Impact of Vanadium Addition on API X100 Steel

Shahrooz NAFISI,^{1)*} Muhammad ARAFIN,^{2)**} Robert GLODOWSKI,³⁾ Laurie COLLINS¹⁾ and Jerzy SZPUNAR^{2,4)}

1) EVRAZ Research and Development, P. O. Box 1670, Regina, SK, S4P 3C7 Canada.

2) McGill University, Dep. of Mining and Materials Eng., Montreal, QC, H3A2B2 Canada.

3) EVRAZ, East Metals North America, 1180 Omega Drive, Pittsburgh, PA, 15205-5005 USA.

4) University of Saskatchewan, Dep. of Mechanical Eng., Saskatoon, SK, S7N 5A9 Canada.

(Received on March 6, 2014; accepted on May 22, 2014)

Laboratory heats of an API X100 steel (Mn–Mo–Nb) with two levels of vanadium (0.004% and 0.063%) were melted and control rolled simulating a coiled plate production process. Extensive microstructural analyses were performed, including optical, EBSD and TEM. Texture analyses of the two alloys were also compared. Mechanical properties were determined for various rolling and pipe axis orientations. Only minor differences in microstructure and texture properties were observed between the two alloys. Yet the 0.063% V alloy had from 8 to 14% higher yield and tensile strengths in all directions, while the toughness and ductility measurements were similar for both alloys. Higher strength of the V added pipeline steel was partially due to its smaller grain size and larger fraction of subgrain boundaries. Some, but perhaps not all, of the strength differences could be related to the observed smaller precipitate size of the higher vanadium steel. The vanadium addition was necessary in this alloy to ensure meeting the required strength properties of X100 steel.

KEY WORDS: API X100; EBSD; TEM; linepipe; texture; mechanical properties; niobium; vanadium.

1. Introduction

There is continued interest in achieving higher strength pipe products, along with achieving the necessary properties in both transverse and longitudinal orientations to the pipe axis, as needed for strain-based design. For spiral welded pipe, this includes testing the 36 degree and 54 degree orientations to the rolling direction. Properties believed to be indicative of this performance include the standard microstructure and mechanical testing, but also texture development that can be key to achieve desired properties in all orientations. In addition, EBSD analysis can now be used to analyze the grain boundary misorientation, considered to be a key to improved strength/toughness combinations.

The addition of microalloying elements such as Ti and Nb plays a critical role during the thermo-mechanical control processing (TMCP) of pipeline steels in obtaining the desired mechanical properties, primarily through grain size refinement. However, for high strength steels additional consideration is necessary such as the use of vanadium which is very effective in increasing the yield and tensile strengths through (1) precipitation and, to a lesser extent, solid solution strengthening, (2) minimizing the recovery of dislocation in bainites during coiling and subsequent cooling, (3) ferrite grain size refinement due to intragranular precipitation of vanadium carbo-nitrides, *etc.*^{1,2)} Addition of

vanadium also has several other advantages in different types of steels, such as promoting homogeneity of microstructure through the thickness due to low solute drag coefficient of vanadium in austenite, delayed fracture resistance due to excellent hydrogen trapping capacity of vanadium carbide precipitates, temper softening resistance, sour corrosion cracking resistance for these very same reasons together with the fact that the dislocation density could be substantially reduced by tempering at high temperature *etc.*^{3–8)}

Several researchers studied the role of vanadium and its precipitates on the mechanical properties and toughness of High Strength Low Alloy (HSLA) steels including linepipe steels.^{9–14)} However, the exact mechanism(s) of vanadium precipitation and their contribution to strength increase are not yet completely understood. For example, while N is highly effective in facilitating the precipitation of V, it is usually kept to a very low level due to toughness concern. Strain induced precipitation of vanadium carbo-nitrides are also expected to be quite limited due to their low dissolution temperature. It is therefore important to explore the possible mechanism(s) through which vanadium containing steel contributes to strength gain in advanced high strength pipeline steel such as X100 which is still at its early stage of development.

