Effects of Nano Precipitates in Austenite on Ferrite Transformation Start Temperature during Continuous Cooling in Nb–Ti Micro-alloyed Steels

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In the present paper, transformation behavior during continuous cooling in non-deformed and hot deformed Nb–Ti micro-alloyed steels was investigated by using the thermal dilation method. Ti content in Nb–Ti bearing steels varied from 0 to 0.031 mass% with Nb content being kept to be constant. Thermal dilatation curves were measured at different cooling rates, from which continuous cooling transformation (CCT) curves were built up. For non-deformed Nb–Ti steels, it was observed that ferrite transformation start temperatures (Ar3) decreased with increasing Ti content up to 0.015 mass%, leveled off in the range of 0.015 to 0.027 mass% Ti, and drastically decreased thereafter. For hot deformed Nb–Ti steels, Ar3 temperature did not exhibit significant difference with Ti addition lower than 0.027 mass%, and decreased drastically by further increasing Ti content. Austenite grain size (Dg), Nb–Ti precipitates and residual strain were taken into account to explain the variation of Ar3 temperatures. Based on the experimental results, mathematical models for the calculation of Ar3 for non-deformed and hot deformed Nb–Ti micro-alloyed steels were developed.

KEY WORDS: Nb–Ti micro-alloyed; CCT curve; Ar3 temperature; transformation; nano precipitate.

1. Introduction

Nb and Ti are micro-alloying elements used in steels to exert effects on recrystallization, grain size, phase transformations, precipitates, and also welding performance in high grade steels,1–25 and play different roles under different conditions. When they are co-doped in C–Mn steels, more complex effects can be generated, which deserve to be more carefully investigated. Jung et al.11 concluded that a small amount of Nb and Ti suppressed the primary ferrite formation, and coarse Nb and Ti particles formed at prior austenite grain boundaries could accelerate ferrite nucleation. Medina et al.12 studied the influence of Ti and N contents on austenite grain size and size of precipitates in steels, and concluded that a minimum Ti content of 0.010 mass% was needed to control austenite gain size. Chen et al.13 found that large complex precipitates were formed in Ti-containing HSLA steels, with thick niobium-rich ‘skin’ wrapping up the small titanium-rich core. Complex precipitation in Nb–Ti micro-alloyed steels was also investigated by numerous authors.14–18 Phase transformations, especially ferrite transformation, which play important roles in determining the properties of hot rolled products, are greatly affected by the precipitation processes. However, the effect of precipitation on phase transformation behavior still needs to be more exactly clarified.

In this paper, the transformation behavior during continuous cooling for four Nb–Ti micro-alloyed steels was systematically investigated, with Ti content being varied from 0 to 0.031% in mass, with Nb content being kept constant. Thermal dilatation curves under different continuous cooling conditions were measured to build up the CCT curves for hot deformed or non-deformed steels. The relationship between Ar3 and Ti content of Nb–Ti steels was developed. Austenite grain size (Dg), Nb–Ti precipitates and residual strain were taken into account to explain the variation of Ar3 temperatures. Based on the experimental results, mathematical models for the calculation of Ar3 for non-deformed and hot deformed Nb–Ti micro-alloyed steels were developed.

2. Experimental Procedures

The steels were melted by using a vacuum induction furnace and cast into ingots, the chemical compositions of the steels are given in Table 1. The ingots were forged into plates, from which specimens with a dimension of 8 mm in diameter and 12 mm in length were machined.

The dilatometric tests were carried out by using a thermal simulator. In each test, a specimen was put in the chamber under high vacuum of 0.1 Torr, being fixed between two anvils, and reheated by induction. An R-type thermocouple was welded on the center of the specimen surface to measure the temperature. During cooling, helium gas was employed as the coolant when cooling rate exceeded 10°C/s, and nitrogen gas was employed when the cooling rate was slower than 10°C/s. Radial expansion of the specimen was measured by a scanning laser beam
across the specimen center, where the thermocouple was welded.

