Phase Transformations, Clustering and Strengthening in Modern Line Pipe Steels

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1. INTRODUCTION

The evolution and advancement of line pipe steels have relied substantially on microalloying additions [1]. Similarly, hot rolled strips and plates have been improved noticeably by adopting microalloying strategies [2,3]. The prominent benefits of microalloying additions entail the suppression of austenite grain growth [4] and recrystallization [5] relevant to high temperature TMCP and welding, and precipitation hardening by random, interphase and strain induced processes [6,7]. Other advantages include controlling phase transformation kinetics; for instance during run-out table cooling [8], and influencing the recovery of dislocations and softening during coiling [2-3,9]. In modern hot rolled products where accelerated cooling in conjunction with low temperature coiling is utilized, a low-carbon bainitic microstructure tends to dominate, as such a tangible strengthening contribution of microalloy carbonitrides is not expected. Moreover, the utility of the Nb and V addition on tailoring austenite decomposition and controlling the softening upon coiling have not been exploited entirely. Relevant to bainitic hot rolled skelps and strips with low to medium carbon content, several advantages of vanadium microalloying have been reported [2,3, 10-12]. However, the underlying mechanism has not been understood clearly as to whether the precipitation, clustering or solid solution effect on phase transformation and tempering is the key factor. Hutchinson [3] found extra strengthening up to 100 MPa in a 0.08 wt% vanadium containing hot strip steel cooled between 400 – 500 °C and argued a higher resistance of bainite to tempering due to vanadium addition. Siwecki [2] discussed the pinning effect of V(C,N) in suppressing the recovery of dislocation tangles, but no direct evidence has been provided. Nafisi [10] reported 60 to 100 MPa gain in strength of a laboratory X100 plate containing 0.063 wt% vanadium without tangible degradation of toughness compared to the reference X100 plate. Benz [13] has found vanadium-based nanoprecipitates during cooling simulation at 550°C with slight effect on hardness evolution of a V-added HSLA steel subjected to Gleeble simulation. Gu has noticed site-specific nanoprecipitates by APT and TEM analysis in a Nb-V-added model alloy exposed to a coiling simulation at 500°C [14].

Our previous work has shown changes in transformation kinetics and in microstructural features of the decomposition products due to vanadium addition in a laboratory X100 line pipe steel [15]. The proposed concept is further explored in this paper by confirming the strengthening role of vanadium for another experimental X70 plate processed by CanmetMATERIALS pilot
Moreover, to deconvolute the individual role of vanadium and niobium, four Ti-free model alloys with simple chemistries but containing different amounts of V and/or Nb have been studied to verify the strengthening mechanism of vanadium in low-carbon bainitic microstructures subjected to a low coiling temperature.

2. EXPERIMENTAL

Two experimental X70 plates were produced by CanmetMATERIALS’ pilot scale vacuum casting and rolling facility. The cast ingots had dimension of 200 mm x 100 mm x 250 mm with the measured composition as shown by Table 1. The summary of the thermomechanical processing steps is also included in the table. These two line pipe steel plates are referred herein to X70-Ref and X70-V to indicate the vanadium microalloying addition of 450 ppm for the latter; all the other composition and processing parameters were identical between the two X70 plates.

Moreover, to deconvolute the role of vanadium from other microalloying additions and to exclude the effect of other alloying elements in commercial line pipe steels (e.g. Cr, Mo, Ni, Cu), four model alloys were designed and produced. The composition and processing history are shown in Table 1. The hot rolled plates with 11 mm thickness were adopted for dilatometry study whereas 0.8 mm sheets were used for Gleeble strip annealing and subsequent room temperature tensile tests. The dilatometer thermomechanical routes entailed continuous cooling experiments to determine CCT diagrams (Route A), and in-situ compression at different coiling temperatures to evaluate the tempering response of the microstructure (Route C). The thermal cycles consist of a leading solutionizing treatment at 1200°C to dissolve microalloy carbonitrides. The trailing cycle at a lower reheating temperature of 1000-1050°C aimed to refine the prior austenite grain size while maintaining microalloying atoms in solution. An option for austenite conditioning (pancaking) was included with 0.3 straining at 850°C prior to cooling. Solid cylinders with 5 mm diameter and 10 mm length were machined from quarter thickness of the plates for the dilatometry study using a quench-deformation Bahr DIL 805 apparatus. Standard size ASTM E8/E8M specimens were cut from Gleeble strip along the rolling direction. These cold-rolled strips, following a complete austenitization and no deformation, were subjected to different coiling temperatures and holding times consistent with the thermal path of “Route C” using a Gleeble 3800 simulator and its strip annealing rig.

