Effect of Distribution of TiN Precipitate Particles on the Austenite Grain Size of Low Carbon Low Alloy Steels*  

By Shoichi MATSUDA** and Naoki OKUMURA**

Synopsis
The effect of TiN particles in low carbon low alloy steels on the austenite grain size was studied in relation to the dissolution, coalescence and reprecipitation. Main results were as follows.

1. Ostwald ripening was observed in the process of coalescence of TiN particles.
2. The main factors controlling the austenite grain size \((R)\) were the volume fraction \((f)\) and the mean size of TiN particles \(\langle r \rangle\) such that \(R = K \cdot \langle r \rangle^2\), where the \(\langle r \rangle\) is the mean distance of TiN particles.
3. This experimentally obtained relationship was theoretically substantiated by a simple model that takes both the effect of distribution of TiN precipitate particles and the nature of the particles into consideration.

I. Introduction
It is well known that the toughness of steel is improved by the austenite grain refinement. There are many ways to obtain a fine grain size. A typical example is to use fine AlN or Nb(CN) precipitate.\(^1,2\)

Gladman\(^3\) has developed a general theory on the mechanism controlling the austenite grain size in which he correlated the critical stage of grain coarsening with the size and the volume fraction of precipitates. There are many experimental evidences concerning the austenite grain refinement using carbides and nitrides. George and Ira\(^i\)\(^n\)\(^4\) determined grain coarsening temperature of the Ti bearing steels as about 1 200°C, which is higher by 100°C than that of the cases of other precipitate particles. Similar experimental results on Ti containing steels were obtained by Bashford and George.\(^5\) It has been suggested from these works that the size and the volume fraction of TiN are the major factors which control the austenite grain coarsening at high temperatures, but no observation has been offered.

The present work is to study the dissolution, coalescence and precipitation of TiN in the austenite temperature range with special reference to the austenite grain size. A simple model is proposed on the mechanism of controlling the austenite grain size by precipitate particles.

II. Experimental Procedures
The chemical compositions of the steels are shown in Table 1. All alloys were melted and cast into 20 kg ingot in a vacuum induction furnace. The amounts of Ti and N were 0.010~0.023% and 0.0064~0.0091%, respectively. The precipitated TiN was analyzed by atomic absorption spectroscopy, the analysis error being ±0.002% as Ti.

The sizes of TiN particles were determined by means of carbon extraction replicas, and at least 10 fields in each of three replicas from each specimen were examined.

III. Experimental Results

1. Process of Dissolution of TiN in the Austenite Temperature Range

Each specimen (40 mm×40 mm×15 mm) was heated in an atmosphere of He to the austenite temperature range at 1 150°C, 1 250°C, 1 350°C or 1 430°C for 1, 4 or 10 hr, and quenched into water. After each heating procedure, the amount of solute Ti was determined as shown in Fig. 1 for steels A and B. Here the amount of solute Ti means the difference between the amount of the precipitated TiN before and after a heat-treatment.

From Fig. 1, it is clearly seen that the solute Ti from 0.004 to 0.006% are obtained as a result of partial dissolution of TiN by the heat-treatment of 1 250°C×10 hr or 1 350°C×1 hr. Even then, Ti as undissolved TiN amounted to one-half the total Ti.

Table 1. Chemical composition of specimens (wt%)

<table>
<thead>
<tr>
<th>Specimen*</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.14</td>
<td>0.31</td>
<td>1.54</td>
<td>—</td>
<td>—</td>
<td>0.023</td>
<td>0.0084</td>
</tr>
<tr>
<td>B</td>
<td>0.12</td>
<td>0.31</td>
<td>2.11</td>
<td>0.50</td>
<td>0.42</td>
<td>0.019</td>
<td>0.0088</td>
</tr>
<tr>
<td>C</td>
<td>0.12</td>
<td>0.28</td>
<td>1.30</td>
<td>—</td>
<td>—</td>
<td>0.020</td>
<td>0.0091</td>
</tr>
<tr>
<td>D</td>
<td>0.15</td>
<td>0.50</td>
<td>1.37</td>
<td>—</td>
<td>—</td>
<td>0.010</td>
<td>0.0064</td>
</tr>
</tbody>
</table>

