titanium bearing particles, and dotted line for manganese sulphides). The resulting size distributions for the totals are different for the two steels at a given cooling rate, and the difference has no clear dependence on cooling rate. Similarly, for a given steel, no clear relationship exists between the size distribution and the cooling rate. This is considered to be due to the fact that most of the particles found in each steel were oxides which were stable even in the liquid steel, and whose distribution did not change from that in as received steel plates.

The degree of stability of particles can be understood quantitatively by comparing the activity product of the particle forming elements with their respective solubility limits shown in Table 5.3. The calculation of the solubility in liquid iron was based on data published by Elliot [38], and the activity of the compounds was assumed to be one. In addition, the first-order interaction coefficients among solutes were taken into account in the calculation. The solubility limits were calculated at 1520 °C which is the peak temperature of the melting tests in the present work. The calculation was performed for TiN, MnS, Al₂O₃, and CaO.
Table 5.4 Calculation for particle forming.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Actual Activity Product for Steel A</th>
<th>Actual Activity Product for Steel B</th>
<th>Solubility Product at 1520 °C in wt%</th>
<th>Particle Forming Temperature for Steel A (°C)</th>
<th>Particle Forming Temperature for Steel B (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ti] + ( \frac{1}{2} [N_2] ) = TiN</td>
<td>6.1 x 10^{-6}</td>
<td>3.7 x 10^{-5}</td>
<td>6.7 x 10^{-4}</td>
<td>1170 (^2)</td>
<td>1410 (^2)</td>
</tr>
<tr>
<td>[Mn] + ( \frac{1}{2} [S_2] ) = MnS</td>
<td>8.7 x 10^{-3}</td>
<td>1.4 x 10^{-3}</td>
<td>2.2</td>
<td>1485 (^3)</td>
<td>1270 (^4)</td>
</tr>
<tr>
<td>2[Al] + ( \frac{3}{2} [O_2] ) = Al(_2)O(_3))</td>
<td>9.7 x 10^{-14}</td>
<td>1.2 x 10^{-13}</td>
<td>1.4 x 10^{-15}</td>
<td>(\ldots) (^5)</td>
<td>(\ldots) (^5)</td>
</tr>
<tr>
<td>[Ca] + ( \frac{1}{2} [O_2] ) = CaO</td>
<td>(\ldots) (^1)</td>
<td>7.2 x 10^{-7}</td>
<td>1.6 x 10^{-11}</td>
<td>(\ldots) (^1)</td>
<td>(\ldots) (^5)</td>
</tr>
</tbody>
</table>

1) Steel A does not contain Ca.
2) Calculated by the solubility product measured by Matsuda et al. [16].
3) Estimated as the temperature at which the steel becomes single phase austenite.
4) Calculated by the solubility product measured by Turkdogan et al. [39].
5) Considered to exist in the liquid steel.

In the table above, a smaller activity product of particle forming elements than the solubility limit of the compounds means that the particle forming elements are soluble in the liquid steel. This is the case for TiN and MnS; however, the activity products of Al\(_2\)O\(_3\) and CaO exceeds the solubility limits, implying that these oxide particles exist in the liquid steel at 1520°C. Although it should be emphasized that this calculation can not be directly applied to the experiments in the current study because the activity of the compounds were assumed to be one (pure compounds) and the experiments were not considered to have attained equilibrium, the calculation does support the stability of oxides in the molten steel. Furthermore, particle forming temperatures for TiN and MnS were estimated with the solubility products in the literature. For TiN, the solubility product in austenite which is expressed by the following equation [16] was used.
Chapter 5. Results and Discussion

\[
\log[\% Ti][\% N] = \frac{-8000}{T} + 0.32 \quad (5.3)
\]

where \( T \) is an absolute temperature. For MnS, the solubility product by Turkdogan et al. [39] shown below was used.

\[
K_s = [\% Mn][\% S]f_s^{Mn}
\]

\[
\log K_s = \frac{-9020}{T} + 2.929 \quad (5.4)
\]

\[
\log f_s^{Mn} = \left(-\frac{215}{T} + 0.097\right)[\% Mn]
\]

For Steel A, the solubility of MnS in \( \delta \)-ferrite was calculated as well based on the free energy change for formation of MnS in \( \delta \)-phase [40]. The results showed that MnS in Steel A was completely soluble in \( \delta \)-phase and not completely soluble in \( \gamma \)-phase and that the change of MnS solubility between the two phases was discontinuous; therefore, the formation temperature was estimated as the temperature at which the steel became single phase austenite. The calculations are based on the equilibrium state; therefore, the results are not directly applicable to the present study. However, the results are helpful to have a rough idea of the particle forming sequence during continuous cooling.

In order to examine the size distributions more quantitatively, it is useful to plot the cumulative percentage on log-normal probability paper [41]. Those plots are shown in Figs. 5.28-5.31. In these figures, all particles are plotted. If the cumulative percentage lies about a straight line in the plot, then the log of the geometric mean of this distribution, \( \log \bar{x_G} \), is given by the 50 percent point, and the log of the geometric standard deviation, \( \log \sigma_G \), is given by the difference between the 50 and 84 percent points [41].
Chapter 5. Results and Discussion

Fig. 5.28 The log-normal probability plot of the second phase particle size distribution for the samples cooled in air.
Fig. 5.29 The log-normal probability plot of the second phase particle size distribution for the samples cooled at 4.5°C/s.
Chapter 5. Results and Discussion

Fig. 5.30 The log-normal probability plot of the second phase particle size distribution for the samples cooled at 1.2°C/s.
Fig. 5.31 The log-normal probability plot of the second phase particle size distribution for the samples cooled at 0.4°C/s.
Chapter 5. Results and Discussion

From these figures, the following statements can be made:

- For the samples air cooled and cooled at 0.4°C/s, no significant difference in size distribution of second phase particles is observed between the two steels.
- For the samples cooled at 4.5°C/s, the particle size distributions are different between the two steels; however, the geometric means for both steels are almost the same.
- For the samples cooled at 1.2°C/s, the geometric means, as well as the particle size distributions, are different between the two steels.

