Influence of Oxide Particles and Residual Elements on Microstructure and Toughness in the Heat-Affected Zone of Low-Carbon Steel Deoxidized with Ti and Zr

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The microstructure and toughness in Fe–0.04%C–1.85%Mn–0.03%Si–0.018%Nb steel deoxidized with Ti and Zr have been studied as functions of particle characteristics, austenite grain size and soluble Ti and Zr contents using a simulated HAZ (heat affected zone) thermal cycle (peak temperature, 1400°C; peak holding time, 60 s; time of cooling from 800 to 500°C, 70 s) and submerged arc welding (heat input of 15 kJ/mm), respectively. Microstructures were studied in samples containing 1.0 to 1.5 μm-diameter oxide particles numbering 500 to 2000 mm–2 and with a soluble oxygen content of 10 to 30 ppm (measured before casting) and soluble Ti and Zr contents of 50–150 ppm. The γ grain size after HAZ thermal cycle in the range between 200 and 600 μm is controlled by pinnning and solute drag. Small γ grain size below 300 μm was obtained with high soluble Ti and Zr contents of 110–160 ppm, whereas large γ grain size above 300 μm was obtained with low soluble Ti and Zr contents of 60–110 ppm. Two types of microstructures that showed high Charpy absorbed energy (VE(–10°C)= 150–250 J and VE(–50°C)= 50–150 J) were observed independent of γ grain size: One is acicular ferrite and a small amount of grain boundary ferrite (GBF) and ferrite side plate (FSP) and the other is GBF, FSP and granular bainitic ferrite. It was observed that low VE(T) values are attributed to the formation of porosity, large-size particles, carbides (+nitrides) and lathe bainitic ferrite.

KEY WORDS: titanium; zirconium; deoxidation; austenite grain size; microstructure refinement; HAZ; acicular ferrite; Charpy absorbed energy.

1. Introduction

Increasing demand for and dwindling supplies of energy resources has pushed the development of oil and natural gas fields into more difficult regions globally. The structural steels used in these fields are fabricated by welding. Their mechanical properties are greatly improved in terms of strength and toughness if their microstructures are largely intragranular acicular ferrite and if the amount of the grain boundary ferrite and sideplate ferrite is minimized. Therefore, the microstructures in weld metal and weld heat affected zone (HAZ) have been widely studied. The microstructure is a function of metal composition, inclusion characteristics (type, number, size and distribution), austenite grain size and cooling rate.

Thewlis1) has performed extensive experiments and observed the relationships among volume fractions of acicular ferrite, austenite grain size and the number, size and composition of inclusions. His results suggest that the maximum fraction of acicular ferrite can be achieved at an optimum austenite grain size, which depends on the alloy elements of the steel weldment and the inclusion type. The balance of ferrite nucleation is shifted from the austenite grain boundaries to the intragranular regions above a critical austenite grain size, which becomes finer in the presence of effective nucleating inclusions. It is considered that the combination of austenite grains with proper size and a high density of effective intragranular inclusions is the key to obtaining a fine microstructure.

Oxide inclusions may influence the γ/α transformation, not only by acting as intragranular nucleation sites during cooling, but also by pinning the migrating austenite grain boundaries and thereby controlling the grain boundary surface area for ferrite nucleation. Many researchers have focused on the effect of specific inclusions on the formation of acicular ferrite in weld metal and HAZ. An extensive
review has been published by Koseki and Thewlis\textsuperscript{30} on this topic. It was found that as Ti and/or Zr contents increase, the amount of intragranular ferrite increases until it reaches a maximum.\textsuperscript{33} The generally held view is that alloying elements such as B in weld metals influence acicular ferrite formation by retarding transformation at austenite grain boundaries ferrite and encouraging transformation on inclusions inside the grains. Furthermore, the grain boundary carbides are formed by excess addition of carbide-forming elements such as B, Zr, Ti, Nb and Cr, and act as nucleation-inhibiting agents at early reaction times, and favor ferrite nucleation when they are coarse.

The transition from acicular ferrite to bainite in Fe–Cr–C weld metal was studied by Babu and Bhadeshia.\textsuperscript{34} It was found that bainitic microstructures begin to dominate with high alloying element content because the allotriomorphic ferrite layers begin to diminish, leaving the austenite grain surface for the nucleation of bainite. This indicates that, by the addition of an appropriate amount of alloying elements, the formation of allotriomorphic ferrite layers causes a reduction in the number density of austenite grain boundary nucleation sites and hence, promotes the preferential formation of acicular ferrite at the expense of bainite.

The present paper presents the results of a systematic study of the influence of oxide particles and soluble Ti and Zr on microstructure refinement in simulated HAZ and on Charpy absorbed energy in HAZ after submerged arc welding of Fe–0.04%C–1.85%Mn–0.03%Si–0.018%Nb steel. Particular attention is paid to the microstructure and toughness in terms of austenite grain size and soluble Ti and Zr contents.

2. Experimental
2.1. Materials
Deoxidants: Pure Ti and Al, Fe–50mass%Zr (Ce) alloy and a Ni–10mass%Mg (Ca) alloy were used for Ti, Al, Zr, Ce, Mg and Ca deoxidations. Percent and ppm represent mass% and mass ppm, hereinafter.

Oxidants: A sintered FeO powder and/or an Fe–O alloy was used in some experiments for additional oxidation of melts and for formation of supplementary particles. Tablets of pressed FeO powder were sintered in an Fe crucible at 150 kW) under N\textsubscript{2} (100 Torr) and Ar (300 Torr) atmosphere. Carbon, Mn and Si were added in appropriate amounts. A quartz sampler was used for the sampling and analysis of C, Mn and Si contents in the melt. Then, other elements except for deoxidants and oxidants were added. After 30 s of final addition, the oxygen activity was measured by an oxygen sensor of ZrO\textsubscript{2}–9mol%MgO electrolyte with the Cr/Cr\textsubscript{2}O\textsubscript{3} reference electrode, and 90 s later the metal was sampled. After 20 s all melt was cast during 40 s into a cylindrical ingot mold.