* all heats vacuum melted

![Fig. 1. Effect of heat treatment temperature on the amount of solute Ti](image)

** Fundamental Research Laboratories, Nippon Steel Corp., Ida, Nakahara-ku, Kawasaki 211.
The solubility product of TiN in the austenite temperature range can be estimated using Table I and Fig. 1 as shown in Fig. 2. It is formulated as follows,

$$\log[\text{Ti}[\text{N}]] = \frac{-8000}{T} + 0.32 \quad \text{for steel A}$$

$$\log[\text{Ti}[\text{N}]] = \frac{-3000}{T} - 2.20 \quad \text{for steel B}$$

where \( T \) is the absolute temperature. It is to be noted that the solubility product of TiN in Si-Mn-Ti-N steels increases with the addition of Cr and Mo. It follows, therefore, that the addition of alloying elements is an effective method for the purpose of controlling the austenite grain size with TiN precipitate particles.

2. Process of Coalescence of TiN in the Austenite Temperature Range

The coalescence of TiN in the austenite temperature range was examined. A typical example of the distribution of TiN particles is shown in Photo. 1. Generally, TiN particles precipitate in steels in cubic or rectangular-prism shapes. In this report the size of a TiN precipitate particle is represented as the length of a side or the geometric average of sides of rectangular-prism shape. The size of TiN for each specimen in each heat treatment is calculated as follows:

$$r = \frac{\sum N_i l_i}{\sum N_i}$$

where \( N_i \) means the number of TiN particles of the size \( l \). The growth of TiN particles due to the coalescence are shown in Fig. 3. There is a considerable difference in the size of TiN particles between steel B (containing Cr and Mo) and steel A or C (no Cr nor Mo). The following empirical equation was obtained for the steels A to C:

$$r = At^{1/3}$$

where, \( r \): the size of TiN particles
\( t \): the heating time
\( A \): a constant which varies with composition of steels

Equation (3) means that volume \((r^3)\) of a TiN particle increases in proportion to the heating time.

The following equation is derived based on the Lifshitz-Wagner’s theory for the Ostwald ripening effect,

$$r = C(D/T)^{1/3}t^{1/3}$$

Fig. 2. Solubility product of TiN in austenite temperature range

Fig. 3. Effect of heating time on mean particle size of TiN

Photo. 1.
TiN distribution.
Heat treatment: 1350°C x 1 hr, WQ.
where, \( T \) and \( t \): the same as before
\( D \): the diffusion coefficient of solute Ti
\( C \): a constant independent of above-mentioned parameters.

With this, we shall now estimate the activation energy \((Q)\) of diffusion by plotting \((1/T)\) vs. \( \log (r^3T) \) as shown in Fig. 4. The slopes of those straight lines give the activation energy of diffusion as \( Q = 100 \) kcal/mol, which is almost the same for each of steels A to C. This estimated value is rather large as compared with 60 kcal/mol which was previously reported.7

The effect of the distribution of TiN particles on the austenite grain size was investigated in detail in the temperature range from 1150°C to 1430°C. The results are shown in Fig. 5, from which the following equation was obtained empirically:

\[
R = K \cdot \frac{r}{f} \tag{5}
\]

where, \( R \): the austenite grain size
\( f \): the volume fraction of TiN
\( r \): the mean particle size of TiN
\( K \): a dimensionless factor, is approximately 1.5 in Fig. 5.

In Eq. (5), the term \( \frac{r}{f} \) gives the mean distance between TiN particles when \( f \) is much less than unity. This should hold true at least for the steels of this study, because the volume fraction of TiN is in the order of \( 10^{-4} \) as estimated from Fig. 1.

It is concluded from Eq. (5) that the most effective method to control the austenite grain size is to reduce the mean particle size \( r \) for a given volume fraction of TiN.