In this study, two laboratory heats of API X100 Mn–Mo–Nb steel were melted and processed to 14 mm hot rolled plates. The primary difference was the addition of 0.06% V to one of the heats. Mechanical testing, microstructural analyses, texture and EBSD studies, and precipitate analysis were all carried out on these two plate steels. Results of

*Corresponding author: E-mail: Shahrooz.Nafisi@evrazna.com

**Current address: CanmetMATERIALS, 3303 33 St. NW, Calgary, AB, T2L2A7, Canada

DOI: <http://dx.doi.org/10.2355/isijinternational.54.2404>

these analyses are reported, and a possible explanation for the observed strengthening contribution of the vanadium is proposed.

2. Experimental Procedure

The steel used in this study was made by hot rolling a laboratory melted 127 mm thick cast ingot down to 14 mm final gauge. The alloy contained 0.06%C, 1.95%Mn, 0.41%Mo, 0.16%Cr, 0.03% Nb, 0.005%Ti, 0.0055%N, and two levels of V, a residual level of 0.004% V (alloy A) and an addition of 0.063% V (alloy B). The slab was reheated at 1180°C for 2.5 hrs and then rolled in two stages; rough rolling above the recrystallization stop temperature, T_{nr} , followed by finish rolling below T_{nr} . The plate was then accelerated cooled to the coiling temperature, then slow cooled to simulate the coiling process. An overall grain refinement was expected by rough rolling 64% in 7 passes above the calculated T_{nr} (958°C)¹⁵⁾ to achieve adequate recrystallization of the as-cast austenite grains. Finish rolling was a 72% cumulative reduction in 6 passes in the austenite region below T_{nr} . The rough rolling was started at about 1125°C and finished about 1010°C. Finish rolling started at 880°C and finished at about 792°C. The rolled steels were then accelerated cooled to about 450°C at 30°C/s, then slow cooled at 15°C/hr for 24 hours (Fig. 1). Ar3 and Ar1 temperatures were measured by Gleeble simulation under cooling rate of 2°C/min and values were measured as 759°C and

Fig. 1. Schematic presentation of thermo mechanical rolling conditions of API X100 steels. (Online version in color.)

647°C for alloy B and 756°C and 637°C for alloy A respectively.

Samples for mechanical testing were cut at different angles from the rolling direction. For microstructural investigation, samples were cut from quarter width and prepared by a diamond saw from quarter thickness of the rolled plate and final polished by colloidal silica. Texture of the specimens was measured using diffractometer and analyzed with the TexTools software.¹⁶⁾ Percent retained austenite measurements were performed using diffractometer with a Cr target X-ray tube. Data were collected and analyzed using the four-peak method as per ASTM E975. Electron backscatter diffraction (EBSD) analysis was conducted by a FEG-SEM with step sizes of 0.5 and 0.1 μm for 1000 and 5000 magnifications respectively.

3. Results and Discussion

3.1. Microstructural Investigation

Typical optical micrographs of the specimens at quarter thickness are presented in Fig. 2. Both specimens contain mainly bainitic ferrite with small amount of quasi polygonal ferrite and MA constituents (martensite-austenite). In addition, percentage of retained austenite was measured by using an XRD diffractometer and it was found that alloys A and B had 0.78% and 2.58% retained austenite respectively (within 5% accuracy).

3.2. Mechanical Properties

High strength line pipe intended for application in a strain-based design requires consideration of properties in both TPA[†] and LPA[‡] orientations. A strain-based design intends to prevent any fracture of the pipe due to its plastic deformation as a consequence of ground movement. This application not only requires good toughness and weldability, but also needs high deformability by high work hardening (low yield to tensile strength (YS/TS) ratio) and high uniform elongation (U.EI). In addition, girth weld strength must overmatch the longitudinal pipe body strength.¹⁷⁾

Selected mechanical properties in various directions are shown in Fig. 3. Regardless of sample directionality, the yield strength (YS) and ultimate tensile strength (UTS) of the specimens from alloy B are higher than the base material, alloy A. Comparing the results to CSA Z245.1-02 spec-

Fig. 2. Selected optical micrographs of various thermomechanical processing. (Online version in color.)