Five different methods for addition of deoxidants/oxidants in the melt were used.

i) \( M \) and \( O–M \) methods. \( M \) method: A Ni–10\%Mg alloy was added (sample M). \( O–M \) method: Initial O content was increased by adding FeO pieces enclosed in an Fe tube and an Fe–50\%Zr alloy was added (sample 54).

ii) Ti/\( M \) and \( O–Ti/M \) methods. Ti/\( M \) method: Ti was added and 1 min later the appropriate amount of \( M (M = Mg, Zr \) and Ce) was added (samples TM, 2 and 4). \( O–Ti/M \) method: Initial O content in the melt was increased by adding FeO pieces, and after 100 s the appropriate amount of Ti and Fe–50\%Zr alloy was added. After sampling and measuring oxygen activity, the melt was cast in a manner similar to that mentioned in the \( M \) method. In some experiments Al was added in an appropriate amount, followed by the method mentioned above.

iii) Ti/\( M–O \) and \( O–Ti/M–O \) methods. Ti/\( M–O \) method: Ti was added, followed by an Fe–50\%Zr alloy. Then, an Fe–0.12\%O alloy was added in order to control the contents of soluble Ti and Zr. \( O–Ti/M–O \) method: Initial O content in the melt was increased by adding FeO pieces and then, Ti was added, followed by an Fe–50\%Zr and Fe–0.12\%O alloy additions. After sampling and measuring the oxygen activity, the melt was cast in a manner similar to that mentioned in the \( M \) method. In some experiments Al was added (sample 44) and instead of Zr an Fe–50\%Ce alloy was added (sample 21).

iv) Ti/\( M1/M2 \) method: After Ti addition, a Ni–10\%Mg alloy was added, followed by an Fe–50\%Zr (or an Fe–50\%Ce) alloy. In some experiments (sample 55), the initial oxygen was increased by adding FeO pieces, followed by Ti, Fe–50\%Zr alloy and Ni–10\%Ca alloy additions. The purpose of this multiple addition of deoxidants was to produce particles with different compositions.

v) Ti–\( M1/O–M2 \) method: This is the combination of the \( iii \) and \( iv \) methods, but the final Fe–0.12\%O alloy was not added. The purpose of this addition method was to produce many particles with different compositions. In all deoxidation methods the soluble oxygen content before Ti addition was in the range of 30 to 60 ppm.

2.3. Simulated HAZ Thermal Cycle
An ingot sample was sliced into 30×15×3 mm. This sample was set on a silica cell connected with a high alumina tube and then lowered to the even temperature zone of 1400°C in a resistance furnace under an overpressure of Ar. A thermocouple (Pt–6\%Rh/Pt–30\%Rh) was located just above the silica cell. After holding for 60 s, the sample was pulled up by limiting the time of cooling from 800 to 500°C (\( \Delta T = 50°C \)) to 70 s. This thermal cycle condition was chosen to simulate the weld heat cycle. Hereafter, we call this test the welding heat treatment “\( WHT \)”. In some experiments the peak holding time was changed.
The Charpy impact test was carried out on the submerged arc-welded sample. The submerged arc welding was conducted under a weld heat input of 15 kJ/mm. This thermal cycle is well simulated to the condition of 3 beads per layer of flux copper backing (FCB) welding.

2.4. Welding Method and Charpy Impact Test
Weld metal was prepared as follows: An ingot sample was forged to a cylindrical shape (30 mm in diameter) after heating at 1200°C for 1 hour. This sample was heated at 900°C for 1 hour, followed by water quenching. Then, it was tempered at 600°C for 1 hour. Submerged arc welding (heat input is 15 kJ/mm) was carried out using 3 electrodes and flux copper backing. A notch was made at the position of the fusion boundary where the HAZ: welded metal ratio was 50:50. Three Charpy impact tests were made for each selected temperature in the range from –10 to –50°C.

### Table 1. Chemical compositions of metal phase.

| Sample number | Deoxidation       | [Ti] sol./insol. | [Mg] sol./insol. | [Zr] sol./insol. | [Ce] sol./insol. | [Al] sol./insol. | T.O   | T.N   | mass ppm |
|---------------|-------------------|------------------|------------------|------------------|------------------|----------------|-------|-------|----------|
| M             | Mg                | 1/13             | 3/28             | –                | –                | 1/40           | –     | –     | 9        |
| TM            | Ti/Mg             | 39/20            | 3/15             | –                | –                | 2/16           | –     | –     | 23       |
| 54            | O–Zr              | 1/4              | –                | 6/15             | –                | 3/2            | 31    | 39    | 41       |
| 4             | Ti/Zr             | 156/8            | –                | 1/126            | 1/4              | 3/29           | 13    | 25    | 33       |
| 22            | O–Ti/Zr–O         | 94/11            | –                | 4/36             | –                | 5/2            | 25    | 36    | 41       |
| 23            | Ti/Zr–O           | 82/14            | –                | 13/25            | –                | 2/2            | 23    | 35    | 38       |
| 31            | O–Ti/Zr           | 137/2            | –                | 3/60             | –                | 19/1           | 18    | 38    | 44       |
| 32            | O–Ti/Zr–O         | 82/7             | –                | 2/23             | –                | 11/12          | 31    | 26    | 30       |
| 33            | O–Ti/Zr–O–O       | 58/3             | –                | 1/10             | –                | 3/19           | 20    | 37    | 26       |
| 34            | Ti/Zr–O           | 58/11            | –                | 1/16             | –                | 3/14           | 43    | 40    | 38       |
| 35            | Ti/Zr–O           | 10/4             | –                | 2/7              | –                | 0/15           | 31    | 37    | 47       |
| 41            | O–Ti/Zr           | 128/12           | –                | 0/100            | –                | 36/8           | 19    | 51    | 60       |
| 42            | O–Ti/Zr           | 91/12            | –                | 1/61             | –                | 16/5           | 23    | 38    | 44       |
| 43            | O–Ti/Zr–O         | 62/0             | –                | 0/21             | –                | 13/14          | 20    | 26    | 46       |
| 44            | O–Al–Ti/Zr–O      | 57/5             | –                | 0/12             | –                | 12/9           | 22    | 31    | 46       |
| 45            | O–Al–Ti/Zr        | 112/0            | –                | 1/76             | –                | 22/5           | 15    | 44    | 48       |
| 51            | O–Al–Ti/Zr–O      | 145/36           | –                | 8/22             | –                | 16/6           | 19    | 25    | 49       |
| 52            | O–Al–O–Ti/Zr      | 144/35           | –                | 5/9              | –                | 13/3           | 26    | 26    | 41       |
| 53            | O–Al–O–Ti/Zr      | 106/15           | –                | 2/0              | –                | 10/5           | 21    | 29    | 36       |
| 2             | Ti/Ce             | 140/26           | –                | –                | 2/120            | 1/10           | 17    | 19    | 35       |
| 21            | O–Ti/Ce–O         | 103/11           | –                | –                | 12/46            | 4/2            | 20    | 37    | 37       |
| 5             | Ti/Mg/Zr          | 37/30            | –                | 0/24             | –                | 2/33           | 20    | 24    | 35       |
| 3             | Ti/Mg/Ce          | 38/15            | –                | –                | 1/36             | 2/21           | 19    | 15    | 34       |
| 55            | O–Ti/Zr–Ca        | 4/9              | –                | 2/0              | –                | 7/4            | 27    | 68    | 59       |
| 25            | O–Ti/Zr–O/Mg      | 46/16            | 0/32             | 6/12             | –                | 2/2            | 22    | 47    | 39       |
| 11            | Ti/Zr–(O/Zr)x2    | 90/8             | –                | 233/581          | 21/3             | 8              | 11    | 41       |
| 13            | Ti/Zr–O/Ce–O/Zr   | 77/4             | –                | 134/381          | 0/65             | 6/2            | 10    | 5     | 36       |
| 15            | Ti/Zr–O–Zr–O/Ce   | 76/2             | –                | 69/245           | 25/178           | 4/35           | 11    | 7     | 42       |
| 12            | Ti/Mg–(O/Zr)x2    | 100/9            | 8/6              | 176/562          | –                | 11/6           | 13    | 17    | 39       |