Fernández et al.\textsuperscript{20) calculated the amount of Nb and Ti precipitated at different temperatures for either Nb or Nb–Ti micro-alloyed steel, which showed that a reheating temperature of 1 220°C was proper for the steels used in this work. Figure 1 shows the schematic drawing for the thermo-mechanical treatment. The reheating temperature for these steels was chosen to be 1 220°C and held for 5 min to be fully austenitized. After reheating, the specimens were cooled down to 900°C at a cooling rate of 5°C/s, being held for 20 s and cooled down to 200°C at different cooling rates from 0.5 to 30°C/s. To study the effect of hot deformation on phase transformation behavior in the steels, a compression with a true strain of 0.693 was applied to the specimen at a strain rate of 0.693 was applied to the specimen at 900°C after being held for 10 s at 900°C, with the laser beam being able to follow the welding spot on the specimen center surface during the deformation.

After thermo-mechanical treatments, all specimens were cut in the middle along longitudinal direction across the thermocouple welding points and prepared for optical metallographic examination in the conventional way to observe the transformed microstructure by using an image analysis system, CCT curves were drawn by the temperatures determined on the dilatometric curves with the help of optical metallographic observations.

To measure the austenite grain sizes prior to transformation, some of the samples were quenched from temperatures just above $A_3$ determined by the dilatometric tests. Carbon extraction replicas from the quenched samples, which were continuously cooled to $A_{13}$ at a rate of 1°C/s before quenching, were prepared to observe the precipitates prior to transformation by TEM (transmission electron microscopy). Compositional microanalyses of the precipitates were carried out by EDX (energy dispersive X-ray spectroscopy).

### Table 1. Chemical compositions of the steels (mass%).

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>N</th>
<th>P</th>
<th>S</th>
<th>Nb</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>0.11</td>
<td>0.17</td>
<td>1.23</td>
<td>0.005</td>
<td>0.006</td>
<td>0.006</td>
<td>0.038</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>T2</td>
<td>0.11</td>
<td>0.18</td>
<td>1.19</td>
<td>0.002</td>
<td>0.005</td>
<td>&lt;0.005</td>
<td>0.04</td>
<td>0.015</td>
</tr>
<tr>
<td>T3</td>
<td>0.12</td>
<td>0.23</td>
<td>1.22</td>
<td>0.002</td>
<td>0.005</td>
<td>&lt;0.005</td>
<td>0.043</td>
<td>0.027</td>
</tr>
<tr>
<td>T4</td>
<td>0.13</td>
<td>0.18</td>
<td>1.25</td>
<td>0.002</td>
<td>0.006</td>
<td>0.005</td>
<td>0.039</td>
<td>0.031</td>
</tr>
</tbody>
</table>

### 3. Results

#### 3.1. Typical Thermal Expansion Curve

Figure 2(a) shows a typical thermal expansion curve of Steel T1 after being hot deformed by a strain of 0.693 at 900°C and cooled to room temperature at a cooling rate of 15°C/s. The microstructure of the sample was observed to be ferrite and bainite, as shown in Fig. 2(b). The determination of ferrite transformation start temperatures was made by judging the turning points in the thermal expansion curves, and bainite phase transformation start temperatures were estimated by using the Lever Rule.

In the first step, the transformed fractions of ferrite and bainite ($f_a$ and $f_B$) at room temperature were measured by metallographic analysis. Then, it was assumed that on the thermal expansion curve (TEC) bainite transformation had started at the point which separated the ferrite and bainite transformations. The whole transformation segment on the TEC was BC, as shown in Fig. 2(a). By using the Lever Rule, the separation point, E, was found by $BE/BC=f_a$. 

Fig. 1. The schematic drawing for the thermo-mechanical treatment.

![Fig. 2. (a) The typical thermal expansion curve; (b) the corresponding microstructure.](http://example.com/fig2.png)

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CE/BC = f_B. By drawing a parallel line to the base line, AB, to intersect with the TEC, a point of F was determined to be the bainite transformation starting point on the TEC, and the corresponding temperature was the bainite transformation starting temperature, Bs.

3.2. The CCT Curves

Figures 3(a) through 3(d) show the CCT curves of the non-deformed and hot deformed Nb–Ti micro-alloyed steels. The regions for the transformations from austenite to ferrite and pearlite were enlarged due to hot deformation. At slow cooling rates, \( A_r^3 \) was raised by about 100°C due to hot deformation, and this increment decreased with increasing cooling rates. The effect of hot deformation on the end temperatures for austenite to pearlite transformation was not significant.

