The Effects of Vanadium, Niobium, Titanium and Zirconium on the Microstructure and Mechanical Properties of Thin Slab Cast Steels

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The evolution of precipitation and microstructure during a simulation of the thin slab direct rolling process, in six vanadium based, low carbon, steels with V, V–N, V–Ti–N, V–Nb, V–Nb–Ti and V–Zr additions was studied by optical microscopy, analytical transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDAX) and parallel electron energy loss spectroscopy (PEELS). Tensile properties and Charpy vee-notch toughness of the final strip were also determined. The effects of microalloying additions and processing conditions, including equalisation temperature (1 200°C, 1 100°C and 1 050°C) and end water cool temperature, on the austenite and ferrite grain sizes, as well as the type and composition of the precipitates, were determined. The relationship between the microstructure and the properties in the steels was also ascertained.

KEY WORDS: vanadium; nitrogen; vanadium–niobium; vanadium–titanium and vanadium–zirconium microalloyed steel; thin slab direct rolling; equalisation temperature; microstructure; precipitation; mechanical properties.

1. Introduction

Thin slab casting and direct rolling (TSDR) technology has brought global changes to manufacture of hot rolled coil, due to its higher productivity and lower energy requirement. However, both the microstructural development during TSDR and the mechanical properties of the final coil may be expected to differ from equivalent steels, which have undergone conventional rolling (CCR).1–4)

Compared with the thick slabs (200–250 mm) used in CCR, thin slabs (30–90 mm) are cast at higher speeds (up to 6 m/min) and the rapid solidification results in reduced segregation.5) In CCR processing, the austenite is metallurgically conditioned by the phase transformations that occur during slab cooling and reheating. The austenite grain size after soaking and at the start of the rolling process is then usually smaller than it was in the original cast slab, being affected by any undissolved inclusions and carbonitrides.6) With TSDR methods, the continuously cast steel is hot rolled following direct charging to an equalisation furnace, without the intermediate stages of cooling to room temperature before rolling, as in CCR. Prior to the commencement of hot rolling, the austenite then has the coarse-grained, dendritic and segregated microstructure of the original casting. In addition, the amount of reduction introduced during rolling in TSDR is frequently less than in conventional practice. Furthermore, the as-cast microstructure prior to rolling is generated at temperatures in excess of 1 450°C, where the equilibrium solubility of microalloyed carbonitrides is very much greater than that at the soaking temperatures used in CCR. Therefore, the as-cast phase may be more highly supersaturated with respect to microalloying elements than the reheated phase in CCR processing. This could be expected to have an effect on precipitation during the processing.

The aim of this project was to investigate the evolution of the microstructure, and particularly the precipitates present during the TSDR process at several stages in the process route; after casting, after equalisation, after the fourth rolling pass and in the final coil. The investigation was carried out using a series of vanadium containing microalloyed steels and the observed microstructure and mechanical properties were related to the chemical composition and the processing conditions.
2. Experimental Procedures

2.1. Materials

The study examined six, low carbon (\(\sim 0.06\%\)), vanadium based, microalloyed steels: V (0.10 % V, 0.007 % N), V–N (0.10 % V, 0.02 % N), V–Ti–N (0.10 % V, 0.01 % Ti, 0.17 % N), V–Nb (0.11 % V, 0.03 % Nb, 0.011 % N), V–Nb–Ti (0.11 % V, 0.31 % Nb, 0.07 % Ti, 0.011 % N) and V–Zr–Ti (0.10 % V, 0.008 % Zr, 0.010 % N), all mass percent. The full chemical composition of the steels is given in Table 1. The thin slab direct rolling processing was simulated at Corus Group, Swinden Technology Centre and a schematic diagram representing the processing is shown in a previous paper. The steels were melted in air and cast into three moulds to produce 50 mm thick, 18 kg ingots and the typical cooling rate at the mid-thickness position of the ingots was 3.5°C/s. The ingots were hot stripped from the mould and the ingot surface temperature at stripping was typically >1 100°C. After stripping, the ingots were wrapped in insulating wool and transferred directly to an equalisation furnace. The ingot surface temperature at charging to the equalisation furnace was 930–1 095°C and the ingots were equalised at 1 050, 1 100 or 1 200°C for 30–65 min prior to rolling. (For Steel V, the ingots were only equalised at 1 100 and 1 200°C.) After equalisation, the ingots were rolled on a laboratory-reversing mill to 7 mm strip using a rolling schedule with 5 passes. After the fourth pass, the strip was held until a temperature of 870°C was reached. The hold period was 25–40 s, which enabled sampling to proceed. The finish rolling temperature was reached. The hold period was 25–40 s, which enabled sampling to proceed. The typical cooling rate at the mid-thickness position of the ingots was about 1 mm for all of the steels. The austenite grain sizes in the as-cast ingots and in the specimens after the fourth pass, as well as the ferrite grain size in the final strip, were measured using a linear intercept method on a optical microscope with a an image analyser. Precipitates in the steels at different stages during the process were studied, using carbon extraction replicas, on an analytical Philips EM-400 TEM with a Phoenix Energy Dispersive X-ray (EDAX) attachment. The composition of the precipitates was analysed using EDAX and by parallel electron loss spectroscopy (PEELS), using a Vacuum Generators HB5 microscope. The size of the precipitates was measured on TEM micrographs, using an image analyser.