* * measured by oxygen sensor before casting.
2.5 Particle Characteristics, γ Grain Size and Microstructure

The planar size distribution of particles on a polished cross section of each sample was observed using a scanning electron microscope (SEM) with an electron probe microanalyzer (EPMA) at a 1 000 times magnification. The particle greater than 0.5 μm in diameter were measured. The particle diameter, \( d_A \), was estimated as the diameter of a circle with the same area as a sectioned inclusion particle using a semi-automatic image analyzer. The spatial size distribution of particles was obtained using a potentiostatic electric extraction method. Since a film filter of 0.05 μm was used, particles above this size were observed. The particles on the film filter after electrolytic extraction were observed by SEM with EPMA at magnifications of 1 000, 2 000, 5 000 and 10 000. The spatial size, \( d_\gamma \), was estimated as the diameter of the equivalent spherical particles, which would have the same area as an imaged particle on an SEM photomicrograph. More details on this size estimation method are given elsewhere.5,6

The composition of spatial particles on a filter with an open pore size of 0.1 or 1 μm was measured using an SEM with an EPMA. The γ grain size was revealed by etching with 3% nital and measured by the method described elsewhere.7,8 The microstructure was observed after etching with a saturated picric acid and a CuCl₂ solution.9

2.6. Chemical Analysis

The samples in Ti and Zr deoxidation experiments were dissolved with 10%AA (10v/v% acetylacetone -1 w/v% tetramethylammonium chloride - methanol solution) using a potentiostatic electrolytic extraction method. The samples in Mg and Ce deoxidation experiments were dissolved with 2%TEA (2v/v% triethanolamine - 1w/v% tetramethylammonium chloride - methanol solution). The solution after filtration and the residue on the film filter were analyzed for their contents of soluble and insoluble elements using inductively coupled plasma-emission spectrometry (ICP-AES). More details are given elsewhere.10 Total oxygen and total nitrogen contents in the metal were determined using an inert gas fusion-infrared absorptiometry and inert gas fusion-thermal conductivity measurement method, respectively.

3. Results and Discussion

The contents of soluble and insoluble M (M=Ti, Mg, Zr, Ce and Al) and those of total O and total N in an ingot sample are summarized in Table 1, together with the values for oxygen activity, \( a_o \), measured by an oxygen sensor before mold casting. The oxygen activities in the samples of M and TM were not measured. The metal composition was as follows: C=0.04%, Si=0.03%, Mn=1.85%, P<0.001%, S<0.001%, Cu=0.39%, Cr=0.1% and Nb=0.018%. The numbers of planar particles with \( d_A > 0.5 \mu m \) and \( l_{max} > 20 \mu m \) \( (l_{max} \) is the maximum length of particle) per unit area on a polished cross section, \( N_A \), and the mean values of spatial particle diameter, \( d_\gamma \), are given in Table 2. The mean γ grain size after WHT (peak temperature, \( T_p=1 400°C \), peak holding time, \( t_p=60 s \) and \( \Delta t_{(85)}=70 s \) ), type of microstructure, area fraction of intragranular ferrite (IGF) and group of

| Sample number | \( N_A \) (d=0.5 μm mm⁻²) | \( N_A \) (\( l_{max} > 20 \mu m \) mm⁻²) | \( d_\gamma \) (μm) | \( D_{cross} \) (μm) | Type of microstructure*** | IGF | Group of \( V \) | E # |
|---------------|-----------------|-----------------|---------|-----------------|-----------------|------|---------|-----|
| M             | 1 619           | 0.098           | –       | 258             | I                | 10   | A       |     |
| TM            | 764             | 0.161           | –       | 359             | I                | 20   | B       |     |
| 54            | 569             | 0.026           | –       | 552             | I                | 15   | C’      |     |
| 4             | 1 094           | 0.000           | 1.00    | 260             | I                | 5    | A       |     |
| 22            | 1 190           | 0.269           | 0.63    | 419             | II               | 55   | A       |     |
| 23            | 2 288           | 0.269           | 0.72    | 354             | II               | 60   | A       |     |
| 31            | 1 948           | 0.323           | 0.55    | 303             | I-(II)           | 35   | A       |     |
| 32            | 1 418           | 0.134           | 1.23    | 440             | I                | 20   | A       |     |
| 33            | 1 662           | 0.269           | 1.55    | 515             | I                | 30   | A       |     |
| 34            | 6 600           | 0.045           | 1.48    | 554             | I                | 2B’   | A       |     |
| 35            | 470             | 0.685           | 1.49    | 268             | I                | 20   | C’      |     |
| 41            | 1 039           | 0.215           | –       | 311             | I                | 15   | A       |     |
| 42            | 8 499           | 0.153           | –       | 471             | II               | 60   | A       |     |
| 43            | 7 14             | 0.045           | –       | 487             | II               | 65   | A       |     |
| 44            | 531             | 0.000           | –       | 556             | II-I             | 45   | A       |     |
| 45            | 8 15             | 0.000           | –       | 347             | I                | 20   | A       |     |
| 51            | 448             | 0.107           | –       | 246             | I                | 20   | A       |     |
| 52            | 727             | 0.051           | –       | 230             | II               | 60   | A       |     |
| 53            | 573             | 0.113           | –       | 288             | II               | 55   | A       |     |
| 21            | 1 721           | 0.000           | 1.02    | 290             | I                | 5    | A       |     |
| 22            | 1 558           | 0.224           | –       | 379             | II-I             | 60   | A       |     |
| 5             | 699             | 0.098           | –       | 530             | I                | 15   | B’      |     |
| 3             | 559             | 0.054           | –       | 410             | II-I             | 55   | B’      |     |
| 55            | 405             | 0.103           | –       | 451             | I                | 10   | C’      |     |
| 25            | 9 666           | 0.635           | 0.89    | 505             | I-(II)           | 35   | C’      |     |
| 11            | 1 428           | 1.343           | –       | 214             | III              | 0    | C’***   |     |
| 13            | 1 172           | 0.180           | –       | 219             | III              | 10   | C’***   |     |
| 15            | 1 244           | 0.307           | –       | 221             | III              | 0    | C’***   |     |
| 12            | 1 269           | 0.215           | –       | 193             | III              | 0    | C’***   |     |