Microstructural features of the pilot plates, dilatometer and Gleeble samples were studied by means of EBSD and TEM. The EBSD scans were conducted using a field-emission gun scanning electron microscope (FEI Quanta-650), with an accelerating voltage of 20 kV. TSL OIM 6.2 software performed the EBSD data processing and quantitative orientation analysis. A Tecnai Osiris 200KV FEG-STEM equipped with a Gatan Enfina EELS system and four windowless Super-X SDD EDX detectors for chemical mapping was used to prepare TEM micrographs. To perform atom probe tomography, a Cameca local electrode 77 atom probe (LEAP) 4000X HR was used in 78 laser pulsing mode and at a pulse rate of 250 kHz. Data analysis and reconstruction were completed using IVAS 3.6.8 software.

<table>
<thead>
<tr>
<th>Elements (wt%)</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ti</th>
<th>V</th>
<th>Nb</th>
<th>Cr</th>
<th>Al</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>X70 – Ref</td>
<td>0.054</td>
<td>0.25</td>
<td>1.74</td>
<td>0.022</td>
<td>0.002</td>
<td>0.060</td>
<td>0.22</td>
<td>0.034</td>
<td>0.0083</td>
</tr>
<tr>
<td>X70 – V</td>
<td>0.054</td>
<td>0.25</td>
<td>1.74</td>
<td>0.022</td>
<td>0.045</td>
<td>0.060</td>
<td>0.21</td>
<td>0.039</td>
<td>0.0083</td>
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<tr>
<td>Processing</td>
<td>Reheating at 1200°C, roughing reduction of 70%, finishing reduction of 75% with FRT = 780°C, laminar water cooling and coiling at 510°C, producing final plate thickness of 15mm.</td>
<td></td>
<td></td>
<td></td>
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</tr>
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</table>

<table>
<thead>
<tr>
<th>Model Alloys</th>
<th>Elements (wt%)</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ti</th>
<th>V</th>
<th>Nb</th>
<th>Cr</th>
<th>Al</th>
<th>N</th>
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</thead>
<tbody>
<tr>
<td>Base V-free</td>
<td>0.063</td>
<td>0.27</td>
<td>1.98</td>
<td>-</td>
<td>0.001</td>
<td>-</td>
<td>-</td>
<td>0.042</td>
<td>0.0041</td>
<td></td>
</tr>
<tr>
<td>V-added</td>
<td>0.056</td>
<td>0.28</td>
<td>2.00</td>
<td>-</td>
<td>0.110</td>
<td>-</td>
<td>-</td>
<td>0.044</td>
<td>0.0039</td>
<td></td>
</tr>
<tr>
<td>Nb-added</td>
<td>0.066</td>
<td>0.24</td>
<td>1.93</td>
<td>-</td>
<td>0.003</td>
<td>0.03</td>
<td>-</td>
<td>0.044</td>
<td>0.0055</td>
<td></td>
</tr>
<tr>
<td>V-Nb added</td>
<td>0.068</td>
<td>0.25</td>
<td>1.91</td>
<td>-</td>
<td>0.104</td>
<td>0.03</td>
<td>-</td>
<td>0.044</td>
<td>0.0058</td>
<td></td>
</tr>
<tr>
<td>Processing</td>
<td>Hot rolled plates: Reheating at 1200°C, roughing reduction of 82%, finishing reduction of 50%, laminar water cooling or air cooling to produce plate thickness of 11mm.</td>
<td>Cold rolled strips: Hot rolling of 11mm plate to 1.8mm strip followed by cold rolling to 0.8 mm thickness.</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</table>
3. RESULTS AND DISCUSSION