As can be seen in Figs. 5.15-5.23, the difference in the as-cast austenite grain size between the two steels at a given cooling rate was the largest at 1.2°C/s, and no significant difference was observed for the rest of the cooling rates. This result can be related to the difference in the size distribution of second phase particles mentioned above. This reasoning will be discussed more thoroughly in later sections.

To examine the cause of the different particle size distributions, two facts should be kept in mind:

1) There is no clear relationship between the size distribution of second phase particles and related factors such as the cooling rate and the type of steel, and
2) Most of the particles found were oxides which are very stable even at high temperatures above the liquidus temperature of the steels, meaning that the size distribution of the oxides would not be changed from the initial stage very much by the heat treatments applied to the samples.

Thus the difference in size distribution among the samples is considered to be due to the uneven distribution of second phase particles in the as received plate steels, rather than the cooling rate and chemical composition.

In order to verify the above supposition, a reproducibility test was carried out with Steel B at the cooling rate of 1.2°C/s; previous results indicated the austenite grain size was clearly finer than that of Steel A at the same cooling rate.
Chapter 5. Results and Discussion

5.5. Reproducibility Test

The thermal history of the repeated test is shown in Fig. 5.32, which also presents the cooling curves of the earlier tests at the same cooling rate.

![Graph showing the cooling curve with a cooling rate of 1.2°C/s.](image)

**Fig. 5.32** The cooling curve for the reproducibility test plotted with the curves for the earlier tests (cooling rate: 1.2°C/s).

In this figure, it can be seen that the cooling rate was well controlled for the reproducibility test. The resulting dendritic structure and the as-cast austenitic macro structure are shown in Figs. 5.33 and 5.34.
Chapter 5. Results and Discussion

Fig. 5.33 The dendritic structure for the repeated test (Steel B, C.R.=1.2°C/s).
Fig. 5.34 The austenitic structure for the repeated test (Steel B, C.R.=1.2°C/s, x6.5).
Chapter 5. Results and Discussion

The secondary dendrite arm spacing was measured from Fig. 5.33, and plotted in Fig. 5.35 together with the secondary arm spacing of the other tests. The secondary dendrite arm spacing of the repeated test is consistent with that of the other tests, and is a measure of the reproducibility of the thermal history.

![Graph showing the relationship between secondary dendrite arm spacing and cooling rate.](image)

**Fig. 5.35** The relationship between secondary arm spacing and cooling rate.

In Fig. 5.34, much coarser austenite grains are observed as compared to the original test results shown in Fig. 5.20. The austenite grains were measured and plotted in Fig. 5.36, together with the grain sizes obtained in the other tests.
Chapter 5. Results and Discussion

Fig. 5.36 The relationship between austenite grain size and cooling rate.

The austenite grain size of the repeat test does not agree with that of the previous test under the same conditions. Instead, it is as coarse as that of the Steel A at the same cooling rate. The size distribution of second phase particles was measured and plotted in Fig. 5.37.
Fig. 5.37 The second phase particle size distribution for the sample of the Steel B cooled at 1.2°C/s.

From Fig. 5.37, it can be seen that the particles are fewer in number than those in the samples of the previous tests obtained at the same cooling rate, as shown in Fig. 5.26.

The cumulative percentage plot on log-normal probability paper for this sample is shown in Fig. 5.38 together with the previous tests obtained at the same cooling rate.
Chapter 5. Results and Discussion

Fig. 5.38 The log-normal probability plot of the second phase particle size distribution for the samples cooled at 1.2°C/s.

The size distribution of the second-phase particles in the sample which was thermally treated to reproduce the test of Steel B cooled at 1.2°C/s, is different than previously obtained and is very close to that obtained for Steel A cooled at 1.2°C/s.

The results of the reproducibility test strongly suggest that the difference in size distribution of second phase particles among the samples is due to the uneven distribution of second phase particles in the as-received steel plates, rather than to cooling rate and chemical composition.
5.6. Volume Fraction of Second Phase Particles

In discussing the effect of second phase particles on the austenite grain size, the volume fraction of second phase particles is important, as well as the mean particle size which is determined by the size distribution, as can be seen in the literature [16, 17].