* \( d_\gamma \) is measured for particles on the film filter with the open pore size of 0.05 μm.
** WHT (1 400°C, 60 s, \( \Delta t_{(85)} \approx 70 s \)).
*** Type of microstructure: I = [GBF+FSP+granular bainitic ferrite (α_B)], II = [Acicular ferrite+GBF+FSP] and III = [Lath bainitic ferrite (α_B)].
# Groups of Charpy absorbed energy at different temperatures from –10 to –50°C: A, B and C values are shown in Fig. 1.
† porosity, ‡ large size particles, *** carbides (and nitrides).

Charpy absorbed energy are given also in Table 2.

3.1. Factors Affecting γ Grain Size
3.1.1. Pinning

The values of Charpy absorbed energy, \( V_E(T) \), measured in the temperature range from –10 to –50°C, were classified
by three groups of A, B and C, as shown in Fig. 1. The mean values of $\nu E(T)$ in the A, B and C groups changed from 170 to 100 J, from 100 to 50 J and from 50 to 30 J, respectively, with decreasing temperature from −10 to −50 °C.

It was found that the number of particles with $d_A > 0.5 \mu m$ is independent of the method of deoxidant addition and considerably scatters from 500 to 2 500 mm$^{-2}$. When the frequency of particles with $l_{\text{max}} > 20 \mu m$ is more than 0.5 mm$^{-2}$, the C group is obtained. The samples with $N_A(l_{\text{max}} > 20 \mu m) < 0.5 \text{ mm}^{-2}$, which correspond to B and C groups, have the porosity, carbide content and microstructure of lath bainitic ferrite as a result of high soluble Ti and Zr contents. In order to have high $\nu E(T)$ values, the method of deoxidant addition and the number of small particles ($d_A > 0.5 \mu m$) are not so significant. However, the elimination of large-size particles, porosity, carbide and microstructure is very important, in addition to the control of soluble elements that influence the formation of upper bainite.

The soluble O contents before casting are plotted against the sum of soluble Ti and $M (M = \text{Zr, Mg and Ce})$ contents in Fig. 2 as a function of the classification of $\nu E(T)$. It is assumed that the soluble O content is equal to the measured oxygen activity, $a_o$. The data points are classified by three regions of “Porosity+Oxides”, “Oxides” and “Carbides (+Nitrides)”. It was confirmed by SEM with EPMA that carbides (+nitrides) are located on $\gamma$ grain-boundaries. These carbides (+nitrides) were formed in samples with high soluble Ti and M contents between 120 and 230 ppm and with low soluble O contents of about 10 ppm. On the other hand, greater porosity and larger-size oxides were formed in samples with soluble Ti contents below 60 ppm and with soluble O content (above 20–30 ppm). Small oxide particles were formed in the samples with intermediate soluble Ti and M contents and soluble O content. These results indicate that high $\nu E(T)$ values (A group) were obtained in samples with soluble Ti and Zr contents, $[\text{Ti+Zr}]_{\text{sol.}}$, between 50 and 150 ppm and with soluble O content, $[\text{O}]_{\text{sol.}}$, between 15 and 25 ppm. It should be noted that the contents of $[\text{O}]_{\text{sol.}}$ and $[\text{Ti+Zr}]_{\text{sol.}}$ affect the composition of the outer layer, which is partially or totally formed on primary deoxidation particles, in addition to the control of $\gamma$ grain growth by pinning.

The $N_A$ values of particles with $d_A > 0.5 \mu m$ are plotted against the $[\text{O}]_{\text{sol.}}/[\text{Ti+M}]_{\text{sol.}}$ ratio as a function of the group of $\nu E(T)$ in Fig. 3, in which the parenthesis indicates the sample number given in Tables 1 and 2. In samples 11–13 and 15 with $[\text{O}]_{\text{sol.}}/[\text{Ti+M}]_{\text{sol.}}$ ratios in the range < 0.1, high values of $N_A (d_A > 0.5 \mu m)$ were obtained due to the formation of intergranular carbides and/or nitrides. It is obvious that the formation of a “Carbides (+Nitrides)” region is promoted at high soluble Ti and Zr contents relative to the soluble O content before solidification. The “Porosity + Oxides” region with small values of $N_A (d_A > 0.5 \mu m)$ had $[\text{O}]_{\text{sol.}}/[\text{Ti+M}]_{\text{sol.}}$ ratios > 0.5, because the formation of porosity is promoted at high soluble O content relative to soluble Ti and Zr content. Therefore, it is important to limit the $[\text{O}]_{\text{sol.}}/[\text{Ti+M}]_{\text{sol.}}$ ratio to the range between 0.1 and 0.4 in order to obtain high $\nu E(T)$ values (A group). It can be seen that the $N_A (d_A > 0.5 \mu m)$ value is not in direct relation to the $[\text{O}]_{\text{sol.}}/[\text{Ti+M}]_{\text{sol.}}$ ratio, since it depends on many factors such as initial O content, the amount of deoxidant and oxidant, the kind of deoxidants, the deoxidation method and so on. However, it can be concluded that the $[\text{O}]_{\text{sol.}}/[\text{Ti+M}]_{\text{sol.}}$ ratio is an important parameter for the prevention
of intragranular carbides (+nitrides) and porosity and the suppression of upper bainite formation together with the control of the outer layer of the deoxidation product.