3. Relation between the Reprecipitation of TiN and the Austenite Grain Size

As mentioned earlier, the precipitated TiN gets dissolved partially by heating at temperatures higher than 1250°C. It is important to understand the process by which the dissolved TiN reprecipitates finely on reheating. Thereupon, the influence of heat treatments on the distribution of TiN particles was investigated for the steels A and B, paying a special attention to the heating rate. The schematic diagrams of heat treatments are shown in Fig. 6.

The very fine TiN particles (\( \sim 0.005 \mu m \)) precipitated in a random and dense manner as shown in Photo. 2 (a) when heated slowly, at a rate of 1.6°C/min, in both steels irrespective of the highest temperature heated to (Fig. 6 (a)). On the other hand, for a heating rate of 200°C/min (Fig. 6 (b)), TiN particles were coarse, 0.01 \mu m, when heated to 1150°C, but only 0.004 \mu m when heated to 650°C as exemplified in Photo. 2 (b). It is to be noted in the latter case that coarse TiN particles of 0.01 to 0.02 \mu m are present making a row. It will be seen in the electron photomicrograph (Photo. 2 (b)) that a zone free from precipitate particles exists on either side of the row.

Calculation of the mean particle size with Eq. (2), the coarse TiN particles existing in the row taken into account, revealed that the greater the mean TiN particle size, the more frequently the rows appear. In order to study the dependence of the frequency of the formation on the heating rate in detail, steel B, which had been heated at 1350°C for 1 hr and quenched, was reheated to 750°C in an induction furnace in the range of heating rate from 8°C/min to 3 \times 10^3°C/min, and the amount of the rows was determined for each case. Here, the total length of the rows per unit area

![Fig. 4. Effect of heating temperature on mean particle size of TiN](image)

**Fig. 4.** Effect of heating temperature on mean particle size of TiN

- Heating time: 10 hr
- \( r \): Mean particle size of TiN
- \( T \): Heating temperature

![Fig. 5. Relation between mean distance of TiN particles and austenite grain size](image)

**Fig. 5.** Relation between mean distance of TiN particles and austenite grain size

- \( R \): Austenite grain size
- \( f \): Volume fraction of TiN
- \( r \): Mean particle size of TiN
- \( K \): Dimensionless constant

![Fig. 6. Schematic diagram of heat treatments](image)

**Fig. 6.** Schematic diagram of heat treatments
(a) Heating rate: 1.6°C/min
(b) Heating rate: 200°C/min
Specimen: Steel B
Heating temperature: 1150°C

Photo. 2.
Effect of heating rate on TiN distribution.
A chain of TiN particles is observed in the upper part of (b) and such a manner of dispersion of TiN particles is termed the row arrangement.

was taken as the amount, which is correlated to the heating rates in Fig. 7. From Fig. 7 it is seen that the rows are likely to occur when the heating rate is large. The reason of the heating rate dependence will be considered in the following section.

In order to see the effects of the distribution of TiN precipitate particles on controlling the growth of the austenite grain in welding, steels A and B were rapidly heated again to 1350°C, but held for less than 1 sec, after completing the heat treatments of Fig. 6. The heat treatment was to simulate the thermal situation of welding. Hereafter this heat treatment is called the simulated heat treatment in this paper. The results are shown in Fig. 8. An austenite grain size as small as ASTM No. 4.7 and No. 5.3 was obtained for the steels A and B, respectively, after the simulated heat treatment. In both cases the pre-treatment was a heating to 1150°C at a rate of 200°C/min.