3. Results

3.1. Evolution of Grain Size during the Processing

The average prior austenite grain size in the 1/4 thickness position of the ingots was about 1 mm for all of the steels. After equalisation, the microstructure and prior austenite grain size were similar to those in the as-cast ingots. The initial coarse as-cast austenite grains were refined in four rolling passes. A recrystallised austenite structure was observed in the steels with the exception of Steel V–Nb, equalised at 1 050°C, which had a mixed austenite grain structure (90% recrystallized grains and 10% deformed grains), indicating that only partial recrystallisation had occurred in this steel. The average prior austenite grain size in the steels after the fourth pass is given in Table 2. A smaller austenite grain size was found in the Ti, Nb or Zr containing steels than in Steel V and Steel V–N, for all the equalisation temperatures. In addition, the austenite grain size was larger in the steels after equalisation at 1 200°C than after equalisation at 1 050 or 1 100°C, except for Steel V–Zr. (Fig. 1).

The microstructure in the final strip of all of the steels consisted of ferrite and pearlite and the average ferrite grain size for the steels is given in Table 2. Ferrite grain sizes in the multiple microalloyed steels were slightly finer than those of Steel V and Steel V–N. Steel V–Zr had the finest ferrite grain size of all, despite having austenite grain size similar to, or coarser than Steels V–Ti–N, V–Nb and V–Nb–Ti. Figures 2(a) and 2(b) show the effects of the equalisation temperature and the end water cool temperature on the ferrite size. There is a weak trend, which indicated that the ferrite grain size became larger as the equalisation temperature increased.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>N</th>
<th>Nb</th>
<th>Ti</th>
<th>Zr</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.062</td>
<td>0.45</td>
<td>1.47</td>
<td>0.015</td>
<td>0.004</td>
<td>0.020</td>
<td>0.007</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>V–N</td>
<td>0.068</td>
<td>0.37</td>
<td>1.40</td>
<td>0.014</td>
<td>0.005</td>
<td>0.025</td>
<td>0.020</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>V–Ti–N</td>
<td>0.065</td>
<td>0.47</td>
<td>1.44</td>
<td>0.015</td>
<td>0.006</td>
<td>0.026</td>
<td>0.017</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>V–Nb</td>
<td>0.061</td>
<td>0.48</td>
<td>1.48</td>
<td>0.015</td>
<td>0.005</td>
<td>0.035</td>
<td>0.011</td>
<td>0.030</td>
<td>0.005</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>V–Nb–Ti</td>
<td>0.056</td>
<td>0.51</td>
<td>1.45</td>
<td>0.016</td>
<td>0.005</td>
<td>0.022</td>
<td>0.011</td>
<td>0.031</td>
<td>0.007</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>V–Zr</td>
<td>0.063</td>
<td>0.53</td>
<td>1.46</td>
<td>0.016</td>
<td>0.006</td>
<td>0.027</td>
<td>0.010</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.008</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Cr:0.09%, Mo:0.02%, Ni:0.07%, Cu:0.07% for all the steels.
sation temperature or end water cool temperature was increased. Figure 2(c) shows the influence of $V/H_{11003}N$ on the ferrite grain size. The data plotted in this figure were obtained from the steels examined in this project and also from some V and V–N steels in previous work.\(^7,8\) All of the steels had the same base composition and were processed under similar conditions. There is a general trend for the ferrite grain size to decrease as the product of $V/H_{11003}N$ increased in Steels V and V–N. Some values of the multiple microalloyed steels follow the trend, while the addition of Zr, Ti or Nb does, under some process conditions, lead to a smaller ferrite grain size than the median.

Figure 3 gives the relationship between the austenite grain size after the fourth rolling pass and the ferrite grain size. It can be seen that the austenite grain size after the fourth rolling pass has only a relatively weak effect on ferrite grain size in the steels.