Ashby and Ebeling [41] suggested that from an examination of extraction replicas the volume fraction of spherical second phase particles could be determined using the following equation based on the log-normal distribution:

\[
\ln f = \ln \frac{\pi}{6} N_s + 2 \ln \bar{x}_d + 2 \ln^2 \sigma_d
\]  

(5.5)

where \( f \) is the volume fraction of second phase particles, \( N_s \) is the total number of particles intersecting a unit area of the sample, \( \bar{x}_d \) is the geometric mean of the particle diameter distribution, and \( \sigma_d \) is the geometric standard deviation of the particle diameter distribution around the mean. \( N_s \) is related to the number of particles per unit area of the replica, \( N_s' \), by \( \alpha N_s = N_s' \); where \( \alpha \) is the fraction of the number of particles extracted on the replica. Although there is no data regarding the value of \( \alpha \), it is meaningful to calculate \( f \) by using \( N_s' \), instead of \( N_s \) in Eq. (5.5) in order to compare the volume fractions of second phase particles observed in the samples obtained in the current work. All of the replicas of the current work were prepared by the same procedure, which means that the values of \( \alpha \) should not vary from sample to sample. The results of the calculation are shown in Table 5.5.
Chapter 5. Results and Discussion

Table 5.5 Calculation of volume fraction of second phase particles on the replicas.

<table>
<thead>
<tr>
<th>Cooling Rate (°C/s)</th>
<th>Steel</th>
<th>N**</th>
<th>$N'$ (μm$^2$)</th>
<th>$\bar{\sigma}_G$ (μm)</th>
<th>$\sigma_G$ (μm)</th>
<th>$\ln f$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.5</td>
<td>A</td>
<td>124</td>
<td>1.71×10^{-3}</td>
<td>0.18</td>
<td>0.37</td>
<td>-8.47</td>
<td>2.1×10^{-4}</td>
</tr>
<tr>
<td>15.9</td>
<td>B</td>
<td>69</td>
<td>9.50×10^{-4}</td>
<td>0.20</td>
<td>0.71</td>
<td>-10.59</td>
<td>2.5×10^{-5}</td>
</tr>
<tr>
<td>4.5</td>
<td>A</td>
<td>76</td>
<td>1.05×10^{-3}</td>
<td>0.28</td>
<td>0.31</td>
<td>-7.31</td>
<td>6.7×10^{-4}</td>
</tr>
<tr>
<td>4.5</td>
<td>B</td>
<td>99</td>
<td>1.36×10^{-3}</td>
<td>0.23</td>
<td>1.43</td>
<td>-9.93</td>
<td>4.9×10^{-5}</td>
</tr>
<tr>
<td>1.2</td>
<td>A</td>
<td>159</td>
<td>2.19×10^{-3}</td>
<td>0.18</td>
<td>0.32</td>
<td>-7.60</td>
<td>5.0×10^{-4}</td>
</tr>
<tr>
<td>1.2</td>
<td>B</td>
<td>73</td>
<td>1.01×10^{-3}</td>
<td>0.53</td>
<td>0.61</td>
<td>-8.33</td>
<td>2.4×10^{-4}</td>
</tr>
<tr>
<td>0.4</td>
<td>A</td>
<td>77</td>
<td>1.06×10^{-3}</td>
<td>0.19</td>
<td>0.36</td>
<td>-8.73</td>
<td>1.6×10^{-4}</td>
</tr>
<tr>
<td>0.4</td>
<td>B</td>
<td>181</td>
<td>2.49×10^{-3}</td>
<td>0.24</td>
<td>0.49</td>
<td>-8.48</td>
<td>2.1×10^{-4}</td>
</tr>
<tr>
<td>1.2*</td>
<td>B</td>
<td>29</td>
<td>4.00×10^{-4}</td>
<td>0.16</td>
<td>0.71</td>
<td>-11.90</td>
<td>6.8×10^{-6}</td>
</tr>
</tbody>
</table>

*) Repeated test.
**) Number of particles in examined area, which was six 110μm×110μm squares.

The calculated volume fractions range from 6.8×10^{-6} to 6.7×10^{-4}. According to Matsumiya et al. [42], who studied the crystallization behavior of inclusions during solidification of a steel which had a similar chemical composition to the steels used in the current study, and which also was considered to have the same degree of cleanliness due to the fact the steel was supplied by the same mill as the steels used in the present work, the weight percent of oxides such as Al$_2$O$_3$ and CaO were of the order of 10^{-2}, which is an approximate volume fraction of 10^{-4}~10^{-3}. Therefore, the calculated values of volume fraction are considered to be reasonable estimations, considering that some of the particles might not be extracted into the replicas and would remain in the samples.

According to classical theory [13], the average austenite grain size in a steel which contains second-phase particles is related to the mean particle radius and the volume fraction of the particles, as can be seen in the following equation:

$$R = K \frac{\bar{F}}{f} \quad (5.6)$$

where $R$ is the average austenite grain radius, $K$ is a constant, $\bar{F}$ is the mean particle radius and $f$ is the volume fraction of the particles. Although it was not clearly stated, $\bar{F}$ is considered to
Chapter 5. Results and Discussion

be the arithmetic average of the radius distribution of second phase particles. Therefore, the arithmetic average of the second phase particles was calculated for each size distribution, and these values are included in Table 5.6 with the other measured parameters of importance to Eq. (5.6).

Table 5.6 Summary of the relationship between $\bar{r}/f$ and $R$.