[†] Transverse to pipe axis, i.e. 36 degree.

[‡] Longitudinal to pipe axis, i.e. 54 degree.

Fig. 3. Tensile strength, yield strength, elongation and charpy results of the tested specimens. (Online version in color.)

Fig. 4. 45 degree plots of ODFs. (Online version in color.)

ification,¹⁸⁾ only alloy B met the yield and tensile strengths criteria for X100 (690<YS<825 and 620<YS<750 MPa in the TPA and LPA directions respectively; 760<TS<970 MPa in both TPA and LPA directions). Figure 3 shows the elongation values. According to CSA Z245.1-02 specification,¹⁸⁾ the minimum elongation should be 10% and 17% for TPA and LPA directions respectively. Both samples met the requirements.

Figure 3 also shows Charpy V-notched (CVN) energy results at various temperatures. At -30°C , the shear areas of both steels was above 85% (transverse to the pipe axis) which meet the required Evraz target specification (although all these samples passed the API specification 5L).¹⁹⁾

According to CSA Z245.1-02,¹⁸⁾ the absorbed energy (based on the full size test specimens) for each Charpy V-notch impact test shall be equal to or greater than 210J in the pipe body and 140J for any individual test (at -5°C). Both samples passed the acceptance requirement.

3.3. Texture

Texture in rolled sheet metals is generally represented as $\{hkl\} \langle uvw \rangle$ which signifies that $\{hkl\}$ planes of the grains lie parallel to the plane of the sheet, with the $\langle uvw \rangle$ direction oriented parallel to the rolling direction (detailed descriptions of the X-ray methods can be found in several

texts, *e.g.* Cullity²⁰). Ray and Jonas²¹) reviewed hot/cold rolling transformations in steels and they explained that amongst the transformation texture components found in controlled rolled steels, the $\{113\} \langle 110 \rangle$ component causes significant anisotropy in both strength and toughness and makes the material brittle along the 45° plane with respect to the rolling direction. By contrast, the $\{332\} \langle 113 \rangle$ component causes less anisotropy in strength and toughness²²) and also leads to more desirable values for these properties. As a result, the strength and toughness of controlled rolled steels could be improved by controlling the deformation of parent austenite grains so as to strengthen the intensity of the $\{332\} \langle 113 \rangle$ component and decrease the fraction of

$\{113\} \langle 110 \rangle$ grains in the final microstructure.

As indicated in **Fig. 4**, in both steels, the intensity of $\{001\} \langle 110 \rangle$ component is fairly low and it is unlikely to pose any problem. The presence of some $\{332\} \langle 113 \rangle$ and $\{113\} \langle 110 \rangle$ orientation components also suggest that austenite grains were indeed in deformed state before the cooling started. It is worth mentioning that intensities of $\{332\} \langle 113 \rangle$ and $\{554\} \langle 225 \rangle$ components are higher in alloy B.

The skeletal plots illustrating the α fiber, γ fiber, and ϵ fiber textures at quarter depth are presented in **Fig. 5**. Differences along the α -fiber were insignificant, however a small difference is observed in ϵ fiber. In the α -fiber, the most intense orientation for both steels is $\{113\} \langle 110 \rangle$. The $\{112\} \langle 110 \rangle$ orientation in α -fiber indicates that the steel may have cooled into the $\alpha + \gamma$ two phase region during hot rolling. Also the same concept is apparent in γ fiber showing higher intensity of $\{111\} \langle 112 \rangle$. However the intensity of $\{111\} \langle 112 \rangle$ for alloy B is a bit higher than alloy A.

The ϵ fiber shows the presence of the desired $\{332\} \langle 113 \rangle$ component in both steels that is likely to counterbalance the undesired $\{100\} \langle 110 \rangle$. In addition, presence of $\{332\} \langle 113 \rangle$ and $\{554\} \langle 225 \rangle$ is more pronounced in alloy B steel than alloy A. The presence of $\{554\} \langle 225 \rangle$ also suggests possible deformation in the $\alpha + \gamma$ region.