### 3.2. Precipitation during the Processing

#### 3.2.1. After Casting (Stage A)

After casting, only oxides and sulphides were observed in the V, V–N and V–Nb steels, but nitrides were observed in the Ti containing steels.\(^3\) For Steel V–Ti–N, the main precipitates after casting were irregularly shaped particles, which were usually present in rows and had a particle size of 40–200 nm. The irregularly shaped particles contained both V and Ti, and had an atomic ratio of $V/(Ti+V)=0.5$. A small number of Ti rich ($V/(Ti+V)=0.07$) cuboid particles were also observed. Most of the Ti rich precipitates had a size ranging from 50 to 350 nm, but a few of the particles were about 1 μm in size. In addition, a few complex and dendritic particles were found and the core and arm of the dendrites had similar $V/(Ti+V)$ ratios, i.e. 0.3–0.4.

For Steel V–Nb–Ti, the main precipitation in the as-cast slab was large dendritic particles, which consisted of V, Nb,

### Table 2. Austenite grain size after the fourth pass and ferrite grain size in the final strip.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Equalisation Temperature ($^\circ$C)</th>
<th>Austenite Grain Size (μm)</th>
<th>End Water Cool Temperature ($^\circ$C)</th>
<th>Ferrite Grain Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>1100</td>
<td>537</td>
<td>520</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>602</td>
<td>520</td>
<td>3.6</td>
</tr>
<tr>
<td>V–N</td>
<td>1050</td>
<td>750</td>
<td>520</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>602</td>
<td>520</td>
<td>5.2</td>
</tr>
<tr>
<td>V–TiN</td>
<td>1050</td>
<td>754</td>
<td>511</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>630</td>
<td>511</td>
<td>6.7</td>
</tr>
<tr>
<td>V–Nb</td>
<td>1050</td>
<td>645</td>
<td>700</td>
<td>8.8</td>
</tr>
<tr>
<td>V–Nb–Ti</td>
<td>1050</td>
<td>642</td>
<td>700</td>
<td>9.8</td>
</tr>
<tr>
<td>V–Zr</td>
<td>1050</td>
<td>642</td>
<td>700</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Fig. 1. Influence of equalisation on austenite grain size after the fourth rolling pass.

Fig. 2a. Effect of equalisation temperature on the ferrite grain size in the final coil.

Fig. 2b. Effect of end water cool temperature on the ferrite grain size in the final coil.

Fig. 2c. Effect of V×N on the ferrite grain size in the final coil.
Ti and N. The atomic ratio of V/(V + Nb + Ti) was 0.25 and of Nb/(V + Nb + Ti), 0.37, with Ti making up the remainder. Again, there was no difference in composition between the core and arm of the dendrites. Some needle-like V–Nb–Ti(N) particles were also found.

For Steel V–Zr, the only particle found to contain Zr was a large particle, in which Zr was the only metallic element. No particles containing V were found at this stage, in this steel.

3.2.2. After Equalisation (Stage B)

(i) 1 200°C Equalisation

No carbonitrides were identified in the Ti free steels. In the Ti containing steels, spherical nitride particles in the matrix were observed in Steel V–Ti–N. The size of these particles was 20–50 nm and the V/(Ti + V) ratio was 0.6.

Cuboid particles on rows and cruciform particles in the matrix were seen in Steel V–Nb–Ti, but the density of the particles was much lower than that after equalisation at 1 050 or 1 100°C. The cuboid particles had a size of 10–70 nm (avg. 35 nm) and the V/(V+Nb+Ti) ratio was 0.29 and Nb/(V+Nb+Ti) was 0.25. The cruciform particles had an arm length of 30–60 nm (avg. 42 nm) and were of similar composition to the cuboid particles.

For Steel V–Zr, the main precipitates were CuS based needle-like particles. Most of the particles were distributed in matrix and a few of them were precipitated on grain boundaries. The particles contained Cu, S, V and Ti, although Ti was not a deliberate addition. Because the specimen holder used in TEM was made from a Cu alloy, it is difficult to analyse the Cu content of the particles. The atomic ratio of V/(Ti+V) of the CuS based particles was 0.40–0.45. No particles containing Zr were identified.

(ii) 1 100°C Equalisation

For the Ti free steels, no carbonitrides were found in either of Steels V or V–N. However in Steel V–Nb, cuboid particles of size 50–110 nm (avg. 68 nm), were observed on prior austenite grain boundaries along with large complex particles in the matrix. The cuboid particles contained both V and Nb and the V/(V+Nb) ratio was 0.29 and the Nb/(V+Nb) was 0.71. The complex particles comprised of V, Nb, Al and O and had a V/(V+Nb) ratio of 0.41 and a Nb/(V+Nb) ratio of 0.59.