The mean values of the γ grain size obtained after WHT, $D_{WHIT}$, are plotted against the $[O]_{sol.}/[Ti+M]_{sol.}$ ratio as a function of the group of $\nu E(T)$ values in Fig. 4, where three regions of “Porosity + Oxides”, “Oxides” and “Carbides (+Nitrides)” are indicated. It is apparent that the mean γ grain size of “Porosity + Oxides” region is high (400 to 600 μm) due to the small number of particles and low content of soluble elements, which do not act extensively as inhibitors for the γ grain growth by pinning and solute drag, respectively. The mean γ grain size of the “Carbides (+Nitrides)” region was low (about 200 μm) due to the high number of carbide particles consisting of mostly ZrC precipitated on grain boundaries and the high content of soluble Zr, which leads to the inhibition of grain growth by solute drag.11) The effect of non-random particles on grain growth is much stronger than that of random particles.7) The grain-growth-inhibiting effects of TiC and ZrC precipitates are discussed elsewhere.12) The γ grain size of the “Oxides” region increases as the $[O]_{sol.}/[Ti+M]_{sol.}$ ratio increases. It was found in a previous study13) that the γ grain size in non-steady state is dependent on the Zener pinning force for a given condition of WHT in the absence of solute drag. However, in the presence of soluble Ti and M, the γ grain size is significantly affected by solute drag.

3.1.2. Solute Drag

The effects of pinning and solute drag on γ grain growth were studied by plotting the γ grain size against the number of particles greater than 0.5 μm as a function of three different content levels of soluble Ti and M (below 100, 100–150 and above 150 ppm) in Fig. 5. The data points are classified by the regions a, b, c and d.

In the a region samples (3, 5, 25, 34, 35, 54 and 55 but not samples 43 and 44) whose $\nu E(T)$ values correspond to the B or C group, the $N_A$ ($d_A>0.5 \mu m$) values were low (about 0.5×10$^3$ mm$^{-2}$) and the soluble Ti and M contents were also low (6 to 60 ppm). The mean γ grain size varies widely (between 250 and 550 μm) due to the presence of porosity and the small number of particles. In the b region (samples 4, 41, 45, 51, 52, and 53), whose $\nu E(T)$ values correspond to the A group, the $N_A$ ($d_A>0.5 \mu m$) values are intermediate (0.5×10$^3$ to 1.1×10$^3$ mm$^{-2}$) and the soluble Ti and M contents are relatively high (110 to 160 ppm). Accordingly, the mean γ grain size in these samples is relatively small (between 200 and 300 μm) due to the effect of both solute drag and particle pinning. In the c region (samples 11, 12, 13 and 15), whose $\nu E(T)$ values correspond to the C-group, the $N_A$ ($d_A>0.5 \mu m$) values are high (1.2×10$^3$ to 1.4×10$^3$ mm$^{-2}$) and the soluble Ti and M contents are very high (150 to 320 ppm). Therefore, the mean γ grain size is smallest (about 200 μm) due to solute drag and pinning by carbide and oxide particles. In the d region (samples 2, 21 and 31), whose $\nu E(T)$ values correspond to the A group, the $N_A$ ($d_A>0.5 \mu m$) values are very high (1.5×10$^3$ to 2.9×10$^3$ mm$^{-2}$) and the soluble Ti and M contents are relatively high (110 to 140 ppm). Therefore, the mean γ grain size is relatively small (300 to 400 μm) due to the effect of both particle pinning and solute drag. In a previous work11) no effect of solute drag on grain growth was observed for Mg and Ti, but a marked effect was observed for Zr and Ce.

The Zener pinning force, $Z_p$, is expressed as follows:

$$Z_p = 3\sigma f_N / d_V ........................................ (1)$$

where $\sigma$ is the grain boundary energy, $V$ is the molar volume of Fe, $d_V$ is the mean particle diameter and $f_N$ is the volume fraction of particles.

In a previous study13) it was confirmed that the γ grain size in non-steady state decreases with increasing the Zener pinning force given by Eq. (1).

The volume fraction of particles, $f_N$, is given by

$$f_N = (\pi/6)d_V^3 N_V .......................................... (2)$$

where $N_V$ is the number of spatial particles per unit volume. By substituting Eq. (2) into Eq. (1), coupled with the relation: $N_V = N_A/d_A$, we have

$$Z_p = (\pi/2)\sigma f_N N_A ....................................... (3)$$

It is clear from Eq. (3) that the γ grain size, which is inversely proportional to the $Z_p$ value, decreases with increasing $N_A$ values at almost same $d_V$ (see Table 2).

In the samples of 22, 23, 32 and 42–44, whose $\nu E(T)$ val-
ues correspond to the A group, the \( N_A (d_A>0.5 \, \mu m) \) values varied in the range between 0.5×10³ and 2.5×10³ mm⁻², and the soluble Ti and \( M \) contents were relatively low (60 to 100 ppm). In this case, the mean \( \gamma \) grain size tends to decrease with increasing \( N_A (d_A>0.5 \, \mu m) \) values. Thus, it can be suggested that the Zener pinning force given by Eq. (3) increases with an increased \( N_A (d_A>0.5 \, \mu m) \) value under a small effect of solute drag. In the present study, the mean \( d_V \) values for the samples 22 (0.63 \( \mu m \)), 23 (0.72 \( \mu m \)) and 32 (1.23 \( \mu m \)) were measured (Table 2). If the mean \( d_V \) values of samples 42–44 were nearly the same as those of samples 22, 23 and 32, the decrease in the mean \( \gamma \) grain size with increasing \( N_A (d_A>0.5 \, \mu m) \) could only be explained by the Zener pinning force.

Thus, it can be concluded that the formation of carbides, oxides and porosity + large-size oxides is in good relation to the \([O]_{sol.}/[Ti+M]_{sol.}\) ratio. Furthermore, the \( \gamma \) grain size after the HAZ thermal cycle is affected not only by particle number and size, but also by the soluble Ti and Zr contents.

### 3.2. Factors Affecting Microstructure and Charpy Absorbed Energy

#### 3.2.1. \( \gamma \)Grain Size

The microstructures observed after WHT were classified into Types I, II and III, which are shown in Fig. 6. The Type I microstructure consists of grain boundary ferrite (GBF), ferrite side plate (FSP), and granular bainitic ferrite \( (\alpha_B) \). The microstructure of Type II is typified by intragranular ferrite (IGF) such as acicular ferrite and lesser amounts of GBF and FSP. The microstructure of Type III consists of mainly lath bainitic ferrite \( (\alpha''_B) \). According to the classification of microstructural constituents by Thewlis, \[^{14}\] GBF is PF(G) (Ferrite veins or polygonal grains aligned with prior austenite grain boundaries), FSP is WF-FS(A) (Primary and secondary Widmanstatten ferrite sideplates), and lath bainitic ferrite is B-FS(A) (Bainitic ferrite with aligned carbide). Granular bainitic ferrite is not classified by him, but this is observed by Habraken and Economopoulos. \[^{15}\] Since the time of cooling from 800 to 500°C was fixed as 70 s in this study, the microstructures of Types I, II and III were determined as functions of factors other than time: \( \gamma \) grain size, content of soluble elements and particle characteristics such as number, size and composition, all of which are interdependent.