Fig. 5. Plots of ODFs, α -fiber, γ -fiber, and ϵ -fiber, at quarter thickness (Square is alloy A and triangle is alloy B). (Online version in color.)

3.4. EBSD Studies

The crystallographic characteristics of the specimens have been examined with the EBSD technique. The EBSD crystal orientation maps are presented in **Fig. 6**. High angle grain boundaries (HAGB) were defined as having misorientation greater than 15° . Generally these types of grain boundaries can be used as a crystallographic criterion showing the main grain boundaries. Low angle boundaries were defined as having misorientation of $2\text{--}15^\circ$. Each color indicates that the crystal orientation changes only from $2\text{--}15^\circ$ with its neighbor points. Anything between these two numbers was defined as subgrain boundaries.

As stated earlier, low and high angle boundaries were defined as $2\text{--}15^\circ$ and $15\text{--}180^\circ$ respectively. Several EBSD analyses were performed and the results concluded in **Fig. 7**. Alloy B has a greater fraction of low angle grain boundaries compared to the base steel, alloy A (at least 6 EBSD mapping were performed on each sample).

The distribution of grain size based on diameter is pre-

Fig. 6. Crystal orientation mapping for various rolling trials (consider 15° as high angle grain boundaries). (Online version in color.)

Fig. 7. Fraction of low and high angle boundaries. (Online version in color.)

Fig. 8. Grain diameter classification. (Online version in color.)

sented in Fig. 8. Both samples have almost the same fraction of grains less than 10 μm however alloy A has higher fraction of grains greater than 40 μm in diameter (definition of grain diameter from software). It is believed that the higher strength of the pipeline alloy B was partially due to its smaller grain size and larger fraction of subgrain boundaries. The content of low angle grain boundaries (misorientation between 2 and 15 degree) of alloy B was $\sim 39 \pm 3\%$, higher than that of steel alloy A ($\sim 34 \pm 4\%$). In other words, alloy B contains higher density of dislocations and sub-boundaries which is beneficial to the strength.

3.5. Correlation between Mechanical Properties and Microstructure

Extraction replicas were prepared and examined using TEM and FEG TEM, both with EDX detectors. The results are presented in Figs. 9–11. In the base steel (alloy A), two types of particles were identified (Fig. 9). One type was large faceted particles (typically greater than 30 nm in size), which were rich in Ti and Nb and likely nitrides, and smaller, spherical particles (<30 nm in size), which were rich in Nb and likely carbonitrides. No V was detected in precipitates as the steel contained only 0.004% V; no Mo was detected in any of the precipitates as well.

In alloy B, two types of precipitates were also identified (Fig. 10); these contained V with concentrations varying

from <1 wt% to ~ 30 wt% - based on comparison with Nb and Ti levels (*i.e.*, the total of Nb+Ti+V=100 wt%). The average size of the V-containing particles was about 15 nm. Particles larger than 35 nm in size were faceted, as well as Nb- and Ti-rich, and contained very little V (<5 wt%). The smaller particles were spherical and contained up to ~ 30 wt% V. They were Nb-rich with V and Ti making up the balance. No Mo was detected in any of the precipitates (Note, for both steels, that larger particles (>300 nm) were not detectable by replica methods).

The size distribution of the particles is summarized in Fig. 11. As indicated, particles in the alloy B steel were much smaller in size and with a narrower size distribution than those in the alloy A. The size distribution of each precipitate type is consistent with the solubility of each steel composition. The TiN precipitates will form shortly after solidification, and a significant portion of those precipitates will remain undissolved even through the reheat process at 1180°C. Based on the ThermoCalc calculation, using the TCFE 6 Database, the mostly Nb-based (Nb, V) (C, N) particles start forming at around 1110°C, while the carbonitride precipitation with V as a major constituent, would not normally start until about 980°C. Note that, the latter precipitates do not form in alloy A since this steel only contains a trace amount of V. However, the combination of pre-existing precipitates containing Ti and Nb, and deformation strain during finish rolling, may have accelerated the co-precipitation process in alloy B. The V containing precipitates, characterized by TEM-EDX analysis in the present investigation, still mainly contained Nb and Ti.