For Steel V–Ti–N, the main precipitation was cruciform particles, which were distributed on both the prior austenite grain boundaries and in the matrix. Fig. 4. The length of the cruciform arm varied from 30 to 150 nm. The cruciform particles were identified as V–Ti(N) and the atomic ratio of V/(Ti+V) was 0.6.

The main precipitation in Steel V–Nb–Ti equalised at 1 100°C was cuboid particles on prior austenite grain boundaries, Fig. 5. Some of the cuboid particles had the appearance of growing cruciform particles. The cuboid particles had a size of 10–60 nm (avg. 27 nm) and a V/(V+Nb+Ti) ratio of 0.32 and a Nb/(V+Nb+Ti) ratio of 0.30, the remainder being Ti. Cruciform particles in the matrix were also observed in Steel V–Nb–Ti and the cruciform arm length was from 10 to 60 nm (avg. 27 nm). Once again, the cruciform particles had a similar composition to the cuboid particles.

Precipitation in Steel V–Zr after equalisation at 1 100°C was also mainly CuS based particles in the matrix. These particles had cuboid or complex morphologies. Most of the CuS based particles contained Ti and V and only a few of the particles were found containing Zr. Atomic ratio of V/(V+Ti+Zr) of the particles was 0.45–0.65 and Zr/(Ti+V+Zr) was about 0–0.02.

(iii) 1 050°C Equalisation

Steel V was not equalised at 1 050°C. Cuboid particles on prior austenite grain boundaries were observed in both of the V–N and V–Nb steels. The cuboid particles in Steel V–N were identified as VN by using PEELS, while the cuboid particles in Steel V–Nb were VN(C, N) and the V/(V+Nb) ratio was 0.35, with Nb making up the remainder. A few VN particles, associated with MnS inclusions were also observed in Steel V–N. The size of the cuboid particles was 10–80 nm (avg. 24 nm) in Steel V–N and 40–100 nm (avg. 62 nm) in Steel V–Nb. AlN was also found at this equalisation temperature in Steel V–N, but it was only associated with MnS or MnN and VN.

For the steels containing Ti, the main precipitation was the same as that in the specimens equalised at 1 100°C. However, the particles in the steels after equalisation at 1 050°C had a smaller particle size, and higher vanadium content. For Steel V–Ti–N, the cruciform arm length was from 20 to 50 nm and the V/(Ti+V) ratio was 0.7. For Steel V–Nb–Ti, the particle size was generally smaller, 10–40 nm (avg. 22 nm) for the cuboid particles and 20–40 nm (avg. 33 nm, arm length) for the cruciform particles. Both types of particle had a V/(V+Nb+Ti) ratio of 0.39 and a Nb/(V+Nb+Ti) ratio of 0.36. In addition, complex particles, which contained V, Ti, N, S and Mn, were also found in the matrix of Steel V–Ti–N.
For Steel V–Zr, the precipitation was once again CuS based particles, containing Ti and V or Ti, V and Zr and having similar morphologies to the particles observed after equalisation at 1000°C. The atomic ratio of V/(V/Ti/Zr) was 0.5–0.7 and Zr/(V/Ti/Zr) was 0–0.1 for the CuS based particles.

3.2.3. After Fourth Pass Rolling and Holding (Stage C)

No major precipitation occurred between the start of rolling and the end of the fourth pass in any of the steels. The particles, which precipitated during casting and equalisation were retained after the fourth rolling pass. However, they grew during rolling/or after rolling. Most of the cuboid particles on the prior austenite grain boundaries, which were observed after equalisation in Steel V–Nb–Ti, developed into cruciform particles. Additionally, a few broken cruciform and dendritic particles were found in both Steel V–Ti–N and Steel V–Nb–Ti at this stage.

3.2.4. After Coiling (Stage D)

Fine precipitates (<15 nm), distributed in the matrix were observed in the final strip for all of the steels and these fine particles are likely to be those responsible for dispersion strengthening. Atomic ratios of V/Metal, Nb/Metal, Ti/Metal, Zr/Metal, N/Metal and C/Metal for the fine particles are given in Table 3 and Fig. 6. It can be seen that the fine particles in ferrite were essentially V-rich nitrides. The V/Metal in the fine particles was higher for the V and V–N steels than that for the multiple microalloyed steels, except for Steel V–Zr, which had the highest value of V/Metal.