It is of interest to note that high \( \nu E(T) \) values were obtained in both Type I and Type II microstructures. High toughness in weld metal and HAZ is generally associated with the formation of microstructures exhibiting a maximum amount of fine acicular ferrite in the intragranular regions with a minimum amount of proeutectoid ferrite at the \( \gamma \) grain boundaries. However, in the present study, high \( \nu E(T) \) values, which correspond to the A group, are obtained even in the Type I microstructure. Furthermore, the Type I and Type II microstructures are observed in a wide range of \( \gamma \) grain sizes, between 250 and 550 \( \mu m \) (Table 2).

The formation of IGF becomes more advantageous with an increased \( \gamma \) grain size due to the decrease in the nucleation sites at grain boundaries compared with the intragranular nucleation sites of oxide particles. This indicates that there is an optimum \( \gamma \) grain size and number of particles. The critical \( \gamma \) grain size, above which nucleation of ferrite is shifted from the austenite grain boundaries to the intragranular regions, is significantly affected by the nucleation potency of the intragranular oxide phase and by the degree of segregation of the \( M \) elements on the grain boundary. It has been shown that the length of GBF and FSP decreases with a decrease in \( \gamma \) grain size, and high \( \nu E(T) \) values are obtained at a \( \gamma \) grain size of about 100 \( \mu m \).\[^{16,17}\] However, these results are different from those in the present study.

In this investigation, the microstructure and \( \gamma \) grain size were measured for samples after WHT. On the other hand, \( \nu E(T) \) values were measured for the submerged arc-welded samples. It was confirmed that the microstructure and \( \gamma \) grain size in the samples after WHT correspond well to those observed in HAZ near the fusion line in the welded samples.

The area fraction of IGF is plotted against the \( \gamma \) grain size in Fig. 7, in which the data points in Ti/Zr deoxidation experiments with high \( \nu E(T) \) values (A group except for 11 and 34) are classified by regions \( a, b, c \) and \( d \) depending on soluble Ti and Zr contents. It can be seen that the area fraction of IGF increases with increasing \( \gamma \) grain size, followed
by going through a maximum except for a few data points (samples 32, 52 and 53). The Type I microstructure with a low area fraction of IGF (5–30%) is formed in two regions: One is the a region, where the γ grain size is small (250 to 350 μm) and the soluble Ti and Zr contents are high (110 to 160 ppm). The other is the d region, where the γ grain size is large (450 to 550 μm) and the soluble Ti and Zr contents are low (60 to 80 ppm). Type II microstructures with a high area fraction of IGF (55–65%) are formed in two regions: the b region, where γ grain size is small (200 to 300 μm) and soluble Ti and Zr contents are high (110 to 150 ppm) and the c region, where the γ grain size is large (350 to 500 μm) and soluble Ti and Zr contents in most samples are low (60 to 100 ppm).

The reason for the increase in area fraction of IGF with increasing γ grain size up to about 400 μm can be explained as follows: the nucleation site of GBF per unit volume decreases with increasing γ grain size if the effect of particle characteristics such as composition (nucleation potency), size and number on IGF formation is not taken into consideration. Furthermore, the grain-boundary segregation of soluble Ti and Zr in this range of relatively small γ grain size suppresses GBF formation, thereby leading to IGF formation. The decrease in the area fraction of IGF with increasing γ grain size above 500 μm may be explained not only by the decreased particle number, but also by the increased segregation of soluble Ti and Zr on the grain boundary and the formation of lath bainitic ferrite.

The γ grain size was measured after WHT whose conditions correspond to submerged arc welding. The Charpy impact test was conducted on these welded samples. It was confirmed that the γ grain size obtained in the samples after WHT was in good correspondence to that observed in HAZ near the fusion boundary in the welded samples. The vE(T) values obtained at –30°C are plotted against γ grain size in Fig. 8, as an example. It can be seen that the vE(T) values for small-size particles, which do not show a clear dependence of particle number (Fig. 3), also show no dependence of γ grain size. A similar trend was observed for other test temperatures. The a region in Fig. 8 except for samples M, 32 and 33 in Table 3 includes the samples of c class (samples 52 and 53) in Table 3. The b region includes all samples of b class and samples 32 and 33 from a class in Table 3.

3.2.2. Residual Deoxidant Elements

In order to study the effect of residual deoxidant elements on microstructure, slice specimens from samples 21 to 23 ([Ti]sol. = 82–103 ppm and [Zr]sol. = 4–13 ppm) and 25 ([Ti]sol. = 46 ppm and [Zr]sol. = 6 ppm) were held at 1400°C for 60 s, 10 min and 30 min, followed by cooling at ΔT(850°C)/70 s. The mean γ grain size and the area fraction of IGF are plotted against holding time at 1400°C in the upper and lower diagrams of Fig. 9, respectively. It can be seen that the γ grain
size increases with increased holding time, whereas the area fraction of IGF decreases. These results correspond well to the tendency shown in Fig. 7 in which high area fraction of IGF in the c region of Type II decreases to a low area fraction of IGF in the d region of Type I with increasing γ grain size from 350–450 to 500–550 μm.

It is well established that the formation of IGF becomes favorable with an increase in γ grain size. This is only predominant in the range of γ grain sizes below 100 μm, because the surface area of grain boundaries per unit volume drastically decreases in this range.1,2) The results shown in Fig. 9 indicate an opposite trend of γ grain sizes in the range above 500 μm. This is explained by the increasing of grain-boundary segregation of residual deoxidation elements with increasing γ grain size, which promotes the formation of lath bainitic ferrite.

The area fraction of IGF is plotted against soluble Ti content as a function of holding time at 1400 °C in the upper diagram of Fig. 10. These results correspond to those in the lower diagram of Fig. 9. It can be seen in the upper diagram of Fig. 10 that the area fraction of IGF reaches a maximum at a soluble Ti content of about 100 ppm. Moreover, the area fraction of IGF for a given soluble Ti content increases with decreased holding time at 1400 °C and, as a result, so does the γ grain size.