Further, the mean TiN particle size was measured after each heat treatment (Fig. 6), and is shown in Fig. 9 as a function of the temperature heated to. It is concluded from Fig. 9 that the mean TiN particle size at the heating rate of 200°C/min is about two times coarser, except for heating temperature of 650°C, than at 1.6°C/min. The austenite grain size after the simulated heat treatment depends on the mean distance between TiN particles before that heat treatment, as shown in Fig. 10, in which the data shown in Fig. 5 are also replotted. It is to be noted that the relation shown in Fig. 5 is applicable to the cases of the simulated heat treatment except for the reprecipitation treatment at a heating rate of 1.6°C/min. The austenite grains after the simulated heat treatment were unexpectedly coarser when heated at 1.6°C/min than any others shown in Fig. 6.

Equation (5) shows that the austenite grain size is in proportion to the mean TiN particle size for a given volume fraction of TiN. In fact the heating rate does not affect the quantity of reprecipitated TiN as shown in Table 2, and all the Ti once held in solution by heating at 1350°C×1 hr, which is estimated as 0.006%, from Fig. 1, seems to reprecipitate fully when re-heated to 1150°C. Therefore, it is thought that there should be no difference in the volume fraction
IV. Discussion

1. Effect of Distribution of TiN Particles on the Austenite Grain Size

As described earlier, Eq. (5), the empirical equation correlating the distribution of TiN particles with the austenite grain size, was obtained for low carbon low alloy steels, but it was subsequently verified by experiments that the equation held true for steels containing either 3.5% Ni or 1.5% Cu.

Gladman\(^3\) has developed a general theory on the effect of precipitate particles on grain growth in metals, in which he focused on the energy changes of grain boundaries accompanying grain growth. One of his conclusions is that grain growth occurs when coalescence causes the particle size to exceed a critical value, and the other is that dissolution of the precipitate is not a necessary requirement for grain growth.

Concerning TiN particles, the austenite grain growth occurs due to dissolution of some of the very fine particles of the size of \(\sim 0.005 \mu m\). This was verified through the simulated heat treatment experiments. For this, a simple model to describe the TiN particles preventing the austenite grain growth has been developed.

Consider the interaction between an austenite grain boundary and a TiN particle from the standpoint of balance of forces. The driving force for grain growth will be provided through equilibration of two forces: the first is a 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 grain boundary which adjoins the TiN particle. It will be recalled that Gladman's theory does not take account of the second of those forces. Thus, he has been led to predicting that the prevention of the grain growth does not depend on the kind of precipitate when the volume fraction and the size of precipitate are the same.

An attempt for correcting this shortage has been made by introducing the nature of the precipitate into the present model.

A schematic illustration of the interaction between an austenite grain boundary and TiN particles is shown in Fig. 11, and Photo. 3 shows such an interaction occurring. For simplicity, a TiN particle is considered to be a sphere of radius \(r\). When the grain \(A\) grows in the direction of the \(Y\) axis, it suffers from the resistive force originated from the TiN particle until finally acquires an equilibrium state. Then we define the contact angle \((2\alpha)\) as follows.

![Fig. 9. Effect of heating temperature and heating rate on mean particle size of TiN](image)

![Fig. 10. Relation between mean distance of TiN particles and austenite grain size](image)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Heating rate** (°C/min)</th>
<th>Total amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>200</td>
<td>0.023</td>
</tr>
<tr>
<td>B</td>
<td>1.6</td>
<td>0.017</td>
</tr>
</tbody>
</table>

\*[Error of analysis: 0.002% Ti]

**Heating temperature: 1150°C

\((f)\) of TiN particles between 1.6°C/min and 200°C/min, if heated to 1150°C. It follows then that if the distribution of TiN particles does not change during the simulated heat treatment, the austenite grains hereafter should be finer for a slower heating rate than for a faster heating rate. This is what Eq. (5) predicts. This experimental results, however, are in a considerable disagreement with the prediction. This fact means that some of the particles precipitated finely in the size of \(\sim 0.005 \mu m\) are ineffective for controlling the austenite grain growth in the simulated heat treatment. Actually, it was observed that fine TiN particles had become scarcer after the simulated heat treatment; a part of them must have been got dissolved. On the other hand, observations by extraction replica technique showed that the distribution of TiN particles did not change for heating rates of 200°C/min or 10°C/min after the simulated heat treatment.