N/Metal in the fine particles is mainly dependent on nitrogen content in the steels, a higher nitrogen content resulting in an increase in this ratio. In addition, a Ti addition, lower equalisation temperature or higher end water cool temperature appeared to decrease the N/Metal. No Zr was found in the fine particles, which were examined in Steel V–Zr by both EDAX and PEELS.

3.3. Mechanical Properties

The mechanical properties for the steels are summarised in Table 4. The contribution to yield strength from dispersion strengthening (DS) was calculated by subtracting the components of yield strength (σy) due to ferrite lattice fraction stress and C+N in solution (σo), solid solution strengthening (σs) and ferrite grain size strengthening (σg) from the measured value using a modified version of the Hall–Petch equation, with the units in MPa. In this analysis, it was assumed that strengthening from dislocations and texture was low and similar for all the steels examined.

\[
\sigma = \sigma_o - (\sigma_i + \sigma_s + \sigma_f) \quad \text{(1)}
\]

\[
\sigma_o = 45 \text{ MPa} \quad \text{(2)}
\]

\[
\sigma_s = 84(\text{Si}) + 32(\text{Mn}) + 38(\text{Cu}) + 43(\text{Ni}) \quad \text{(3)}
\]

\[
\sigma_f = 18.1 \text{ d}^{-1} \quad \text{(4)}
\]

The lower yield strength (LYS) and ultimate tensile strength (UTS) in the final strip were in the range from 416 to 632 MPa and 543 to 740 MPa, respectively. The elongation (EL) varied from 10 to 27% and showed no significant dependence on either equalisation temperature or end cool temperature. However, there was a trend for the elongation value to decrease with an increase in the product of V/N.

The lower values (EL=10% and 15%) of Steel V–N equalised at 1050°C were due to the test pieces breaking quite a distance from the middle of the gauge length. The 13J-impact transition temperature (13J ITT) obtained from sub-standard test specimens varied from −120 to −40°C, while Charpy Energies (J@) absorbed at −20°C varied between 20–76 J.

Figures 7 and 8 display the influences of equalisation temperature, end water cool temperature and V/N on the lower yield strength, dispersion strengthening and Charpy vee-notch toughness in the steels. The data plotted on Figs. 7(c) and 8(c) for V and V–N steels are from the steels of this study and also from some steels of previous work.
There were increases in both the lower yield strength and dispersion strengthening with increasing equalisation temperature, decreasing end water cool temperature and increasing $V/N$. The use of Ti in the V–N and V–Nb steels resulted in a reduction in the yield strength and dispersion strengthening. However the addition of Zr to the V steel slightly increased the lower yield stress of the steel, but had no effect on dispersion strengthening. The toughness was relatively insensitive to both equalisation and end water cool temperatures. There was, however, a trend for the ITT to increase as the product of $V/N$ increased. As can be observed in Fig. 9, this increase in ITT was almost entirely due to the increase in dispersion strengthening. It is noticeable from this figure that, at the same level of dispersion strengthening, the steels containing Ti have a similar level of toughness to the steels which are Ti-free.

4. Discussion

4.1. Grain Size

The absence of the $\gamma\rightarrow\alpha\rightarrow\gamma$ phase transformations before rolling and a frequently smaller total reduction in thickness
in TSDR processing would be expected to have an effect on grain refinement during the processing. However, the present study has shown that the initial coarse austenite grain size (=1 mm) was refined after four rolling passes, and resulted in a fine ferrite grain size (4.5–7.8 μm) in the final strip. The fine and uniform austenite grains obtained after the fourth pass implies that recrystallization occurred and that repeated recrystallization eliminated the initial, coarse, as-cast structure. The results also indicated that the precipitates, in austenite, at high temperatures had no major effect on retarding recrystallization, but they appeared to prevent recrystallized austenite grain growth during and after rolling, especially in the multiple microalloyed steels. The only steel which exhibited incomplete recrystallization after the fourth rolling pass was the V–Nb steel equalised at 1 050°C. This is probably due to the well-documented effect of Nb inhibiting recrystallization by a solute drag mechanism and/or precipitation during rolling. The multiple microalloyed steels showed a larger austenite grain size compared with Steel V and Steel V–N.

The equalisation temperature had a small influence on the austenite grain size after the fourth pass (Fig. 1) and there was a slight increase in the austenite grain size with increasing equalisation temperature, with the exception of Steel V–Zr. As the equalisation temperature increased, the rolling temperature for the first four rolling passes also increased. The rolling temperature affects both the rate at which recrystallization occurs and the rate of austenite grain growth after recrystallisation. Consequently, a larger austenite grain size was developed after the fourth rolling pass in the steels following 1 200°C equalisation.