<table>
<thead>
<tr>
<th>Cooling Rate (°C/s)</th>
<th>Steel</th>
<th>$\bar{r}$ (μm)</th>
<th>$f$ (mm)</th>
<th>$\bar{r}/f$</th>
<th>$R$ (mm)</th>
<th>$R/\bar{r}/f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.5 A</td>
<td>0.23</td>
<td>2.1x10^{-4}</td>
<td>1.10</td>
<td>0.42</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>15.9 B</td>
<td>0.24</td>
<td>2.5x10^{-5}</td>
<td>9.34</td>
<td>0.45</td>
<td>0.048</td>
<td></td>
</tr>
<tr>
<td>4.5 A</td>
<td>0.20</td>
<td>6.7x10^{-4}</td>
<td>0.29</td>
<td>0.75</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>4.5 B</td>
<td>0.37</td>
<td>4.9x10^{-5}</td>
<td>7.49</td>
<td>0.85</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>1.2 A</td>
<td>0.24</td>
<td>5.0x10^{-4}</td>
<td>0.48</td>
<td>1.5</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>1.2 B</td>
<td>0.45</td>
<td>2.4x10^{-4}</td>
<td>1.87</td>
<td>0.90</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>0.4 A</td>
<td>0.21</td>
<td>1.6x10^{-4}</td>
<td>1.27</td>
<td>1.7</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>0.4 B</td>
<td>0.24</td>
<td>2.1x10^{-4}</td>
<td>1.15</td>
<td>1.5</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>1.2* B</td>
<td>0.24</td>
<td>6.8x10^{-6}</td>
<td>34.7</td>
<td>1.4</td>
<td>0.040</td>
<td></td>
</tr>
</tbody>
</table>

*) Repeated test.

The average austenite grain radius, $R$, as a function of $\bar{r}/f$ is plotted in Fig. 5.39.
Chapter 5. Results and Discussion

Fig. 5.39 The relationship between \( R \) and \( \bar{r}/f \).

Although various values of \( K \) in Eq. (5.6) have been reported for different alloy system, consisting of a metal matrix and second-phase particles, as Nishizawa reviewed [43], the value of \( K \) was a constant in each system. In the present work, both Steel A and Steel B consisted of a steel matrix and oxide particles accounting for the majority of the second-phase particles: for this condition the value of \( K \) was expected to be constant for a given cooling rate. However, as shown in Table 5.6, the values of \( \frac{R}{(\bar{r}/f)} \), which corresponds to \( K \) are different for each steel, except for the cooling rate of 0.4°C/s. This suggests that the particle pinning phenomenon restraining the grain growth of as-cast austenite grains at the high temperature can not be described by the classical Eq. (5.6) except for the cooling rate of 0.4°C/s, in which \( K \) is equal to 1.3 for both samples. For the higher cooling rates, such as air cooling and 4.5 °C/s, the effect of second phase particles on austenite grain size is smaller than that of a slower cooling rate (0.4°C/s) as can be seen in the small gradients of the lines which give the relationship between \( R \)
Chapter 5. Results and Discussion

The experimental observations can be explained as follows:

1) For the low cooling rate of 0.4°C/s, the balance between the driving force for austenite grain growth and the energy barrier of pinning could be close to equilibrium. Matsuda and Okumura [16] have reported that for this condition, when \( f \) is much less than unity, as is the case in the present study, the austenite grain size is related to \( \bar{r}/f \) which gives the mean particle distance.

2) For high cooling rates, such as air cooling and 4.5 °C/s, the effect of cooling rate on the austenite grain growth behavior is predominant compared to that of pinning by second phase particles. The higher the cooling rate, the lower the temperature of complete transformation to austenite \( (T_y) \) [7] below which austenite grain growth occurs rapidly [5]. Thus at higher cooling rates, the temperature region in which austenite can grow is smaller and lower compared to that obtained at a lower cooling rates [7]; this results in reduced austenite grain growth at the high cooling rates.

Although the measured dependence of the austenite grain size on \( \bar{r}/f \) is not well described by Eq. (5.6) for the high cooling rates, such as air cooling and 4.5 °C/s, the qualitative trend is consistent with the conventional theory; namely, the larger \( \bar{r}/f \), the larger the austenite grain size. However, two of the data points for a cooling rate of 1.2 °C/s, clearly show negative slope in Fig. 5.39. This phenomenon is considered to be due to the different way that the second phase particles affect the austenite grain growth for the medium cooling rate, as compared to that obtained for the slow cooling rate at which Eq. (5.6) is valid and that obtained for high cooling rates at which the cooling rate affects the austenite grain size more than does the particle size and distribution.

To pursue this possibility, the particle size distribution of the two samples cooled at 1.2 °C/s has been examined more thoroughly. From Figs. 5.26 and 5.30, the following points can be described:
Chapter 5. Results and Discussion

- The number of particles in Steel A is larger than that in Steel B; however, most of the particles in Steel A are smaller than 1 μm.
- The number of particles which have a diameter of approximately 1 μm, those between 0.6 μm and 3 μm, is larger in Steel B than in Steel A.
- The average particle diameter is larger for Steel B than for Steel A.

From these observations, it is suggested that the fine particles which are effective for pinning austenite grain growth in the classical theory, as can be described by Eq. (5.6), are not capable of pinning the coarse as-cast austenite grains. In order to test this supposition, the particles which existed on grain boundaries were examined for the sample of Steel B cooled at 1.2 °C/s; this steel showed a smaller austenite grain size than Steel A at the same cooling rate. The results are summarized in Table 5.7 and the corresponding photographs of the particles are shown in Figs. 5.40-5.55.