Fig. 9. Effect of heating temperature and heating rate on mean particle size of TiN
2\omega = \frac{s}{r} \quad \text{(6)}

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

\[
JF = \Gamma (1 + \hat{\omega}) \int_{0}^{\omega} 2\pi r \sin \omega \cdot rd\omega - \Gamma (r \sin \omega)^2 \quad \text{(7)}
\]

where, \( JF(r, \omega) \): the increment of the interface energy per TiN particle
\( \Gamma \): the grain boundary energy per unit area \((\approx 800 \text{ erg/cm}^2\) according to Kaznec and Kamenska\(^{30} \))
\( \hat{\omega} \cdot \Gamma \): the interaction energy between the austenite grain and the TiN particle.

It is evident that Eq. (7) holds for any kind of precipitate particles with the parameter \( \hat{\omega} \) denoting the nature of the particular particle.

From Eq. (7), the resistive force is reduced as

\[
T(\omega, r) = d(JF)/dY = 2\pi r \Gamma (1 + \hat{\omega} - \cos \omega) \quad \text{(8)}
\]

\[
Y = r - r \cos \omega \quad \text{(9)}
\]

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

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

\[
2\Gamma/R \quad \text{(10)}
\]

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 originated from TiN particle, whereby,

\[
2\Gamma/R = N \cdot T(r, \omega) \quad \text{(11)}
\]

where \( N \) is the number of TiN particles per unit area of grain boundary. When we substitute Eqs. (8) and (10) into Eq. (11), we obtain the relation between the austenite grain size and the mean distance of TiN particles,

\[
R = \left\{ \frac{4}{3} \frac{1}{(1 + \hat{\omega} - \cos \omega)} \right\} (r/f) \quad \text{(12)}
\]

where the volume fraction of TiN particles \((f)\) is equal to \(4/3 \pi r^3/(r/N)\), and \((r/f)\) means the mean distance of the particles. It is recognized that the empirically obtained Eq. (5) has been substantiated by Eq. (12), where the dimensionless factor \( K \) is defined as

\[
K = \frac{4}{3} \frac{1}{1 + \hat{\omega} - \cos \omega}
\]

It will be noted that \( K \) depends on the nature of the precipitate particles through \( \hat{\omega} \) and \( \omega \); it was 1.5 in the case of TiN (Figs. 5 and 10). In Fig. 12, the relation between \( \hat{\omega} \) and \( \omega \) is shown for \( K = 1.5 \). Figure 13 shows the relation between the contact angle \( (\omega) \) and the size of TiN particles, where the term \( \hat{\omega} \) is much less than unity (Fig. 12). Therefore, it is concluded that the increase in the interface energy of grain boundary is the main factor controlling the austenite grain growth with the TiN precipitate particles.

2. The Coalescence of TiN Particles in the Austenite Temperature Range

The results of Fig. 5 show that the austenite grain size is controlled by the distribution of TiN particles, and an austenite grain can grow when they coalesce together. Therefore, it is important to know the coalescence rate of TiN particles in austenite.

Research Article
This study is believed to be the first ever to report that the mean size of TiN particles does increase with the holding time at 1350°C in accordance with the experimentally determined Eq. (3). Further, the observation that, at 1350°C, the contents of dissolved Ti and dissolved N do not change, however long the heating time may be, should be considered as a proof that a process, in which finer TiN particles get dissolved and coarser TiN particles grow, namely, the process known as the Ostwald ripening, is taking place like cementites in steels.

The rate theory on the effect has not been well established. However, several experimental results have confirmed that the Lifshitz–Wagner's formula holds for various particular precipitates in metals, even though the diffusion of the elements composing the matrix is neglected in their theory. Oriaani and Ardell deduced independently an equation on coalescence rate that takes diffusion of elements of the matrix into account. Their theory predicts that the time dependence of coalescence is not to be represented by a simple power law, e.g., the one-third power law of the Lifshitz–Wagner's theory.