The change in austenite grain size with the different equalisation temperatures was not reflected in any significant change in ferrite grain size obtained in the final coil. There is a weak trend for the ferrite grain size to increase as the equalisation temperature increased and the end cool temperature decreased, Figs. 2(a) and 2(b). Also the ferrite grain size in the steels decreased as the V/N product increased, Fig. 2(c). Most of the values of the ferrite grain size for multiple microalloyed steels were below the trend line of the V and V–N steels, but were within the scatter band of the V and V–N steels.

### 4.2. Precipitation

Because the carbides and nitrides of titanium, zirconium, niobium and vanadium are isomorphous and mutually soluble, the equilibrium precipitate in the multiple microalloyed steels should be mixed compounds of V–Ti(C,N), V–Nb(C,N), V–Nb–Ti(C,N) or V–Zr(C,N), depending on the composition of the steel. Based on the solubility equations of the carbides and nitrides in V, Nb and Ti microalloyed steels, which are recommended by Tukdogan and Rose, the solution temperatures of the carbonitrides and the weight percent of the precipitates in the steels at various temperatures were calculated, using the ChemSage thermodynamic software package, Fig. 10. As a result of the observations of the precipitation in the steels, it was assumed that AlN was dormant in all of the steels, except Steel V–N after 1 050°C equalisation and they all Zr precipitated in Steel V–Zr during casting, as Zr oxides or Zr nitride. The solution temperatures of the carbonitrides are 1 049°C in Steel V–N, 1 106°C in Steel V–N, 1 158°C in Steel V–Nb, 1 339°C in steel V–Nb–Ti and 1 443°C in Steel V–Ti–N. The solution temperature of V(C,N) in Steel V–Zr is 1 072°C. It can be seen that Nb, and especially Ti additions increased the solution temperatures of the carbonitrides in the steels. The thermodynamic indications are in a good agreement with the experimental observations, of the nitrides or carbonitrides which precipitated during and/or after casting in the Ti containing steels.

According to the solubility equation for ZrN given by Evans and Pelhike, the solution temperature of ZrN in Steel V–Zr should be 1 221°C. However, only one particle containing Zr was found in the as-cast specimen. This may have been because the particles were large and did not readily extract. Additionally, it was observed that no Zr compounds were identified in the later stages of the processing. This suggests that Zr precipitation might have been completed during casting. Furthermore, no co-precipitation of Zr and V was found in the as-cast specimen of Steel V–Zr. Complex precipitates of Ti–Zr and Ti–Nb–Zr carbonitrides were reported by He and Baker in controlled rolled Zr microalloyed steels, but the content of Zr in the steels they used was 0.016% which is double of the Zr content used in Steel V–Zr. Thus, it is probable that the Zr content in Steel V–Zr was too low to have a significant effect on precipitation.

No major precipitation occurred in the steels between the start of rolling and the end of the fourth rolling pass, despite the rolling temperature being below the calculated solution temperatures of the carbonitrides in the steels. Nucleation and growth of strain induced precipitation is affected by rolling conditions such as temperature, strain, strain rate and interpass time. Within the parameters used in the present rolling schedule, it is unlikely that the conditions required for significant strain induced precipitation occurred.

The calculated equilibrium solution temperature of AlN was 1 119°C for Steel V, 1 290°C for Steel V–N, 1 241°C for Steel V–Ti–N, 1 263°C for Steel V–Nb, 1 090°C for Steel V–Nb–Ti and 1 194°C for Steel V–Zr. These temperatures were all higher than the minimum equalisation temperature i.e. 1 050°C. However, AlN particles were only observed in Steel V–N after 1 050°C equalisation and they were always associated with MnS or MnS–VN particles. AlN has a close packed hexagonal structure and nucleates with some difficulty in austenite. Its nucleation is controlled by kinetics as well as thermodynamics. The presence of AlN in Steel V–N may be due to the high solution tempera-
ture of AlN, resulting in a higher driving force for nucleation of AlN in this steel compared with the other steels. However, the fact that its nucleation was always associated with other particles suggests that these particles assisted by lowering the energy barrier for nucleation. In the other steels in this work, the stability of titanium (or niobium) vanadium nitrides was greater than that of heterogeneously nucleated AlN, even though MnS particles were present in all the steels. So the nitrogen was invariably combined with the transition metals in preference to aluminum.