**Table 5.7 The particles found on grain boundaries in Steel B cooled at 1.2°C/s.**

<table>
<thead>
<tr>
<th>Particle number *</th>
<th>Elements detected</th>
<th>Corrected Diameter ** (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Ca-O-1</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>2.7</td>
</tr>
<tr>
<td>Al-Ca-O-2</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>4.4</td>
</tr>
<tr>
<td>Al-Ca-O-3</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>2.5</td>
</tr>
<tr>
<td>Al-Ca-O-4</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>6.0</td>
</tr>
<tr>
<td>Al-Ca-O-5</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>3.9</td>
</tr>
<tr>
<td>Al-Ca-O-6</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>2.2</td>
</tr>
<tr>
<td>Al-Ca-O-7</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>2.8</td>
</tr>
<tr>
<td>Al-Ca-O-8</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>2.7</td>
</tr>
<tr>
<td>Al-Ca-O-9</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>1.8</td>
</tr>
<tr>
<td>Al-Ca-O-10</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>1.8</td>
</tr>
<tr>
<td>Al-Ca-O-11</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>2.2</td>
</tr>
<tr>
<td>Al-Ca-O-12</td>
<td>Al, Ca, Mn, Si, Ti</td>
<td>1.0</td>
</tr>
<tr>
<td>Al-1</td>
<td>Al, Mn, Si, Ti</td>
<td>2.5</td>
</tr>
<tr>
<td>Al-2</td>
<td>Al, Mn, Si, Ti</td>
<td>0.9</td>
</tr>
<tr>
<td>Al-3</td>
<td>Al, Mn, Si, Ti</td>
<td>1.2</td>
</tr>
<tr>
<td>Al-4</td>
<td>Al, Mn, Si, Ti</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*) Corresponds to the identification number of photographs, implying the constituents of particles.

**) The particle diameter was measured on photographs at x6000 magnification. The scale on these photographs was calibrated using a standard specimen examined at the same SEM conditions. This revealed that the scale was 11.3% shorter than the actual length requiring the values listed in Table 5.6, to be corrected accordingly.
Chapter 5. Results and Discussion

Fig. 5.40 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.

(a) Low magnification.

(b) High magnification.

(Particle No.: Al-Ca-O-1)
(a) Low magnification.

(b) High magnification.

Fig. 5.41 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.
(Particle No.: Al-Ca-O-2)
Chapter 5. Results and Discussion

Fig. 5.42  SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s. (Particle No.: Al-Ca-O-3)
Chapter 5. Results and Discussion

(a) Low magnification.

(b) High magnification.

Fig. 5.43 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.
(Particle No.: Al-Ca-O-4)
Chapter 5. Results and Discussion

Fig. 5.44 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.

(a) Low magnification.

(b) High magnification.

(Particle No.: Al-Ca-O-5)
Chapter 5. Results and Discussion

(a) Low magnification.

(b) High magnification.

Fig. 5.45 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.

(Particle No.: Al-Ca-O-6)
Chapter 5. Results and Discussion

Fig. 5.46 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.
(Particle No.: Al-Ca-O-7)
Chapter 5. Results and Discussion

(a) Low magnification.

(b) High magnification.

Fig. 5.47 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.
(Particle No.: Al-Ca-O-8)
Chapter 5. Results and Discussion

(a) Low magnification.

(b) High magnification.

Fig. 5.48 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.

(Particle No.: Al-Ca-O-9)
Chapter 5. Results and Discussion

(a) Low magnification.

(b) High magnification.

Fig. 5.49 SEM photographs of particles on boundaries in Steel B cooled at 1.2° C/s.

(Visible: Al-Ca-O-10)
Chapter 5. Results and Discussion

Fig. 5.50 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.

(a) Low magnification.

(b) High magnification.

(Particle No.: A1-Ca-O-11)

(Particle No.: Al-Ca-O-11)
Chapter 5. Results and Discussion

Fig. 5.51 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.
(= Particle No.: Al-Ca-O-12)

(a) Low magnification.

(b) High magnification.
(a) Low magnification.

(b) High magnification.

Fig. 5.52 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.
(Particle No.: Al-1)
Chapter 5. Results and Discussion

Fig. 5.53 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.

(a) Low magnification.

(b) High magnification.

(Particle No.: Al-2)
Chapter 5. Results and Discussion

Fig. 5.54 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.

(a) Low magnification.

(b) High magnification.

(Particle No.: Al-3)
Chapter 5. Results and Discussion

(a) Low magnification.

(b) High magnification.

Fig. 5.55 SEM photographs of particles on boundaries in Steel B cooled at 1.2°C/s.
(Particle No.: Al-4)
Chapter 5. Results and Discussion

All of the particles were considered to be oxides judging from their rounded shape and their chemical compositions. The size of the particles was quite large, most being larger than 1 μm, which supports the supposition that the fine particles are not effective in pinning the coarse as-cast austenite grain boundaries. This can be explained by the influence of thermal activation on the interaction between particles and migrating grain boundaries. Gore et al. [44] reported that the thermally activated unpinning of boundaries was found to become significant at small particle sizes, \( \ll 1 \mu m \), and high temperatures such as above 870°C. In the present study, the lower limit of particle size observed was 0.05 μm.

5.7. Application of Gladman's Model

To support the previous discussion, Gladman's model [17] was applied to calculate the energy barrier of unpinning as a function of particle diameter. The calculation conditions were as follows:

1) The maximum particle radius for which the calculation was carried out was 10 μm.
2) The average austenite grain radius of the matrix was assumed to be \( R_0 = 0.4, 0.8, \) and 1.4 mm.
3) The volume fraction of particle, \( f \) was taken to be 0.001.
4) The ratio of the radii of growing grains to matrix grains, \( Z \) was examined for values of 1.0, 1.2, 1.4, 1.6, 2.0, 3.0, 4.0, 5.0, 6.0, and 8.0.
5) The surface energy per unit area of boundary of austenite, \( \gamma \), was assumed to be 0.8 J/m².