3.1 Experimental X70 plates

The microstructures of the two X70 plates are illustrated by the EBSD micrographs of Figure 2. Irregular ferrite grains dominate the microstructure along with a small fraction of granular bainite. The density of low-angle boundaries identified with 1 to 14 degree misorientation, was slightly higher in X70-V. Further, slight grain refinement was observed due to vanadium addition resulting in a mean grain diameter of 4.97 $\mu$m versus 5.66 $\mu$m measured at quarter thickness for X70-V and X70-Ref, respectively. There was evidence of a higher meso-strain stemming from more dislocations in X70-V steel, based on KAM and GOS analysis of EBSD scans. The mean KAM values based on 3-neighbour analysis were 1.2 and 1.8 degree misorientation for X70-Ref and X70-V, respectively. Since the dislocation density can be estimated from KAM and directly is proportional to $\theta_{KAM}$ [16], this implies the presence of 30% more dislocations in the V-added plate. The GOS maps of Figures 2c and 2d also indicate the presence of grains with higher strains in the X70-V sample that is consistent with the higher KAM value.

Comparing the tensile properties of the two X70s in Figure 3a, it is obvious that the addition of vanadium has improved the overall strength without any drawback on elongation. The yield strength of X70-V was 575 MPa compared to that of the reference steel, 532 MPa and the UTS value of V-added steel was 652 MPa versus 610 MPa of the X70-Ref, showing about 40 MPa gain in both yield and ultimate strength due to vanadium microalloying. The CVN transition curves of the two X70 plates are plotted in Figure 3b. The reference X70 has superior impact toughness attributes as indicated by a higher upper shelf energy of 400 J and a lower ITT of -80°C, compared to that for X70-V. Nevertheless, the impact toughness properties of X70-V is respectable with an upper shelf energy of 280 J and ITT of lower than -50°C.

The tensile flow curves at room temperature indicate the properties of the X70 plates following the coiling where the products of austenite decomposition during run-out table rapid cooling is subjected to a subsequent prolonged slow cooling. Several microstructural changes are expected during coiling including tempering of the transformation products as well as precipitation of carbonitrides depending on the coiling temperature. As such, it is insightful to determine the strength evolution throughout the coiling stage and to better understand the strengthening effect of vanadium in the fresh transformation products and after tempering during subsequent coiling. The in-situ compression tests as depicted by Route C of Figure 1 were conducted and the summary of the strength evolution is presented in Figure 4. The strength of fresh transformation products, measured after one minute holding at the coiling temperature, in X70-V is clearly higher than the X70-Ref counterpart for both 500°C and 600°C coiling simulation. Upon further holding at the coiling temperature the strength tends to drop, however the V-added steel demonstrated more resistance to this softening, as indicated by the percentage softening value beside each curve. The plateau of the softening curve for X70-V after prolonged coiling at 600°C could be related to a potential vanadium precipitation which offsets the recovery of the dislocation substructure. The sluggish recovery of bainitic microstructures in vanadium containing steels has been reported by Hutchinson in low carbon hot strip steels containing 0.08 wt% V [3]. Consistent with our findings of Figure 4, Hutchinson noticed substantial softening during coiling due to the recovery of the dislocation substructure of the bainite matrix. The softening and strength loss were found to be more substantial at coiling temperatures above 500°C, however with vanadium microalloying the final strength of the steel strip was insensitive to coiling temperature which was attributed to the pinning and stabilization of dislocations by V(C, N) [3].
Figure 2. EBSD micrographs showing Orientation Map (OM) and Grain Orientation Spread (GOS) of the experimental X70 hot-rolled plates (a) X70-Ref OM, (b) X70-V OM, (c) X70-Ref GOS, and (d) X70-V GOS.

Figure 3. Tensile and CVN properties of the experimental X70 line pipe skelps. The abrupt stress rise around 3% strain in (a) is related to a change in strain rate.
3.2 Model alloys

