Cooling Rate Effects on the As-Cast Titanium Nitride Precipitation Size Distribution in a Low-Carbon Steel

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INTRODUCTION

With high yield strength, toughness and good weldability, microalloyed steels are widely used in the automotive, pipeline and transportation industries. An understanding of the thermodynamics and kinetics of microalloy precipitation during casting and cooling can be important to microstructure control. Titanium nitride (TiN) precipitation is considered here, as TiN has high stability and may precipitate at temperatures near the liquidus. Titanium nitride precipitates may remain stable at elevated temperatures during later processing, suppressing grain growth during solid state processing or in weld heat-affected zones. Smaller precipitates have a greater effect on the grain boundary pinning and therefore the TiN size distribution is important.

Sage and Cochrane previously evaluated the relationship between cooling rate and titanium nitride precipitate size. An inverse linear relationship between particle size and logarithmic cooling rate during/after solidification was reported. The scope of the present study was to examine TiN formation during casting over an expanded range of cooling rates applicable to newer processes.

BACKGROUND

Previous research by Sage and Cochrane examined vanadium and titanium containing steels for welding applications in the off-shore and construction industries. Both vanadium nitrides (VN) and titanium nitrides contributed to the production of a fine grain size. Since titanium nitrides have the ability to control the austenite grain size during the welding process, these particles have an important role of maintaining toughness in the heat-affected zone. Titanium nitride precipitates form in the liquid during casting, so Sage and Cochrane investigated different sized ingots and different locations within these solidified ingots, associated with different post-solidification cooling rates. For their cooling rate study, three trial heats were used, as shown in Table I.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ti</th>
<th>V</th>
<th>Al</th>
<th>N [ppm]</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.14</td>
<td>1.65</td>
<td>0.44</td>
<td>0.006</td>
<td>0.052</td>
<td>0.026</td>
<td>120</td>
<td>0.011</td>
<td>0.017</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>1.56</td>
<td>0.25</td>
<td>0.012</td>
<td>0.039</td>
<td>0.027</td>
<td>80</td>
<td>0.009</td>
<td>0.017</td>
</tr>
<tr>
<td>3</td>
<td>0.12</td>
<td>1.60</td>
<td>0.38</td>
<td>0.013</td>
<td>0.047</td>
<td>0.030</td>
<td>80</td>
<td>0.009</td>
<td>0.016</td>
</tr>
</tbody>
</table>
The temperature at each location during and after solidification was monitored and the cooling rate was determined. Particle sizes were determined with a transmission electron microscope on extraction replicas. Results from that study are summarized in Figure 1.

![Figure 1. Titanium nitride particle size as a function of the post solidification cooling rate (PSCR).](image)

It was found that the particle size decreases with increasing cooling rate and suggested that this relationship could be represented by the negative log-linear trend shown in Figure 1. Sage and Cochrane stated that in the higher cooling rate conditions, no large particles were found. For the cooling rate conditions of 8, 14, and 16 °C/min however, it was indicated that some particles larger than 1 µm were found. The error bars in the plot were included to represent the upper and lower limit of the particle size ranges, excluding the largest particles assumed to precipitate in the interdendritic liquid.

**EXPERIMENTAL PROCEDURE**

For this study, a low carbon steel with the chemical composition shown in Table II was used, as reported by the manufacturer. This commercially thin-slab cast material was provided by Nucor Steel, Hickman, AR and has near stoichiometric titanium and nitrogen levels. The material was machined into 10 mm thick and 121.5 mm long specimens for melting and casting simulation. A thread was machined on each end, to be able to strain the sample while heating it. For the casting simulations a Gleeble® 3500 simulator was employed with a pocket jaw mobile conversion unit using solid water cooled copper 10 mm round bar grips, which provide efficient heating and cooling.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
<th>V</th>
<th>Al</th>
<th>N</th>
<th>S</th>
<th>P</th>
<th>Cu</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0.046</td>
<td>1.23</td>
<td>0.012</td>
<td>0.045</td>
<td>0.013</td>
<td>0.022</td>
<td>0.005</td>
<td>0.022</td>
<td>0.007</td>
<td>0.003</td>
<td>0.006</td>
<td>0.090</td>
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</table>

For temperature monitoring, an “R-type” thermocouple was welded at the mid-length of the specimen. To contain the molten steel, a quartz tube, 31 mm in length and 10.2 mm internal diameter, was slid over the sample. To prevent oxidation while melting the sample, the Gleeble® chamber was evacuated and flushed with argon twice before heating in an argon atmosphere at a pressure 225 Torr below atmospheric. The complete setup can be seen in Figure 2.
Each sample was heated by electrical resistance to 1526 °C until the central region (~10 mm in length) of the sample was fully molten. The dwell time at this temperature was kept as short as possible to avoid chemical reactions with the quartz containment tube. Subsequently the sample was cooled to a temperature of 1000 °C at one of the three cooling rates selected to represent a particular production process and position within the casting. The cooling rates were as follows:

- Centerline cooling rate of a thick slab, 240 mm: 0.1 K/s
- Columnar region cooling rate of a thin slab, 50 mm: 5.0 K/s
- Near surface cooling rate of a thin strip: 600 K/s

For the low (0.1 K/s) and medium (5 K/s) cooling rates, grip cooling was sufficient. For the high cooling rate (600 K/s) however, rapid cooling was achieved by spraying gaseous helium onto the sample surface. Initially, a thin strip surface cooling rate of 1700 K/s was planned. It was found using the Gleeble® 3500 casting setup in this temperature regime, that 600 K/s was the maximum achievable cooling rate. Once the specimen was cooled to 1000 °C, each sample was “quenched” by shutting off the Gleeble’s heating power and then grip cooling to room temperature. Schematic thermal profiles for the casting simulations are shown in Figure 3.
The quenching temperature of 1000 °C was chosen based on an analysis of the titanium nitride solubility. Using the solubility product expression in Equation 1 below, less than 1 wt pct of titanium should remain in solution in austenite under equilibrium conditions at a temperature of 1000 °C.

\[
\log K_{\text{TiN}} = \log[\%\text{Ti}][\%\text{N}] = -\frac{15.790}{T} + 5.40
\]  

In Equation 1, \(K_{\text{TiN}}\) is the solubility product of titanium nitride, \([\%\text{Ti}]\) and \([\%\text{N}]\) are the solute concentrations of Ti and N in austenite, respectively in wt pct and \(T\) is the temperature in Kelvin.

After processing, each specimen was cut into smaller pieces. The central region, where the temperature was recorded, was sectioned for metallography, mounted in Bakelite®, ground to 600 grit and polished down to 1 µm using a diamond suspension. The samples were lightly etched for 30 seconds using a 2 pct nital solution and then subsequently coated with a thin carbon film for replication. Only the near-surface portion of the cross-sectional area, close to the thermocouple position was coated. Then each sample was etched in a 5 pct nital solution for a few minutes, to release the replicas, which were captured on Cu grids. Specimens were examined by transmission electron microscopy (TEM) in bright-field using a FEI (Phillips) CM 200. At least two different replicas were examined for each condition. On each replica, at least three grids were examined and ImageJ® software was used to measure the titanium nitride particle size. For each particle, two measurements were taken and averaged, as shown using the example in Figure 4. For the cooling rates of 0.1, 5 and 600 K/s, 120, 330, and 885 precipitates were measured, respectively. Most of those precipitates were of cuboidal shape with some minor variations. Some precipitates were found to show less distinct edges. Due to the much greater stability of TiN compared to TiC at the investigated range of temperature (liquidus – 1000 °C) and the fact that some excess nitrogen was present, it was presumed that the cuboidal precipitates are TiN.

At elevated temperatures, the possibility of reactions between the atmosphere and melt was of concern. Therefore, the formation of oxides was suppressed by running the simulation in an argon atmosphere. Reactions between the quartz tube and the melt at elevated temperatures were still possible, so the chemical composition of a melted and resolidified sample was compared to the composition of an untested casting specimen as shown in Table III. It is noted that the levels of C, Si, and Ti were not substantially changed after remelting. It was therefore concluded that any reactions between the quartz tube and specimen are not significant.

**Table III. Composition for an Untested and Tested (Remelted and Solidified) Gleeble Casting Sample in wt pct.**

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untested</td>
<td>0.048</td>
<td>1.28</td>
<td>0.024</td>
<td>0.030</td>
<td>0.040</td>
<td>0.016</td>
<td>0.025</td>
</tr>
<tr>
<td>Tested</td>
<td>0.053</td>
<td>1.21</td>
<td>0.029</td>
<td>0.054</td>
<td>0.039</td>
<td>0.013</td>
<td>0.022</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>Nb</th>
<th>V</th>
<th>Al</th>
<th>S</th>
<th>P</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untested</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>0.016</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.078</td>
</tr>
<tr>
<td>Tested</td>
<td>0.012</td>
<td>&lt;0.001</td>
<td>0.016</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.089</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Figure 5 shows representative titanium nitrides found in the three steels cooled at different rates during and after solidification. All three micrographs were recorded at the same magnification and therefore show quite effectively the dramatic differences in TiN particle size between the three different cooling rates representing different industrial casting processes. Clearly, the TiN particle size is diminished at faster cooling rates, as expected, and consistent with the general trend reported in prior work.1

![Figure 5](image)

Figure 5. Representative TEM micrographs of carbon extraction replicas for the (a) 0.1 K/s, (b) 5 K/s, and (c) 600 K/s cooling rates. The inset in (c) shows the small precipitates at higher magnification.

Overall, the precipitates appeared similar when viewing different regions of the carbon extraction replicas. While the precipitates in Figure 5 do not necessarily represent the precise average particle size for the specific cooling rate condition, they were typical and represent the overall differences between the three conditions. In the low cooling rate samples (0.1 K/s, Figure 5a) larger titanium nitride particles were present. Several particles reached a size in the range of 1 to 2.5 microns. Those particles were visible under a conventional light optical microscope. In the case of the high cooling rate (600 K/s, Figure 5c) the much smaller particles were often grouped in clusters of up to 30 precipitates. An example of fine particle clustering is shown in Figure 6. It is believed that the clustering of small precipitates happened during, and is an artifact of, the preparation of the replicas.8

![Figure 6](image)

Figure 6. TiN particles formed in the 600 K/s cooling condition: clustering of the particles was observed.