These conditions were chosen to simulate the sample of Steel B cooled at 1.2 °C/s. The results are shown in Figs. 5.56-5.58.
Chapter 5. Results and Discussion

Matrix Grain Radius=0.4mm, f=0.001

(a) Ratio of radii of growing grains to matrix grains: Z=1.0, 1.2, 1.4

Matrix Grain Radius=0.4mm, f=0.001

(b) Ratio of radii of growing grains to matrix grains: Z=1.4
Chapter 5. Results and Discussion

(c) Ratio of radii of growing grains to matrix grains: \( Z = 1.6, 2.0, 3.0 \)

(d) Ratio of radii of growing grains to matrix grains: \( Z = 4.0, 5.0, 6.0, 8.0 \)

Fig. 5.56 Effect of particle size on the barrier to grain growth. The average austenite grain radius = 0.4 mm, the volume fraction of particles = 0.001, and the surface energy per unit area of boundary of austenite = 0.8 J/m².
Chapter 5. Results and Discussion

Matrix Grain Radius = 0.8 mm, f = 0.001

(a) Ratio of radii of growing grains to matrix grains: Z = 1.0, 1.2, 1.4

Matrix Grain Radius = 0.8 mm, f = 0.001

(b) Ratio of radii of growing grains to matrix grains: Z = 1.4
Chapter 5. Results and Discussion

Fig. 5.57 Effect of particle size on the barrier to grain growth. The average austenite grain radius = 0.8 mm, the volume fraction of particles = 0.001, and the surface energy per unit area of boundary of austenite = 0.8 J/m².
Chapter 5. Results and Discussion

Matrix Grain Radius=1.4 mm, \( f = 0.001 \)

(a) Ratio of radii of growing grains to matrix grains: \( Z = 1.0, 1.2, 1.4 \)

Matrix Grain Radius=1.4 mm, \( f = 0.001 \)

(b) Ratio of radii of growing grains to matrix grains: \( Z = 1.4 \)
Chapter 5. Results and Discussion

Fig. 5.58 Effect of particle size on the barrier to grain growth. The average austenite grain radius = 1.4 mm, the volume fraction of particles = 0.001, and the surface energy per unit area of boundary of austenite = 0.8 J/m².
Chapter 5. Results and Discussion

For $Z$ (the ratio of the radii of growing grains to the matrix grains) = 1.0 and 1.2, the energy barrier increases as the particle diameter increases regardless of the average austenite grain size of the matrix up to the particle diameter of 10 $\mu$m employed in the calculation. However, if $Z$ is greater than 1.4, it can be seen that there is a specific particle diameter corresponding to a maximum energy barrier for each condition. Denoted this particle diameter as $r^*$, it can be seen that $r^*$ varies depending on the average austenite grain size and $Z$ which represents the heterogeneity of the austenitic structure. One qualitative explanation is as follows:

1) As reviewed in Chapter 2, the total energy change associated with the unpinning of a single particle, $E_r$, is

$$E_r = E_p + E_i = \gamma \cdot (\Delta A) + \frac{2\pi r^2 \gamma}{3R_0 f} \left(\frac{2}{Z} - \frac{3}{2}\right)$$ (see Eq. (2.27));

therefore, if $Z < 4/3 = 1.33$, the second term of the equation above, which represents the energy release per particle due to grain growth, becomes positive, which means that there is an increase in boundary area and the heterogeneity is not large enough for grain growth to occur. As a result, the total energy change associated with the unpinning of a single particle, $E_r$, increases monotonically as the particle diameter, $r$, increases as shown in Eq. (2.27). $\Delta A$ is also a function of $r$, as can be seen in Eqs. (2.19) and (2.20), where, $\Delta A$ increases as $r$ increases. Therefore, the energy barrier to grain growth increases monotonically as the particle diameter increases. In the case of $Z = 1.4$, which is slightly greater than $4/3 = 1.33$, the energy barrier to grain growth increases monotonically as $r$ increases up to $r = 10 \mu$m for $R_0 = 0.8\text{mm}$ and 1.4 mm; however, the energy barrier is expected to decrease at some point as $r$ increases further, as is seen in the case of $Z = 1.4$ and $R_0 = 0.4\text{mm}$.

2) If $Z > 4/3 = 1.33$, there is a decrease in the boundary area, which is a requirement for grain growth to occur, and the second term of Eq. (2.27) becomes negative. For this condition, the balance between the increase in the area of grain boundary due to the distortion exerted by a pinning particle and the decrease in the area due to grain growth should be
Chapter 5. Results and Discussion

considered. For particles of small diameter, the first term, namely the increase in the area due to the distortion is dominant, resulting in a larger energy barrier for larger particles. On the other hand, as the particle diameter increases, the number of particles per unit area of grain boundary may decrease, assuming the volume fraction, \( f \), is constant. As a result, the second term, the energy release per particle due to grain growth, becomes larger and dominant in Eq. (2.27), resulting in a decrease in the energy barrier for larger particles.