The area fraction of IGF after WHT is plotted against soluble Ti content in Ti/Zr deoxidation experiments in the lower diagram of Fig. 10 for different groups of VE(T). The area fraction of IGF tended to increase, followed by going through a maximum with increasing soluble Ti content, although the data points scatter considerably. These results are in good agreement with those observed in previous Ti/Zr deoxidation experiments3) under a constant γ grain size.

The present results are interpreted based on previous results3) as follows: With increasing soluble Ti content from 0 to 100 ppm, the IGF area fraction increases and primary ferrite decreases due to the fact that grain-boundary segregation suppresses the formation of GBF. With further increase of soluble Ti content, IGF is replaced by lath bainitic ferrite due to the high degree of grain-boundary segregation. The scatter of data points in Fig. 11 arises from the fact that the influence of the γ grain size on the degree of grain-boundary segregation, which is discussed in a previous study,1) is not taken into consideration.

The area fraction of IGF increases with increasing γ grain size (from 200 to 400 μm), as shown in Fig. 7, and the γ grain size increases as the [O]sol./[Ti+M]sol. ratio increases, as shown in Fig. 4. Therefore, the area fraction of IGF increases as the [O]sol./[Ti+M]sol. ratio increases from 0.1 to 0.3, as shown in Fig. 11. The a region on this figure includes the samples with Type I microstructures containing soluble [Ti+Zr(Ce)]sol.=110–210, b-60–150 and c-10–60 ppm. It can be seen from the results in Fig. 11 that there are two methods to obtain high VE(T) values: One is to choose the b region, where the [O]sol./[Ti+M]sol. ratio is 0.2 to 0.3 and the microstructure is Type II with a high area fraction of IGF (>50%). Another is to choose the a region, where the [O]sol./
[Ti+M]\text{sol.} ratio is 0.1 to 0.2 and the microstructure is Type I with a low area fraction of IGF (5–35%). The reason why the \textit{b} region has high $\gamma E(T)$ values is clear, since high fracture toughness is obtained by a fine microstructure with high area fraction of acicular ferrite. However, the reason why the \textit{a} region also has high $\gamma E(T)$ values is not straightforward. The microstructures of samples in these \textit{a} and \textit{b} regions are different; namely, the area fraction of IGF in the \textit{b} region (with large $\gamma$ grain size and low soluble content of Ti and M element) is higher than that in the \textit{a} region (with small $\gamma$ grain size and high soluble content). But high $\gamma E(T)$ values are obtained in both regions. In view of the degree of grain-boundary segregation, the conditions for large $\gamma$ grain size and low soluble content and those for small $\gamma$ grain size and high soluble content are appropriate to the promotion of IGF formation, although their IGF area fractions are considerably different.

In the aforementioned discussion of the effect of solute element on microstructure, the total solute content in the matrix obtained from chemical analysis is used. However, the chemical hardenability should be discussed based on the solute content at grain boundaries. This has been discussed in a previous paper.3)

The values of $\gamma E(–30^\circ C)$ are plotted against soluble Ti and M ($M=Zr$, Ce and Mg) contents in Fig. 12, as an example. A similar trend was observed for other test temperatures. It is clear that $\gamma E(T)$ values scatter considerably and are independent of soluble Ti and M contents. These results are similar to those in Fig. 8, indicating no dependence of $\gamma E(T)$ values on $\gamma$ grain size. However, the result that the IGF% is related to the soluble Ti content for a given $\gamma$ grain size, as shown in the upper diagram of Fig 10, is different from that shown in Fig 12.

The $\gamma E(–30^\circ C)$ values are plotted against the [O]\text{sol.}/[Ti+M]\text{sol.} ratio in Fig. 13, as an example. The samples of M and TM are not included because their oxygen activities were not measured. These results are in good agreement with those shown in Fig. 11 in which the IGF% is plotted against the [O]\text{sol.}/[Ti+M]\text{sol.} ratio. It is seen that the samples of zones “Holes” and “Carbides” have low $\gamma E(–30^\circ C)$ values, because porosity, large size particles and carbides (+nitrides) become sites of crack initiation and/or help to propagate cracks in the sample. There are three regions \textit{a}, \textit{b} and \textit{c} whose $\gamma E(–30^\circ C)$ values are high. These three regions correspond to the \textit{a} (except for samples 32 and 33), \textit{b} and \textit{c} classes in Table 3.

It can be concluded that high $\gamma E(T)$ values are obtained at high IGF% in the case of large $\gamma$ grain size and relatively small soluble Ti and Zr contents and also at low IGF% in the case of small $\gamma$ grain size and high soluble Ti and Zr contents. These results can be explained by the suppression of ferrite formation on grain boundaries by the segregation of some soluble elements, with the content on the grain boundaries depending on the $\gamma$ grain size, the width of the grain boundaries and solute content.

3.2.3. Oxide Composition

For the most part in this study, we used complex deoxidation processes such as Ti addition, followed by $M$ ($M=\text{Mg, Zr and Ce}$) addition, etc., except for a few samples with single-deoxidant addition (samples M and 54). The particle size distributions obtained for different particle compositions of sample 23 (Ti–Zr–O) are shown in Fig. 14 as an example. It is seen that the particle compositions of Zr–Ti oxides and Zr–Ti–Mn oxides without Al are observed. As shown in the top diagram of Fig. 14, a bimodal curve is observed for total particle distribution. The curve on the left-hand side (with $d<0.8 \mu m$) corresponds to crystallization and precipitation during cooling. The curve on the right-hand side (with $d>0.8 \mu m$) corresponds to a primary deoxidation product. These particles except for Ti and Zr in sample 23 are multi-phase, and it is not certain that the initial particle composition is homogeneous and becomes heterogeneous by crystallization and/or precipitation during cooling.

The results shown in Fig. 14 are not useful to the study of the effect of inclusion composition on microstructures under a given solute element, austenite grain size and cooling rate. This is because the microstructure is influenced not only by the particle size, but also by the particle surface composition consisting of nucleation sites such as in the Ti-rich phase. It has been reported18–23) with respect to the inclusion size that a certain minimum inclusion size is required for intragranular ferrite nucleation and that inclusions smaller than this size are not effective as nucleation sites.