3.2.1 Phase Transformation behaviour of model alloys

The austenite decomposition response of the model alloys during cooling and coiling can be evaluated based on their CCT diagrams. Examples of CCT diagrams that include measured Ac1 and Ac3 temperatures, are illustrated in Figure 5. The plots show that the addition of 0.1 wt% vanadium has raised the austenite formation temperatures Ac1 and Ac3 compared to the base alloy, i.e., an increase of 24°C was measured for Ac3 temperature upon heating at 0.5°C/s (see Table 2). However, during cooling, the vanadium addition noticeably shifts the bainite and martensite transformation domains to a much lower temperature range. For example, Ar3 temperature for bainite start formation at 30°C/s cooling has decreased from 655°C to 599°C comparing the base versus the V-added variants; a 57°C shift. As it is summarized in Table 2, a 44°C lower Ms temperature was also noticed in this V-added alloy compared to the base. Even with the presence of Nb, the transformation start temperature of bainite and martensite has shifted to lower temperatures with vanadium microalloying. Namely, the bainite start temperature Ar3 (30°C/s) of Nb-added alloy decreased from 650°C to 630°C by addition of V in the Nb-V-added variant, while Ms (150°C/s) changed from 501°C to 465°C. A gradual shift to a lower decomposition temperature for austenite containing incremental values of Nb in solution has been reported previously [8, 17]. The CCT diagrams of Figure 5 demonstrate similar effects of vanadium in the low-carbon model alloys prominently at the higher cooling rates relevant to bainite formation. However, it is not seen at higher start temperatures associated with ferrite formation and its subsequent growth where interphase precipitation of vanadium is likely to occur. It is difficult for vanadium atoms to redistribute or precipitate during fast cooling paths where bainite forms. As such the shift in the transformation temperature range of bainite can be attributed to vanadium atoms in solid solution and its potential interaction with carbon. Further, it is noted that a lower bainite transformation temperature is seen despite the thermodynamic effect of vanadium on ferrite stabilization as illustrated by the more than 30°C higher Ac3 in the V-added compared to the V-free model alloy, as shown in Table 2.

Table 2. Summary of the transformation temperatures of the model alloys measured by dilatometry.

<table>
<thead>
<tr>
<th>(in °C)</th>
<th>V- free</th>
<th>V - added</th>
<th>Nb-added</th>
<th>Nb-V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac1 (0.5°C/s)</td>
<td>871</td>
<td>905</td>
<td>882</td>
<td>893</td>
</tr>
<tr>
<td>Ac1 (0.5°C/s)</td>
<td>721</td>
<td>755</td>
<td>697</td>
<td>707</td>
</tr>
<tr>
<td>Ar1 (10°C/s)</td>
<td>662</td>
<td>636</td>
<td>652</td>
<td>649</td>
</tr>
<tr>
<td>Ar1 (30°C/s)</td>
<td>656</td>
<td>599</td>
<td>650</td>
<td>630</td>
</tr>
<tr>
<td>Ar1 (50°C/s)</td>
<td>636</td>
<td>571</td>
<td>646</td>
<td>617</td>
</tr>
<tr>
<td>Ar1 (80°C/s)</td>
<td>608</td>
<td>545</td>
<td>616</td>
<td>552</td>
</tr>
<tr>
<td>Ms</td>
<td>518</td>
<td>476</td>
<td>501</td>
<td>465</td>
</tr>
</tbody>
</table>
3.2.2 Microstructure characterization results of model alloys

The EBSD micrographs of V-free and V-added model alloys from dilatometer samples which have been cooled at 30°C/s and subjected to different coiling simulations are presented in Figure 6. The cooling rate of 30°C/s is representative of run-out table laminar cooling for skelps with 10-20 mm thickness. As expected from the measured CCT diagrams, the 30°C/s thermal path resulted in a bainitic microstructure mainly in lath morphology along with some granular bainite. The colors represent Euler angles and thus lattice orientations. Black lines mark the grain boundaries with misorientation angle above one degree. It is seen that at 550°C coiling a single-variant bainite is dominant in each grain/packet, while occasional multi-variant laths can be detected within a single packet for the samples coiled at 500°C. The density of laths with low angle boundary (LAB) misorientation appears to decrease at the higher coiling temperature. Further, the V-added alloy tends to show a higher fraction of these LABs.

At higher magnifications, TEM micrographs reveal the underlying dislocation substructure within the bainite laths and the micro-constituents associated with the lath or grain boundaries. For instance, Figure 7 shows the TEM micrograph of the V-free alloy which was coiled for thirty seconds at 500°C (Route B). A sub-micron lath morphology for bainite is seen. Further, Mn and carbon-rich cementite was frequently found at lath/packet boundaries as verified by analyzing selected area diffraction patterns and EDX composition maps (Figure 7b-c). The TEM micrographs of the V-added specimen coiled for one hour at 500°C are shown in Figure 8. The overall features were very similar with the V-free specimen showing bainite substructures and the presence of cementite as well as martensite-austenite (MA) micro-constituents at lath/packet boundaries. No traces of any vanadium carbonitride precipitation was found in the V-added or Nb-V-added model alloys which were coiled at or below 550°C.
Figure 6. EBSD micrographs of the base V-free and V-added model alloys coiled at 500°C and 550°C for a short (30 s) and longer (one hour) holding time. Colors are associated with Euler angle representing different crystal orientations.