Thus, the presence of a particle diameter associated with a peak energy barrier, \( r^* \), can be understood. The results of \( R_0 \) and \( r^* \) are summarized in Table 5.8 and the \( r^* \) vs. \( Z \) is plotted in Fig. 5.59. It can be seen that \( r^* \) increases as \( Z \) decreases, and that \( r^* \) increases as \( R_0 \) increases.

<table>
<thead>
<tr>
<th>( R_0 ) (mm)</th>
<th>1.6</th>
<th>2.0</th>
<th>3.0</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
<th>8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>1.4</td>
<td>0.74</td>
<td>0.40</td>
<td>0.36</td>
<td>0.34</td>
<td>0.30</td>
<td>0.28</td>
</tr>
<tr>
<td>0.80</td>
<td>2.9</td>
<td>1.4</td>
<td>0.90</td>
<td>0.72</td>
<td>0.68</td>
<td>0.62</td>
<td>0.58</td>
</tr>
<tr>
<td>1.4</td>
<td>5.4</td>
<td>2.6</td>
<td>1.5</td>
<td>1.3</td>
<td>1.2</td>
<td>1.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 5.8 The values of \( r^* \) (\( \mu m \)) for various \( R_0 \) and \( Z \).

![Fig. 5.59 Effect of austenite grain size and heterogeneity on \( r^* \).](image-url)
Chapter 5. Results and Discussion

Although the particle size used in Gladman's model is the average of the size distribution of particles, which assumes that all of the particles have the same radius, \( r \), occupying the volume fraction, \( f \), in the matrix, these results provide information as to the particle size that is effective for pinning the coarse as-cast austenite grains and helps to explain the preponderance of larger particles found on the austenite grain boundaries (Table 5.7).
6. Conclusions

The results of this research can be summarized as follows:

1) Ti enriched particles whose diameters were in the range of 0.1 - 0.5 μm did not effectively inhibit the as-cast austenite growth.

2) Oxides with larger diameters than TiN particles were effective pinning particles for the grain boundaries of as-cast austenite grain, in the temperature region of 1200 to 1300°C.

3) The higher cooling rates examined in this study, 4 ~ 20 °C/s, reduced austenite grain growth more effectively than second phase particles.

It is thought that the amount and the size of TiN particles in Steel B were not large enough for pinning the coarse as-cast austenite grains in the experimental condition examined in this work. However, if more titanium is added to a steel, titanium nitrides may form during solidification resulting in their larger diameters [45], which will be favorable in terms of pinning austenite grain boundary and reducing grain growth.

The experimental results presented in this thesis suggest that the size and composition of second phase particles which are effective for the pinning of grain growth may vary depending on the temperature where the grain growth takes place and on the grain size of the matrix.

The cooling rates applied in this research, correspond to those at the mid-thickness of slabs whose thickness is 10 ~ 20 mm in a thin slab casting process, as shown in Eq. (1.1). For thicker slabs, slower cooling rates would be expected at the mid-thickness, even though the cooling rates in the surface region will remain high. For this reason, a relatively thick slab, whose thickness is e.g. 50 mm, second phase particles will be effective to producing a fine microstructure throughout the thickness.

The following recommendations are made for future work:
Chapter 6. Conclusions

1) Quantify the effect of cooling rate on the amount and particle diameter of oxides forming during melting.

2) Find a proper condition for the formation of TiN particles which are effective for pinning as-cast austenite grain boundaries at the high temperatures following solidification.

3) Relate the as-cast austenitic structure to the ferritic structure and the presence of second phase particles which form at different temperatures.
References


References


[22] A Nippon Steel Corporation Internal Report, (Unpublished work)


References


Appendix (The Program for Gladman Model)

A.1 Flowchart

Start

Input austenite grain radius (Ro) and Z

Input particle radius (r)

Calculation of pinning energy for a given boundary displacement (S)

S > S_max?

Yes

Determine the minimum and the maximum for the pinning energy (PE_min, PE_max)

Calculate the energy barrier for unpinning (PE_max - PE_min)

Print to output file

r > r_max?

Yes

Need another calculation for another Z and Ro?

No

Stop
Appendix

A.2 Source Code

************************************************************************
C Program to calculate the energy barrier for grain growth
************************************************************************
C MAIN PROGRAM
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

DIMENSION GS(10), ZZ(10)

C GS:Austenite grain size; dimension:micron
GS(1)=400.D0
GS(2)=1000.D0
GS(3)=1200.D0
GS(4)=1400.D0
GS(5)=1600.D0
GS(6)=1800.D0
GS(7)=2000.D0
GS(8)=2200.D0
GS(9)=2400.D0
GS(10)=2600.D0

ZZ(1)=1
ZZ(2)=1.2D0
ZZ(3)=1.4D0
ZZ(4)=1.6D0
ZZ(5)=2.D0
ZZ(6)=3.D0
ZZ(7)=4.D0
ZZ(8)=5.D0
ZZ(9)=6.D0
ZZ(10)=8.D0

C*
DO 10 I=1,10
DO 20 J=1,10

RO=GS(I)
Z=ZZ(J)

OPEN (UNIT=5, FILE='PIN.TXT', STATUS='UNKNOWN')
WRITE (5,501) RO, Z
501 FORMAT (4H R0=,1F6.1,3H Z=,1F3.1)
CALL ENERGY(RO,Z)