Additions of Ti to the steels also changed the morphology of the precipitates. For the Ti containing steels, dendritic particles were observed after casting. In addition, cruciform particles precipitated during equalisation, but they were not observed in the Ti free steels. Previous studies\(^{24-27}\) reported that the observation of cruciform particles is a feature of microalloyed steels having an addition of Ti, usually in association with V and/or Nb. The distribution and size of the cruciform particles were different in Steels V–Ti–N and V–Nb–Ti. The cruciform particles formed on the grain boundaries and in the matrix of Steel V–Ti–N during equalisation at 1 100°C and 1 050°C, but they are precipitated mainly in the matrix of Steel V–Nb–Ti. The size of the cruciform particles was smaller in Steel V–Nb–Ti than in Steel V–Ti–N. It is believed that Nb restricted the growth of the cruciform particles in Steel V–Nb–Ti, due to the slower diffusion rate of Nb in austenite compared with V or Ti.

It has been reported\(^{24,27-30}\) that, in conventional rolled V–Ti or Nb–Ti micro-alloyed steels, the complex Ti–V or Ti–Nb particles often had a nitride core (Ti rich) plus hemispherical carbides caps or a carbide coating (V or Nb rich). However, this was not observed in the present study and may be due to the different processing conditions between conventional rolling and thin slab direct rolling.

**Figures 11(a)–11(c)** display both the V/Metal ratio calculated thermodynamically and the experimentally measured V/Metal ratio, for the carbonitrides in the V–Ti–N, V–Nb and V–Nb–Ti steels. It can be noted that both the theoretical calculations and experimental results show that when the particles formed in austenite at higher temperatures they were rich in Ti and, to a lesser extent, in Nb. However, they were rich in V when they formed in austenite at lower temperatures. Furthermore, the precipitates were much richer in V when they nucleated in ferrite, (V/Metal=0.81–0.9 theoretical, V/Metal=0.69–0.88 experimental). Additionally, theoretical predictions of the V/(Ti + V) and V/(V + Nb + Ti) ratios in the precipitates reflect the experimental results very well for the Ti containing steels, except for the V/(V + Nb + Ti) ratio of the fine particles formed at 600°C in Steel V–Nb–Ti. This latter result is considered to be due to the difficulty of extracting fine particles with a size smaller than 4 nm from bulk specimens. The average size of the particles, which have been examined, may be larger than the actual average size of the fine particles existing in ferrite of the steels. These larger particles may have formed at temperatures higher than 600°C and, consequently, have a lower V/(V + Nb + Ti) ratio than would have been expected for steels cooled at 600°C.

For Steel V–Nb, the experimental V/(V + Nb) ratios of the particles formed in both austenite and ferrite were lower than that indicated theoretically by ChemSage calculations.
larger than for VC and the larger chemical driving force makes VN or N-rich V(C,N) the preferred precipitation as long as there is sufficient nitrogen in the matrix. Zajac et al.\textsuperscript{29,31} pointed out that the majority of V(C,N) can be carbon rich in ferrite only when the nitrogen content in solution is below about 0.005% and, even then, it is unlikely to occur because it would require the reaction to proceed to equilibrium at a low temperature and a low driving force. Because there was no major precipitation during rolling of the steels, the nitrogen in solution before the γ→α transformation would be greater than that indicated by the ChemSage calculation for the equilibrium condition. This could result in the forming of N-rich V(C,N) particles in ferrite. Another possibility is the loss of carbon from the particles during the PEELS analysis by radiation damage, but this was shown to be most unlikely since a significant number of small particles were found to be essentially stochiometric nitrides.\textsuperscript{32}

There are several factors, which may affect the N/Metal ratio of the fine particles. The N/Metal atomic ratio in the precipitates is mainly related to the nitrogen content in the steels. For the steel, which had higher nitrogen content, the fine particles also had a higher average value of N/Metal ratio. The end water cool temperature also had an effect on the N/Metal ratio of the fine particles.\textsuperscript{33} For the same steel, fine particles in specimens with lower end water cool temperatures had a higher average value of N/Metal ratio than those with higher end water cool temperatures. For example, in Steel V–N, lowering the end water cool temperature from 720 to 511°C raised the N/Metal ratio of the fine particles by ~0.1. In addition, lowering the equalisation temperature and making a Ti addition appeared to decrease the N/Metal in the fine particles. There should be more N precipitated as nitrides in austenite during lower temperature equalisation than higher temperature equalisation, hence reducing the amount of N available for the fine particles in ferrite. In similar manner, a Ti addition to the steels resulted in more N being out of solution at higher temperatures in austenite.

4.3. Mechanical Properties and Toughness

Adding Ti to the steels resulted in a decrease in the lower yield strength. The lower level of the yield strength in the Ti containing steels is directly related to a reduction in the contribution from dispersion strengthening, Figs. 7(a)–7(c).