Figure 7. TEM micrographs of V-free model alloy sample coiled at 500°C for 30 seconds. (a) Bright field image, (b) and (c) EDX carbon and manganese maps, respectively. Cementite at lath/packet boundaries was confirmed by SAD.

Figure 8. TEM micrographs of the V-added model alloy sample coiled at 500°C for one hour. Top left shows the bright field image and the color images illustrating distribution of carbon (orange), manganese (blue) and vanadium atoms (red) throughout the microstructure.
Atom probe tomography was conducted on samples coiled at 500°C and 550°C for up to ten hours. An example of the APT analysis and reconstruction is presented in Figure 9 for the V-added alloy coiled ten hours at 500°C. The reconstruction shows iso-surfaces for entities with more than 1 at% vanadium (in light blue) and objects with more than 5 at% carbon (in red). As such, a cementite particle can be readily identified. This is consistent with TEM findings and validate that cementite exists in both fresh and coiled specimens. Further, a high number density of vanadium-clusters can be observed blue spherical particles. These vanadium rich clusters have a mean radius of 1.1 nm. Composition analysis of the clusters revealed both V-C and V-N entities. The summary of size and number density measurements of these V-C and V-N clusters with coiling time and temperature is given in Table 3. The radius of these clusters increases with prolonged coiling, however V-C clusters tend to go through coarsening (decrease of number density) whereas V-N clusters demonstrate a growth process (increase of both radius and density). Vanadium rich particles have been found by Gu [14] in the same Nb-V model alloy coiled at 500°C. However, due to a different thermal path, the microstructure in that study consisted of ferrite and bainite compared to an entirely bainitic microstructure in this work. Gu identified vanadium-rich particles with 5 nm size in the bainitic region and much smaller clusters in ferrite grains arranged frequently in parallel arrays implying interphase nucleation. Consistent with the reconstruction map of Figure 9a, Gu has seen a high density of vanadium-rich nanoprecipitates in the vicinity of cementite particles.

Figure 9. (a) Carbon and vanadium iso-surface in V-Added alloy, and (b) vanadium iso-surface in V-Nb-added model alloy (coiled for ten hours at 500°C).

Table 3. Quantitative analysis of vanadium clusters based on APT data of V-added model alloy.

<table>
<thead>
<tr>
<th></th>
<th>Radius, nm (SD ~0.3 nm)</th>
<th>No. density, ( \mu )m(^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 hr</td>
<td>10 hrs</td>
</tr>
<tr>
<td>V-C</td>
<td>0.97</td>
<td>1.11</td>
</tr>
<tr>
<td>V-N</td>
<td>0.85</td>
<td>1.08</td>
</tr>
</tbody>
</table>

3.2.3 Mechanical properties of the model alloys

The tensile flow curves of the base V-free and V-added model alloy coiled at 500°C for ten minutes and five hours are shown in Figure 10. The tensile tests were conducted at room temperature using the cold-rolled samples treated by Gleeble strip annealing setup (cf. Figure 1, Route B without deformation). A higher flow curve of V-added steel compared to the base steel is obvious throughout the entire span of the straining and regardless of coiling time. For instance, there is a 77 MPa gain in UTS of 10 min coiled samples with vanadium addition. The total elongation of V-added steel is somewhat lower than the base alloy. The elastic to plastic transition appears to be smooth and continuous for the samples with a short hold time at the cooling temperature, i.e. 10 min. However, with prolonged coiling of five hours there is clear evidence of discontinuous yielding and occurrence of yield point phenomena. The upper yield point is very pronounced in the base alloy coiled for five hours. This can be better examined in Figure 10b which illustrates the initial elastic-plastic region of the flow curves and the inclusion of a 0.5% offset line. It is worthwhile to note that the discontinuous yielding and yield point phenomenon are almost absent for the short cooling time with the V-added sample showing very round and smooth elastic to plastic transition and V-free steels demonstrating a very subtle kink during yielding. On the other hand, very prominent upper and lower yield points are noticed.
for the prolonged coiled base alloy (5 hours hold at 500°C), whereas a less pronounced upper and lower yield point can still be detected for the V-added steel. It should be noted that both base V-free and V-added alloys demonstrated softening as they were exposed to a longer coiling period.