It has been observed that titanium oxide particles are most

![Fig. 12. Effect of soluble Ti and M ($M=\text{Zr, Mg and Ce}$) content on Charpy absorbed energy at –30°C.](image)

![Fig. 13. Effect of [O]\text{sol.}/[Ti+M]\text{sol.} ratio ($M=Zr$, Mg and Ce) on Charpy absorbed energy at –30°C: a, b and c regions correspond to a (except 32 and 33), b and c classes given in Table 3.](image)
efficient in nucleating acicular ferrite, because during cooling the Ti$_2$O$_3$ particles act as substrates for precipitation of TiN and MnS.\textsuperscript{24) Nucleation is enhanced by an increase in the thermodynamic driving force for nucleation through manganese depletion of the austenite matrix local to the inclusion. Such a local depletion zone due to MnS precipitation stabilizes the ferrite phase over the parent austenite, thus causing nucleation of IGF.

In the present experiment the Mn-depleted zone (MDZ) around the Ti$_2$O$_3$-containing particles due to the precipitation of MnS was not considered in the IGF formation because the sulfur content was below 10 ppm. However, it appears that the formation of MDZ around the Ti$_2$O$_3$-containing particles due to the Mn absorption into the particles is the likely mechanism of IGF formation\textsuperscript{25,26) together with the precipitation of TiN on Ti$_2$O$_3$-containing particles, which act as effective nucleation sites due to their high coherency with ferrite. One of the probable explanations for this is that the oxygen potential determined by the Ti/Ti$_2$O$_3$ equilibrium increases locally due to the decrease in the soluble Ti content as a result of TiN precipitation. Consequently, the Mn absorption into particles implies that the formation of a Ti$_2$O$_3$–MnO solid solution becomes favorable when the oxygen potential around the TiN precipitated on Ti$_2$O$_3$-containing particles is increased.

With respect to the effects of surface composition and surface area of Ti$_2$O$_3$-containing particles on microstructure, it has been reported that a titanium-rich phase which particularly covers the inclusion is responsible for the nucleation of acicular ferrite. The efficiency of the inclusions for the nucleation of acicular ferrite is related to the total external surface area of the titanium-rich phase covering the inclusions per unit area of metal.\textsuperscript{21) In a previous study\textsuperscript{19} single-deoxidant addition of Ti or Mg was made in the presence or absence of N. It was found that the area fraction of intragranular ferrite for a given austenite grain size and soluble Ti content increased in the order of ZrO$_2$(+Ti$_2$O$_3$) < Ti$_2$O$_3$, MgO(+Ti$_2$O$_3$) < TiN. The composition of the outer layer of primary deoxidation particles is of key importance for IGF formation. For this reason the content of soluble oxygen as well as Ti and Mn before casting should be reasonably high to allow for crystallization and/or precipitation of Ti$_2$O$_3$ and MnO on primary deoxidation particles. In the presence of reasonably high soluble contents of oxygen, nitrogen and Ti, the composition of the outer layer consists of Ti$_2$O$_3$, MnO, MO$_X$ ($M$ = Zr, Mg or Ce) and TiN. Furthermore, the control of the number and size of deoxidation particles, which affects the control of the $\gamma$ grain size, is important for the grain-boundary segregation, which in turn influences the microstructure to a considerable degree.

### 3.3. Relationship between Microstructure and Charpy Absorbed Energy

Figure 15 shows the relationship between the $\gamma$E(T) classification and the type of microstructure. Samples with small size particles are classified as $a$, $b$ and $c$ regions which correspond to $a$, $b$ and $c$ class in Table 3. It was found that high toughness was obtained with microstructures of Type I, consisting of GBF, FSP and granular bainitic ferrite, and Type II, consisting of IGF and small amounts of GBF and FSP. The $a$ region compatible with the Type I microstructure has a small $\gamma$ grain size (250–350 $\mu$m) and high contents of soluble Ti and Zr (110–160 ppm). The $b$ and $c$ regions compatible with the Type II microstructure have small $\gamma$ grain size (200–300 $\mu$m) and high soluble Ti and Zr contents (110–150), and large $\gamma$ grain size (350–500 $\mu$m) and low soluble Ti and Zr contents (60–100 ppm), respectively. It can be seen that the microstructures and Charpy absorbed energies are in close relation to the $\gamma$ grain size and solute content. However, when the effect of solute elements on the microstructure is studied, the content of solute elements on the grain boundaries, not soluble elements in the matrix, must be considered in view of the lowering of grain-boundary energy and grain-boundary precipitation. The concentration of elements on grain boundaries cannot be obtained without

![Fig. 14. Particle size distributions obtained by electrolytic extraction method in Ti/Zr–O experiment (Exp. 23).](image)

![Fig. 15. Relationship between groups of Charpy absorbed energy and type of microstructure shown in Fig. 6: $a$, $b$ and $c$ regions correspond to $a$, $b$ and $c$ classes given in Table 3.](image)
knowledge of the grain-boundary widths. This problem regarding the effect of grain boundaries was considered by Akselsen et al.\textsuperscript{27)} for the study of HAZ properties of boron-containing low-carbon steels using non-equilibrium grain-boundary segregation. This problem has also been discussed via the introduction of a new hardenability parameter in a separate paper.\textsuperscript{3)}

4. Conclusions

The influence of deoxidation products used with Ti and \( M (M = \text{Zr, Mg and Ce}) \) and soluble Ti and \( M \) contents on microstructure and toughness was studied in Fe–0.04\%C–1.85\%Mn–0.03\%Si–0.018\%Nb steel using a simulated HAZ thermal cycle and submerged arc welding, respectively. The following conclusions were drawn.

(1) Austenite grain size after HAZ thermal cycle is affected not only by particle number and size, but also by soluble Ti and Zr contents.

(2) There are three types of microstructures: Type I is GBF, FSP and granular bainitic ferrite; Type II is acicular ferrite and lesser amounts of GBF and FSP; and Type III is lath bainitic ferrite.

(3) The area fraction of IGF increases with increased \( \gamma \) grain size from 200 to 350 \( \mu \)m, has a maximum in the range between 350 and 450 \( \mu \)m, and then decreases.

(4) High \( \gamma \varepsilon(T) \) values are obtained for the Type II microstructure with high IGF (45–65%) in the cases of larger \( \gamma \) grain size (350–500 \( \mu \)m) with lower soluble Ti and Zr contents (60–100 ppm) and of small \( \gamma \) grain size (200–300 \( \mu \)m) with higher soluble Ti and Zr contents (110–150 ppm). Similarly, high \( \gamma \varepsilon(T) \) values are obtained for the Type I microstructure with low IGF (5–35%) in the case of smaller \( \gamma \) grain size (250–350 \( \mu \)m) and higher soluble Ti and Zr contents (110–160 ppm).

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