Dispersion strengthening in steel is dependent on the volume fraction, particle size and inter-particle spacing of fine particles in ferrite. In the present study, the fine particles in ferrite were essentially, V-rich nitrides. Therefore, the volume fraction of fine particles should depend mainly on the amounts of V and N which were available to precipitate in ferrite. ChemSage calculations predicted that the addition of Ti to the steels promoted precipitation of carbonitrides in austenite at a much higher temperature, resulting in more V and N being out of solution before γ→α transformation, Fig. 12 and therefore, decreased the volume fraction of the fine particles, Fig. 13. This result is supported by the composition of the particles observed in Steels V–Ti–N and V–Nb–Ti after the casting and equalisation. Furthermore, the Nb containing steels showed a higher volume fraction of the fine particles than the Nb free steels.

The size and inter-particle spacing of the fine particles are controlled by the nucleation and growth rates. The essential parameter governing the variation in nucleation rate is the chemical driving force for precipitation, while that governing growth is the diffusion rate. It is well known that, in vanadium micro-alloyed steels, nitrogen has a strong effect in increasing the driving force for precipitation, which results in a finer V(C,N) particle size, higher density of V(C,N) particles and decreased particle coarsening tendency in steels with higher nitrogen content.\textsuperscript{24,31} The slower growth rate of V(C,N) in high N steels, was explained as resulting from greater particle nucleation rate, thereby producing earlier impingement of V-denuded zones and so slowing down the precipitate growth. According to thermodynamic calculations, there should be less N left in solution in the Ti containing steels before the γ→α transformation than in the Ti free steels. Therefore, the chemical driving force for nucleation of the fine particles in ferrite should also be smaller in the Ti containing steels, leading to a lower density, larger inter-particle spacing and coarser size of the fine particles. This effect could also be responsible for the lower dispersion strengthening obtained in the Ti containing steels.

The effect of Ti in reducing the yield strength in V or Nb micro-alloyed steels has also been found in previous work.\textsuperscript{5,27,35} Crowther and Morrison\textsuperscript{35} revealed that the addition of 0.01% Ti to V and V–Nb microalloyed steels resulted a significant reduction in yield strength, accompanied by an improvement in the Charpy toughness. He and Baker\textsuperscript{27,34} reported that a small Ti addition (0.01–0.022%) was found to lower the yield strength of niobium-bearing steels in both the as-rolled and normalized conditions. The reduction of yield strength was due to the presence of larger, complex Ti–Nb carbonitrides in austenite. However, the work of Bodnar et al.\textsuperscript{29} has shown that Ti–Nb–V steel ex-
hibited a superior balance of strength and toughness compared with Ti free steels. This improved balance of mechanical properties for the Ti-bearing steel was due to a suitable refinement in the mean ferrite grain size and a reduction in precipitation strengthening increment.

5. Conclusions

The evolution of microstructure and mechanical properties in six micro-alloyed low carbon V–N, V–Ti–N, V–Nb, V–Nb–Ti and V–Zr steels, produced by simulating the thin slab direct rolling route has been studied. It has been demonstrated that:

1. The thin slab direct rolling process, as used in the simulation, is capable of reducing an as-cast austenite grain size of ~1 mm to an austenite grain size of 16–51 μm after the four rolling passes, resulting in a ferrite grain size of 4.2–7.8 μm in the final coil, largely independent of this austenite grain size.

2. The addition of Ti to Steel V–N and Steel V–Nb increased the solution temperature of the carbonitrides in the steels, resulting in precipitation of V–Ti(N) or V–Nb–Ti(C,N) during and/or after casting, and during equalisation. No significant precipitation occurred during rolling.

3. The vanadium content in the precipitates increased with decreasing precipitation temperature and the highest vanadium content was found in the fine particles (~15 nm), which formed in ferrite. The fine particles are considered to be responsible for dispersion strengthening. In addition, the precipitates in both austenite and ferrite were essentially nitrides.

4. A good combination of high yield strength (LYS = 420–630 MPa), good toughness and good ductility was obtained in all the steels. The yield strength slightly increased with an increase in equalisation temperature, with a higher value of V×N and with a lower end water cool temperature.

5. The addition of Ti to the V–N and V–Nb steels decreased the yield strength as a result of the formation of V–Ti(N) or V–Nb–Ti(N) particles in austenite, which reduced the amount of V and N available for subsequent precipitation as fine particles in ferrite. The addition of Nb to the V steel increased the yield strength due to a combination of a slight reduction in ferrite grain size and increased dispersion strengthening. The addition of Zr had no significant effect on precipitation of (V,C,N) in the steel, but it reduced the ferrite grain size, which improved the toughness of the steel.

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