The effect of holding time at coiling temperature on the evolution of flow curves for the V-added steel is illustrated in Figure 10c. Two obvious trends can be seen; firstly, the overall strength decreases with extending the coiling time up to one hour followed by a strength gain upon further coiling to five hours. This gain is about 27 MPa using 0.5% offset method. Secondly the smooth and continuous yielding at the shortest coiling period is replaced with an obvious discontinuous yielding in the sample coiled for the longest time.

![Figure 10](https://example.com/figure10.png)

**Figure 10.** Stress-strain flow curve of the base V-free and V-added model alloys coiled at 500°C for different coiling hold times. Note: Cold rolled samples were fully austenitized without any pancaking deformation and subjected to different coiling simulations using Gleeble annealing rig (see Figure 1, Route B).

### 3.3 Strengthening Analysis

The tensile flow curve of the model alloys demonstrate clearly higher strength values of the V-added alloy compared to the base V-free counterpart. It is shown in Figure 10b, for the samples held shortly at the coiling temperature of 500°C, i.e. 10 minutes, there is a 74 MPa difference in flow stress measured at 0.5% offset. Here the flow stress of the base and V-added alloys are 360 MPa and 434 MPa, respectively. The TEM and APT characterization of these steels for this short coiling time revealed no fine carbonitride precipitation of vanadium, nor niobium. As such, the gain in strength can be attributed to the microstructural features of the bainite matrix. The refinement of bainite lath/platelet and additional dislocation substructure of the bainite have been proposed previously in the literature [15]. This possible mechanism can be further explored and verified for the base V-free and V-added model alloys. Table 2 indicates the transformation start of bainite is 656°C and 599°C at 30°C/s and shows the vanadium addition resulted in a lower Ar3 temperature. The calculated bainite lath thickness and bainite dislocation density for these two transformation temperatures are illustrated in Table 4. The data from Singh [18] for the temperature dependency of lath thickness and the formulation of Bhadeshia for dislocation density [19] were used. The estimated lath thickness is consistent with the TEM observations of these model alloys. The contribution of lath thickness to the flow strength can be estimated using \( \sigma_{\text{lath}} (\text{MPa}) = 115/\lambda \), where the lath thickness \( \lambda \) is in \( \mu \text{m} \) [19]. The contribution from dislocation structure is estimated using Taylor’s formula \( \sigma_{\text{dis}} (\text{MPa}) = 0.48\mu b \rho \). Here \( \mu \) is shear modulus, \( b \) is the magnitude of the Burgers’s vector and \( M \) is the Taylor factor, and \( \rho \) is the dislocation density. Table 4 shows that an additional 33 MPa due to lath refinement and 40 MPa gain due to a higher dislocation density are expected for the V-added alloy as the result of the lower transformation temperature. The combined contribution is about 72 MPa which is very close to the difference determined experimentally, i.e., 74 MPa for samples coiled for 10 min at 500°C.

Although the fresh bainite at the early stages of coiling tends to undergo softening, as seen in Figure 10c, at prolonged coiling beyond a few hours, e.g., five hours, a gradual increase of flow curve with coiling time was found. For instance, the flow stress of the V-added model alloy measured at 0.5% offset increases from 423 MPa to 500 MPa with additional coiling time from one hour to five hours. This can be attributed to formation of strengthening particles at longer coiling periods. Here, the quantitative information from APT of the V-added steel as presented in Table 3 can be used to estimate the strengthening
contribution of V-C and V-N clusters. The vanadium clusters with a size in the order of few nanometers are expected to be shearable causing the gliding dislocation line intersecting the pinning cluster to bend slightly. The bend angle scales with the strength of the pinning particle [20]. Adopting the correction of Foreman-Making for the weak obstacles:

$$\Psi(\beta) = \beta^{3/2}\left[0.8 + \frac{2}{5\pi}\cos^{-1}(\beta)\right]$$

The strength contribution of the clusters can be estimated using:

$$\sigma_{\text{cluster}} = \frac{M\mu b}{L}\Psi(\beta)$$

where $\beta$ is the strength of one cluster with respect to the dislocation line tension. Assuming a very weak cluster strength, i.e. $\beta = 0.1$, and using the quantitative data of size and volume fraction for V-C and V-N clusters, the strength contribution of combined clusters was estimated and is presented in Table 4. It is seen that a value of 29 MPa is estimated for such a population of V-based clusters, which is close to the strengthening gain at longer coiling times. At higher coiling temperatures, e.g., 600°C, the formation of VC and/or VN is expected and the analysis of strengthening should explicitly account for the contribution of these precipitates. This is relevant for the softening curve of X70 experimental plates which is presented in Figure 4.

Table 4. Estimate of strengthening contributions.

<table>
<thead>
<tr>
<th></th>
<th>V-free</th>
<th>V-added</th>
<th>$\Delta\sigma$, MPa @25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_r_3$, °C</td>
<td>656</td>
<td>599</td>
<td></td>
</tr>
<tr>
<td>$\lambda$, µm</td>
<td>0.40</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>$\sigma_{\text{uth}}$, MPa</td>
<td>290.18</td>
<td>322.51</td>
<td>32.33</td>
</tr>
<tr>
<td>$\rho$, m⁻¹</td>
<td>4.2E+14</td>
<td>6.74E+14</td>
<td></td>
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<tr>
<td>$\sigma_{\text{dis}}$, MPa</td>
<td>150.37</td>
<td>190.52</td>
<td>40.16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Clusters mean size: $2r$, nm</th>
<th>Clusters volume fraction: $f_{\text{volume}}$</th>
<th>Clusters interspacing: $L$, nm</th>
<th>$\sigma_{\text{cluster}}$, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-C</td>
<td>2.20</td>
<td>0.000198</td>
<td>102.85</td>
</tr>
<tr>
<td>V-N</td>
<td>2.16</td>
<td>0.000293</td>
<td>84.55</td>
</tr>
<tr>
<td>$\sqrt{\sigma_1^2 + \sigma_2^2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta\sigma_{\text{total}}$, MPa</td>
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</tr>
</tbody>
</table>

4. CONCLUSIONS

The implications of vanadium microalloying in low-carbon, high-strength steels with irregular ferrite and/or bainite microstructures were studied. The main findings are as follows:

- Vanadium addition in the amount of 0.045 wt% to a 0.05C-0.022Ti-0.06Nb (wt%) experimental X70 line pipe steel processed by CanmetMATERIALS pilot facility showed a 40 MPa gain in tensile strength with an ITT lower than -50°C. EBSD analysis has revealed a slight grain refinement and a more dislocated microstructure compared to the X70-Ref plate. Further, interrupted coiling simulation by means of in-situ warm compression method confirmed a lower tendency of softening during coiling due to vanadium microalloying, i.e., V reduces temper softening in bainite.

- In 0.06C-0.28Si-2Mn (wt%) model alloys, vanadium microalloying of 0.1 wt% resulted in a substantially lower transformation temperature of bainite upon cooling between 5 to 80°C/s. For instance, a more than 55°C shift toward a lower $A_r_3$ temperature for bainite formation was found when cooling at 30°C/s for a V-added alloy compared to a
V-free variant. The respective lower bainite transformation temperature due to vanadium addition was about -20°C when the model alloy contains 0.03 wt% Nb. A lower Ms temperature was also found for vanadium model alloys despite a ferrite stability as exhibited by the higher Ac3 temperature of V-added versus V-free steels.

- Microstructure analysis by TEM did not reveal V(C, N) precipitates for samples coiled at 500 to 550°C, however APT confirmed the presence of V-N and V-C clusters of 2 to 3 nm in size, distributed in the bainite matrix and some evidence of cluster formation on bainite lath boundaries.
- Vanadium additions of 0.1 wt% in the model alloys with entirely bainite microstructures has shown a noticeable gain more than 70 MPa in the tensile strength. Further, vanadium microalloying influenced the initial yielding response of the alloy as it promoted continuous yielding and eliminated the occurrence of a sharp yield point compared to V-free samples.
- The strengthening effect of vanadium was analyzed by accounting for bainite lath refinement, increased dislocation density and contribution of V-clusters.

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