3.3. The Relationship between \( A_r^3 \) and Ti Content in Nb–Ti Micro-alloyed Steels

Figures 4(a) and 4(b) show the relationships between \( A_r^3 \) and Ti content for non-deformed and hot deformed Nb–Ti micro-alloyed steels, respectively. With increasing cooling rate, the \( A_r^3 \) curve moves down. For non-deformed Nb–Ti micro-alloyed steels, Fig. 4(a), \( A_r^3 \) temperatures decreased when Ti content increased from 0 to 0.015 mass%, with the decreasing rates having been measured to be 18.7°C and 14°C per 0.01 mass% Ti at cooling rates of 0.5°C/s and 5°C/s, respectively. \( A_r^3 \) temperatures leveled off in the range of 0.015 to 0.027 mass% Ti. When Ti content increased from 0.027 to 0.031 mass%, \( A_r^3 \) temperatures decreased abruptly, with the decreasing rates having been measured to be 82.5°C and 87.5°C per 0.01 mass% Ti at cooling rates of 0.5°C/s and 5°C/s, respectively.

For hot deformed Nb–Ti micro-alloyed steels, Fig. 4(b), \( A_r^3 \) temperatures showed no significant difference for the steels containing Ti lower than 0.027 mass%. When Ti con-
tent was more than 0.027 mass%, A$_3$ temperatures decreased abruptly, with the decreasing rates having been measured to be 125°C and 132.5°C per 0.01 mass% Ti at cooling rates of 0.5°C/s and 5°C/s, respectively, greater than that of non-deformed by about 50%.

3.4. The Austenite Grain Size Prior to Ferrite Transformation

Figure 5 shows the average austenite grain sizes in non-deformed and hot deformed Nb–Ti steels prior to ferrite transformation. For non-deformed Nb–Ti steels, the average austenite grain sizes were measured to be 74 μm, 160 μm, 149 μm and 142 μm for steels T1, T2, T3 and T4, respectively. For hot deformed Nb–Ti steels, the average austenite grain sizes were obtained through both measurement and calculation by using Eq. (1) (the hollow dots in Fig. 5):21)

$$d_{ae} = 1.06 \cdot d_f \cdot (1 - R\% / 100)^{1/3} \cdot \exp(-\varepsilon) \quad \text{eq. (1)}$$

Where, $d_{ae}$ (μm) is the austenite grain size prior to deformation, R% is the volume fraction of material undergone static recrystallization within a period of time from the finish of hot deformation, and ε is the amount of strain. For hot deformed steels T2, T3 and T4, as shown in Fig. 6, no recrystallized grains were observed (leading to R% = 0). For the samples of the same steel subjected to the same amount of deformation, their austenite grain sizes were obtained at similar level at different cooling rates if no recrystallization has taken place. Figure 5 shows that the calculated austenite grain sizes are in good agreements with the measured values.

3.5. The Residual Strain

Residual strain is stored in austenite if recrystallization is not complete after hot deformation, and can increase the deformation stored energy to enhance the ferrite transformation.22) Table 2 shows the residual strain in Nb–Ti steels prior to ferrite transformation. For hot deformed steels T2, T3 and T4, the residual strain was considered to be equal to the deformation strain of 0.693 because no recrystallized grains were observed (R% = 0). For hot deformed steel T1, the recrystallization models developed by Dyja and co-workers26) were used to estimate the softening fractions at different cooling rates.

3.6. Precipitates Prior to Ferrite Transformation

Yuan et al.23) calculated the precipitation start times ($t_{0.05}$) of steel T1 by using the Dutta–Sellars model24) and the method proposed by Jonas et al.25) The results showed that precipitation could hardly occur before transformation in non-deformed steel T1, while coarse Nb precipitates were likely to form in hot deformed steel T1 before ferrite transformation started. Figure 7(a) shows that precipitates in the size of 30–50 nm (Arrow A) formed in hot deformed steel T1. Figure 7(b) shows the EDX analysis of the precipitates observed in Fig. 7(a), which indicates that the precipitates are rich in Nb, in good agreements with the calculation results.