Particle size distributions can be seen in Figure 7. The particle size distributions in Figure 7 are suggestive of bimodal characteristics, and the overlaid curves fitted to the data include a log-normal distribution at small particle sizes and a normal distribution for larger particles. In the case of the 0.1 K/s cooling condition, the particle sizes range from 9 to 2400 nm. Approximately 90 pct of all measured particles are found in the log-normal part, whereas about 10 pct of the precipitates are larger than 1000 nm. Most of the particles, however, are smaller than 250 nm. It is believed that the large precipitates may have formed in the interdendritic liquid, whereas the small particles formed in the solid.9 The medium cooling rate condition (5 K/s) exhibits smaller particles compared to the 0.1 K/s cooling rate. The precipitate sizes range from 3 to 883 nm. The bimodal character was again evident. With increasing cooling rate, not only did the overall particle size decrease, but also the range of the distribution decreased. For the high cooling rate condition (600 K/s) an even smaller range of particle sizes was found. The largest precipitate measured was 58 nm and the smallest particles were around 3 nm. Such fine TiN particles could contribute to precipitation strengthening, and suggest a potential new TiN strengthening mechanism that might be applicable for example, to thin strip products.
In order to obtain an overall particle size value for each of the three cooling conditions, average sizes were calculated from the distributions that were fitted to the data. Average sizes for the fine and coarse components of each distribution are presented in Table IV. In Sage and Cochrane’s earlier study,¹ the larger particles were presumed to have formed in the interdendritic liquid, and were excluded from their analysis since those particles do not contribute as effectively to grain size control as smaller particles. To compare the results of the current study to those of Sage and Cochrane, the average particle size from the log-normal distribution was used to characterize each steel.

Figure 7. Titanium nitride precipitate size distribution for the (a) 0.1, (b) 5, and (c) 600 K/s cooling conditions, including experimental data and fitted curves. Note changes in scale of abscissa.
Table IV. Mean Particle Size for Fine and Coarse TiN Distributions in Each Cooling Condition. The Standard Deviation and Fraction of Particles in Each Component of the Distribution are also shown.

<table>
<thead>
<tr>
<th>Cooling Condition</th>
<th>Fit to Fine Distribution</th>
<th>Standard Deviation</th>
<th>Fraction of Particles</th>
<th>Average Particle Size [nm]</th>
<th>Fit to Coarse Distribution</th>
<th>Standard Deviation</th>
<th>Fraction of Particles</th>
<th>Average Particle Size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 K/s</td>
<td>Log-normal</td>
<td>1.21</td>
<td>0.92</td>
<td>101.0</td>
<td>Normal</td>
<td>0.11</td>
<td>0.08</td>
<td>1897.0</td>
</tr>
<tr>
<td>5 K/s</td>
<td>Log-normal</td>
<td>1.49</td>
<td>0.84</td>
<td>22.5</td>
<td>Normal</td>
<td>0.22</td>
<td>0.16</td>
<td>537.0</td>
</tr>
<tr>
<td>600 K/s</td>
<td>Log-normal</td>
<td>0.27</td>
<td>0.89</td>
<td>6.7</td>
<td>Normal</td>
<td>0.30</td>
<td>0.11</td>
<td>22.8</td>
</tr>
</tbody>
</table>

The average particle size is plotted in Figure 8 versus cooling rate for the present work, along with the prior results of Sage and Cochrane. The overall trend of decreasing particle size with increasing cooling rate is illustrated. For low cooling rates, the average particle size is quite comparable to results from Sage and Cochrane. The medium (5 K/s) and high (600 K/s) cooling rate data expand the range of cooling rates beyond the earlier work, and show that the trend becomes non-linear over the wider range of cooling rates. As mentioned previously, the TiN distributions obtained at the high cooling rate may be of special interest in the context of thin-strip casting.

![Figure 8](image-url)

Figure 8. Titanium nitride particle size as a function of the post solidification cooling rate. The current data (black squares) as well as Sage and Cochrane’s data (open diamonds) are included.

**CONCLUSIONS**

The expected general trend of increasing particle size with decreasing cooling rate was confirmed over the range of cooling rates representing thick-slab through thin-strip processing. The range of cooling rates reported by Sage and Cochrane was successfully expanded and now also gives valuable information for future products subjected to accelerated cooling rates during solidification, e.g. thin strip. The presence of nano-scale titanium nitrides at high cooling rate suggests that a new strengthening mechanism may be available to enhance the properties of rapidly-cooled steels. The increased super saturation associated with faster solidification may have interesting implications for other compounds that can precipitate at high temperatures in austenite. For example, it may be possible to employ higher Nb additions, utilize MnS for beneficial purposes, etc.

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References