The increase in strength properties from the 0.06% V addition (60 to 90 MPa) rivals that of conventional VN precipitation strengthening of ferrite/pearlite steels with similar V additions.²³⁾ While alloy B had a higher volume of small precipitates (<10 nm), they do not appear to approach the volume fraction necessary for effective precipitation strengthening to this degree, and they most likely occurred as Nb-V precipitates in the austenite prior to transformation. Typically, precipitates that occur in the austenite prior to transformation do not contribute as effectively to strengthening as those that occur during or after austenite decomposition. The other microstructural strengthening factors—bainitic ferrite grain size, texture, grain boundary misorientation—are generally very similar with only a few advantages to the V containing steels.

Siwecki *et al.*¹⁾ found that a base alloying of 1.4% Mn, 1.0% Cr and 0.25% Mo is required to form a fully bainitic structure during the cooling after finish rolling of a 8 mm 0.04%C hot strip steel. It was proved that addition of 0.08%V and 0.01–0.02%N can change the yield strength from 680 to 740–790 MPa after coiling at 400°C. It was claimed that this strength gain could be mainly attributed to the fine V carbonitride precipitates retarding the recovery of dislocation structure in bainitic ferrite and, to a lesser degree, due to precipitation strengthening. Siwecki *et al.*¹⁾ believe that these precipitates were extremely small and located within the dislocation substructure. It is unlikely that the relatively larger Nb–Ti(C,N) co-precipitates identified in this investigation, which most likely precipitated in the prior austenite, would retard the recovery of dislocation in bainites. However, such bainite strength retention mechanism

Fig. 9. Alloy A. (Online version in color.)

Fig. 10. Alloy B (note that Cu in the EDX spectra is from the Cu grid). (Online version in color.)

Fig. 11. Particle size distributions (same area). (Online version in color.)

through dislocation pinning might be operative in the vanadium containing steel. Although the extremely small V(C, N) precipitates, necessary to activate the mechanism, were not identified in the present investigations, the TEM analysis revealed that the V-containing carbonitrides in alloy B (Fig. 11) were indeed of ultra-small size and of spherical

shape with the smallest particle size containing the highest vanadium concentration (these particles were still predominantly Nb and Ti). As mentioned earlier, the ThermoCalc prediction for the V-containing steel did suggest the formation of carbonitride precipitates with V as a major constituent—these particles might be small enough to prevent the dis-

location recovery in bainite but difficult to positively identify by TEM extraction replicas. The relatively larger fraction of low-angle boundaries in alloy B (Fig. 7) also indicates higher dislocation density in this steel suggesting that the V-containing precipitates might actually have prevented dislocation-recovery, at least to some extent. From the above discussion, it is apparent that the higher strength level in the V-containing steel may not be attributed to one single mechanism alone, rather the combination of precipitation and solid solution strengthening, smaller grain size and retardation of dislocation recovery effect.

4. Conclusions

(1) In a 0.06%C, 1.95%Mn, 0.41%Mo, 0.03%Nb chemistry, control rolled and accelerated cooled to a simulated coiling temperature of 450°C, it was necessary to add vanadium to achieve the yield and tensile strength property requirements of CSA Z245.1-02 for API X100 steel.

(2) The addition of 0.06%V resulted in an increase of both yield and tensile strengths of 60 to 95 MPa in all tested directions, 0°, 36°, 54° and 90°.

(3) Charpy toughness and elongation results were nearly identical for the steels with and without the vanadium addition.

(4) The microstructure of both the base and vanadium microalloyed material contained mostly bainitic ferrite with small amounts of quasi polygonal ferrite and MA constituents. The V containing steel had slightly higher retained austenite (2.58% vs. 0.78%).

(5) Texture analysis indicated very similar results, with some slight indications of more desirable components in the vanadium added steel, *i.e.* {332}<113> and {554}<225>.

(6) EBSD analyses indicated the presence of higher fraction of low angle boundaries as well as lower grain size in the vanadium steel than the base material. It is believed that the higher strength of the pipeline steel B was partially due to its smaller grain size and larger fraction of subgrain boundaries.