Figures 8(a) through 8(d) show Nb–Ti precipitates with EDX analysis in non-deformed and hot deformed steel T3. Figure 8(a) shows a coarse precipitate in the size of about 130 nm in non-deformed steel T3. Figure 8(b) shows the EDX analysis of the coarse precipitates observed in Fig. 8(a), which indicates that the precipitates are rich in Nb and Ti. For hot deformed steel T3, in addition to a few coarse Nb–Ti precipitates like the coarse one in Fig. 8(a), precipitates in the size of 30–50 nm (Arrow A) and some nano precipitates (Arrow B) in the size of about 5–6 nm were also observed, as shown in Fig. 8(c). EDX analysis indicates that they are all rich in Nb and Ti. Figure 8(d) shows the EDX analysis of the coarse precipitates (Arrow A) observed in Fig. 8(c).
Figures 9(a) and 9(b) show Nb–Ti precipitates in non-deformed and hot deformed steel T4, respectively. The Nb–Ti precipitates in the size greater than 100 nm can be still observed in non-deformed and hot deformed steel T4, like the precipitate in the non-deformed steel T3 shown in Fig. 8(a). Figure 9(a) shows that there are nano precipitates (indicated by Arrow A) formed in non-deformed steel T4.

Figure 9(b) shows that there are precipitates (indicated by Arrow B) in the size of 30–50 nm and a number of nano precipitates (Arrow C) in the size of 5–6 nm in hot deformed steel T4. EDX analysis indicates that they are all rich in Nb and Ti, Fig. 9(c) shows EDX analysis of nano Nb–Ti precipitates (Arrow C) observed in Fig. 9(b).
4. Discussion

4.1. Precipitates in Nb–Ti Steels

Three types of precipitates which formed before ferrite transformation were observed in 0.04 mass% Nb–(0–0.031 mass%) Ti micro-alloyed low carbon steels, which were processed by reheating + continuous cooling or reheating + hot deformation + continuous cooling. These precipitates were measured to be rich in Nb and Ti. The coarse Nb–Ti precipitate in the size greater than 100 nm has been observed in all non-deformed and hot deformed Nb–Ti steels with Ti content varying from 0.015 to 0.031 mass%. The formation of these precipitates was independent of hot deformation and cooling process. They were identified to be undissolved Nb–Ti precipitates. The strain induced Nb–Ti precipitates in the size of 30–50 nm were observed in hot deformed Nb–Ti steels with Ti content varying from 0–0.031 mass%, whose compositions depended on Ti contents in steels. The Nb–Ti precipitates in the size of 5–6 nm were observed in steel T4. When 50% hot deformation was performed, these nano precipitates were found in steel T3, showing that hot deformation can also enhance the formation of the nano Nb–Ti precipitates. It can be seen that the quantity of nano precipitates increases with increasing Ti content in steel and deformation amount applied to steel.

4.2. Effects of Nano Precipitates in Austenite on $\text{A}_3$

Figures 10(a) and 10(b) show the austenite grain size and the measured $\text{A}_3$ at a cooling rate of 1°C/s for non-deformed Nb–Ti steels and hot deformed Nb–Ti steels, respectively. For non-deformed Nb–Ti steels, Fig. 10(a),
austenite grain size increased from 74 μm for steel T1 to 160 μm for steel T2, and decreases to 149 μm for steel T3, which could have been the main reason for the variation of \(A_{\gamma3}\).

For steels T3 and T4, their austenite grain sizes were measured to be 149 μm and 142 μm, respectively, and should almost have similar effects on \(A_{\gamma3}\). The \(A_{\gamma3}\) temperature almost showed no significant difference. Therefore, there should be an increasing factor to counteract the decreasing effect on \(A_{\gamma3}\) caused by increasing austenite grain size. It can be seen that more residual strain was stored in steel T2 than steel T1 by 0.033, Table 2, which should have increased the deformation energy to promote ferrite transformation.\(^{22}\) According to the results given by Hwu and Lenard,\(^{22}\) however, a higher energy to promote ferrite transformation, resulting in the increase of \(A_{\gamma3}\).