20 CONTINUE
10 CONTINUE

STOP
END
Appendix

SUBROUTINE ENERGY (R0,Z)
************************************************************************
C This subroutine calculates the energy barrier for grain growth.
************************************************************************
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON /A01/ PI
DIMENSION ET(20001), H(100), PR(100)
CALL DATAIN (N,GAMMA,F)
OPEN (UNIT=5, FILE='PIN.TXT', STATUS='UNKNOWN')
WRITE (5,501) N,GAMMA,F
501 FORMAT (3H N=,112,7H GAMMA=,1F3.1,3H F=,1F6.4)
R=0.D0
PR(1)=R
H(1)=0.D0
C*
DO 30 J=2,101
R=R+0.1D0
PR(J)=R
CALL INIT (S,ET,ET_MAX,ET_MIN)
DO 10 I=2, 20001
C*
S=S+0.001D0
IF (S.GT.(2.D0*R)) GO TO 20
CALL AREA_B (S,R,N,AREA)
CALL ENE_GG (S,R,GAMMA,R0,F,Z,E1)
CALL ENE_TO (1,AREA,GAMMA,E1,ET)
IF (I.GE.3) CALL MINMAX (I,ET,ET_MAX,ET_MIN)
10 CONTINUE
20 H(J)=ET_MAX-ET_MIN
IF ((J.GT.10).AND.(H(J).LE.0.D0)) GO TO 40
30 CONTINUE
40 CALL OUTPUT (J,PR,H)
RETURN
END

SUBROUTINE DATAIN (N,GAMMA,F)
Appendix

************************************************************************
C This subroutine reads the input data to run the program.
************************************************************************

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON /A01/ PI

DATA PI/3.141592D0/

C Dimension of S: micron, R: micron, R0: micron
C S=0.0
C R=0.0350D0
C R0=1800.D0

N=4
C Z=8.D0
F=0.001D0

C Dimension of GAMMA: Joule/m**2
GAMMA=0.8D0

RETURN
END

SUBROUTINE INIT (S,ET,ET_MAX,ET_MIN)
************************************************************************
C This subroutine initializes some values.
************************************************************************

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

DIMENSION ET(20001)

S=0.D0
ET_MAX=0.D0
ET_MIN=0.D0

DO 10 I=1, 1000
  ET(I)=0.D0
10 CONTINUE

RETURN
END

FUNCTION ASH(X)
************************************************************************
C This subroutine calculates the inverse function of hyperbolic sine.
************************************************************************

IMPLICIT DOUBLE PRECISION (A-H,O-Z)

ASH=DLOG(X+DSQRT(X**2.D0+1.D0))

RETURN
END
Appendix

SUBROUTINE AREA_B (S,R,N,AREA)
************************************************************************
C This subroutine calculates the change in the area of the grain boundary including the effect of the distorted planar boundary.
************************************************************************
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON /A01/ PI

AREA=0.D0

A=S*DSQRT(R**2.D0-(0.5DO*S)**2.D0)
T1=ASH(A/2.DO/DBLE(FLOAT(N))**2.D0/R**2.D0)
T2=ASH(S**2.D0/2.DO/A)
T3=DSQRT(1.D0+(2.DO*(DBLE(FLOAT(N))**2.D0)*(R**2.D0)/A)**2.D0)
T4=DSQRT(1.D0+(2.DO*A/(S**2.D0))**2.D0)

AREA=-0.5DO*PI*A*(T1-T2-T3+T4)

A_INIT=PI*(DBLE(FLOAT(N))*R)**2.DO-PI*(R**2.D0)

AREA=AREA-A_INIT

C Dimension of AREA: (micron)**2

RETURN
END

SUBROUTINE ENE_GG (S,R,GAMMA,RO,F,Z,E1)
************************************************************************
C This subroutine calculates the energy release per particle due to grain growth.
************************************************************************
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
COMMON /A01/ PI

El =2.DO*S*PI*(R**2.D0)*GAMMA/(3.DO*RO*F)
E1=E1*(2.DO/Z-1.5D0)/(10.D0**12.DO)

RETURN
END

SUBROUTINE ENE_TO (I,AREA,GAMMA,E1,ET)
************************************************************************
This subroutine calculates the total energy change associated with the unpinning of a single particle.
************************************************************************
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

DIMENSION ET(20001)

118
Appendix

\[ ET(I) = \text{AREA} \times \text{GAMMA} / (10. \times D0^{12} \times D0) + E1 \]

RETURN
END

SUBROUTINE MINMAX (I, ET, ET_MAX, ET_MIN)
************************************************************************
C This subroutine calculates the minimum and maximum values of
C the total energy change which is a function of grain boundary
C displacement.
************************************************************************
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

DIMENSION ET(20001)

D1 = ET(I-1) - ET(I-2)
D2 = ET(I) - ET(I-1)
PROD = D1 \times D2

IF ((D1 > 0.D0) .AND. (PROD < 0.D0)) ET_MAX = ET(I-1)
IF ((D1 < 0.D0) .AND. (PROD < 0.D0)) ET_MIN = ET(I-1)

RETURN
END

SUBROUTINE OUTPUT (JJ, PR, H)
************************************************************************
C This subroutine outputs the results.
************************************************************************
IMPLICIT DOUBLE PRECISION (A-H,O-Z)

DIMENSION PR(100), H(100)

OPEN (UNIT=5, FILE='PIN.TXT', STATUS='UNKNOWN')

DO 10 J = 1, JJ-1
WRITE (5,502) PR(J), H(J)
502 FORMAT (1F5.2,1E14.6)
10 CONTINUE

RETURN
END