The growth rate of TiN particles by coalescence was rather small in steel B containing both Cr and Mo than in other steels. The results shown in Fig. 4 indicate, on the other hand, that the activation energy of diffusion does not change distinctly on addition of Cr and Mo. Thus, whether Cr and Mo in a steel work to make diffusion rate of Ti smaller or make the interface energy between the TiN particle and the matrix lower remains to be clarified.

3. On the Row Arrangement of TiN Precipitate Particles

As described in III. 2., it was observed that the greater the heating rate of reprecipitation, the more frequent was the occurrence of the TiN particle rows. The features of the row arrangement are as follows. The first is that the TiN particles in the rows are larger than those distributed randomly in the matrix, and the other is that a precipitate free zone exists on either side of a row. The mechanism of formation of the row arrangement may be qualitatively understood as follows.

Figures 14 and 15 show a schematic C-curve for the precipitation of TiN and a distribution of solute Ti and N as quenched from 1350°C, respectively. In general, microscopic nonuniformities in distribution of solute elements can be considered to exist in any specimen due, for example, to the original cast structure. In Figs. 14 and 15, the dotted lines represent, with regard to a certain locality in the specimen where
the solute concentration is higher than the mean, a C-curve and the solute distribution, respectively.

A C-curve is determined by the degree of supercooling at temperatures higher than the temperature of nose and by the diffusion rates of those elements which are to precipitate at lower temperatures. Therefore, in such a location of a specimen where solute concentration is unusually high, the nose of a C-curve is shifted to the shorter time side because the degree of supercooling is considerably higher there.

Now consider two cases: the case of high heating rate which corresponds to (a) in Fig. 14 and the case of low rate which is (b). In the case of (a), precipitation begins at time $t_1$ at the locality of high solute concentration, but at that time no precipitation is yet possible in other low concentration places, where precipitation is held up until time $t_2$. In the mean time, the already precipitated TiN particles continue to grow drawing solute atoms from surroundings according to the Fick’s first law. At time $t_2$, however, TiN particles start precipitating at other sites, and the amount of solute migrating to the previously precipitated TiN particle becomes less, causing the lowering of the growth rate. In this way the TiN particle rows can be formed.

On the other hand, no such preferential precipitation is possible in the case of slow heating rate (case (b)) since the precipitation is controlled mainly by the diffusion rate of the solute Ti: random and uniform distribution of TiN should result. From the standpoint of controlling the austenite grain size, the precipitated particles should preferably be uniform in size since the particle volume fraction is dictated by the solubility product. It is submitted then that much can be done by controlling the heating process of TiN reprecipitation.

V. Conclusion

(1) The interrelationship between the distribution of precipitated TiN particles and the austenite grain size in low carbon low alloy steels has been determined, both empirically and theoretically, as

$$R = K \cdot (r/jf)$$

where, $R$: the radius of the austenite grain
$r$: the size of TiN particles
$f$: the volume fraction of TiN particles
$K$: the numerical factor which depends on the kind of precipitate particle, and is approximately 1.5 for TiN particle.

(2) The TiN particles can coalesce when heated in the austenite range, the mean size increasing with holding time as

$$r = At^{1/3}$$

where, $r$: the mean size of TiN particles
$t$: the holding time
$A$: a constant, particularly with regard to the holding time.

This one-third power law agrees well with the Lifshitz-Wagner’s theory on the Ostwald ripening effect.

(3) When once quenched from 1350°C, fine TiN particles ($\sim 0.005 \mu m$) precipitate on re-heating to 650°C to 1150°C. At the same time coarser particles ($0.02 \sim 0.03 \mu m$) precipitate forming rows in such a way as the faster the heating rate, the more frequent is the occurrence of the rows. This feature is explained qualitatively, assuming microscopic nonuniformities in the concentration of solute Ti and N which affect the C-curve for precipitation. Although the origin of the concentration nonuniformity is uncertain, any heterogeneity like, for example, the remnant cast structure can be the cause.

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