The \(A_{\gamma3}\) decreasing rates being measured to be 0.015 mass%, the decreasing rates being measured to be

\[
A_{\gamma3} = 660 \exp \left( -\frac{\sqrt{D_T}}{6.7} \right) - 216C_R^{0.1} + 13716([\text{Nb}] + [\text{Ti}])^2 - 111998([\text{Nb}] + [\text{Ti}])^2 + 373 + \delta T
\]

\[
\delta T = \frac{1}{S_{0.05}}(\Delta C) + 87699([\text{Nb}] + [\text{Ti}])^2 + 587 + \delta T
\]

For non-deformed steels T1, T2 and T3, \(\delta T=0^\circ\mathrm{C}\). For non-deformed steel T4, \(\delta T\) has been obtained to be \(-38^\circ\mathrm{C}\). For hot deformed steels, precipitation induced by hot deformation start time, \(t_0.05\), which is calculated by using the Dutta–Sellars model,\(^{24}\) and residual strain in austenite, \(\Delta \varepsilon\), were also taken into account. The equation is expressed as:

\[
A_{\gamma3} = 370 \exp \left( -\frac{\sqrt{D_T}}{6.7} \right) - 316C_R^{0.1} + 10569([\text{Nb}] + [\text{Ti}])^2 + 66 \times \left( \frac{1}{S_{0.05}}(\Delta C) + 87699([\text{Nb}] + [\text{Ti}])^2 + 587 + \delta T \right)
\]

For hot deformed steels T1, T2 and T3, \(\delta T=0^\circ\mathrm{C}\). For hot deformed steel T4, \(\delta T\) was obtained to be \(-51^\circ\mathrm{C}\).

Figure 11 shows comparisons of the measured and calculated values, indicating that the models have good accuracies to predict the \(A_{\gamma3}\) values for Nb–Ti micro-alloyed steels.

5. Conclusions

(1) For non-deformed Nb–Ti micro-alloyed steels, \(A_{\gamma3}\) decreased when Ti content increased from 0 to 0.015 mass%, the decreasing rates being measured to be
18.7°C and 14°C per 0.01 mass% Ti at cooling rates of 0.5°C/s and 5°C/s, respectively. $\Delta r_3$ almost had no change with Ti content in the range of 0.015–0.027 mass%. The decreasing rate was measured to be 82.5°C and 87.5°C at cooling rates of 0.5°C/s and 5°C/s with Ti content in the range of 0.027–0.031 mass%, respectively.

(2) For hot deformed Nb–Ti micro-alloyed steels, when Ti content increased from 0 to 0.027 mass%, $\Delta r_3$ almost had no change, and drastically decreased with further increasing Ti content. The decreasing rates were measured to be 125°C and 132.5°C per 0.01 mass% Ti at cooling rates of 0.5°C/s and 5°C/s, respectively, greater than that of non-deformed.

(3) Three types of Nb and Ti rich precipitates, including undissolved coarse precipitate in the size greater than 100 nm, the precipitate in the size of 30–50 nm and the precipitate in the size of about 5–6 nm, which formed before ferrite transformation were observed in 0.04 mass% Nb–0.031 mass% Ti micro-alloyed low carbon steels processed by reheating and continuous cooling or reheating, hot deformation, and continuous cooling.

(4) The undissolved coarse precipitates have no obvious effect on ferrite transformation. In non-deformed and hot deformed 0.039 mass% Nb–0.031 mass% Ti micro-alloyed steels, nano precipitates were formed in austenite before ferrite transformation, which could have retarded ferrite transformation, leading to a decreased $\Delta r_3$ temperature.

(5) Modeling of $\Delta r_3$ for Nb–Ti micro-alloyed steels has been developed based on the experimental results. For non-deformed Nb–Ti steels,

$$A_{\Delta r_3} = 660 \exp \left( -\frac{D_T}{6.7} \right) - 216C^{0.1}_R + 13 \text{716}([\text{Nb}]+[\text{Ti}])$$

$$-111998([\text{Nb}]+[\text{Ti}])^2 + 373 + \delta T$$

For hot deformed Nb–Ti micro-alloyed steels,

$$A_{\Delta r_3} = 370 \exp \left( -\frac{D_T}{6.7} \right) - 316C^{0.1}_R + 10 \text{569}([\text{Nb}]+[\text{Ti}])$$

$$-87 \text{699}([\text{Nb}]+[\text{Ti}])^2$$

$$+66 \times \frac{1}{S_{0.05}} + \Delta \varepsilon + 587 + \delta T$$

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