(7) TEM analysis of both steels indicated precipitation of Ti–Nb(C,N) precipitates all cases. The vanadium steel had finer particle size distribution, with V contained up to 23% in the finest particles (less than 10 nm). The precipitate size/composition relationships can be rationalized based on the solubility of Ti, Nb and V nitrides and carbides.

(8) While the smaller particle size in V-containing steel

would contribute to strength gain but the observed magnitude of strength increase may not be completely attributed to this observation alone. The improved strength might have also come from the retardation of the recovery of the dislocation structure by extremely fine V(C, N) or V–Nb(C,N) precipitates during the coil cooling cycle as proposed by Siwecki *et al.*¹⁾ although such precipitates could not be identified in the TEM analysis.

Acknowledgements

The authors would like to thank J. Bowker, C. Galvani, B. Voyzelle from CANMET, Natural Resources Canada, D. Ivey and R. Eslahpazir from University of Alberta for TEM work, as well as Y. Bian and J. Jackson from Evraz.

REFERENCES

- 1) T. Siwecki, J. Eliasson, R. Lagneborg and B. Hutchinson: *ISIJ Int.*, **50** (2010), 760.
- 2) G. Yong and D. Han: Proc. Int. Seminar on Production and Application of High Strength Seismic Grade Rebar Containing Vanadium, Vanitec (Vanadium International Technical Committee), UK, (2010), 1.
- 3) R. Glodowski: Int. Seminar on Application Technologies of Vanadium in Flat Rolled Steels, Vanitec Publication, UK, (2005), 43.
- 4) C. Mendibide and T. Sourmail: *Corros. Sci.*, **51** (2009), 2878.
- 5) H. Asahi, D. Hirakami and S. Yamasaki: *ISIJ Int.*, **43** (2003), 527.
- 6) M. Ueda, T. Omura and T. Abe: NACE Corrosion Conf., paper # 5089, Nace International, Houston, Texas, (2005).
- 7) H. Wei-jun, D. Han and W. Yu-qing: *J. Iron Steel Res. Int.*, **10** (2003), 63.
- 8) R. Lagneborg, T. Siwecki, S. Zajac and B. Hutchinson: *Scand. J. Metall.*, **28**, (1999) No. 5, 186.
- 9) Y. M. Kim, S. Y. Shin, H. Lee, B. Hwang, S. Lee and N. J. Kim: *Metall. Mater. Trans. A*, **38** (2007), 1731.
- 10) G. Yang, X. Sun, Z. Li, X. Li and Q. Yong: *Mater. Design*, **50** (2013), 102.
- 11) P. H. M. Hart and P. S. Mitchell: *Weld. Res. Suppl.*, **74** (1995), 239.
- 12) W. B. Morrison: Proc. of the Vanitec Symp. 2000, The Vanadium International Technical Committee, Vanitec Limited, Westerham Kent, England, (2000), 25.
- 13) T. N. Baker: *Mater. Sci. Technol.*, **25** (2009), 1083.
- 14) M. C. Zhao, K. Yang and Y. Shan: *Mater. Sci. Eng. A*, **335** (2002), 14.
- 15) D. Q. Bai, S. Yue, W. P. Sun and J. J. Jonas: *Metall. Trans. A*, **24** (1993), 2151.
- 16) TexTools Software, Resmat Corporation, Montreal, QC, (2000).
- 17) A. Glover: Proc. of Int. Dreamer's Conf., Scientific Surveys Ltd., UK, (2002), 33.
- 18) N. Ishikawa, M. Okatsu, S. Endo and J. Kondo: Proc. of IPC2008, 7th Int. Pipeline Conf., ASME, USA, (2008).
- 19) Specification for Line Pipe, API SPECIFICATION 5L, American Petroleum Institute, USA, (2013).
- 20) B. D. Cullity: Elements of X-ray Diffraction, Addison-Wesley, Reading, MA, (1978).
- 21) R. K. Ray and J. J. Jonas: *Int. Mater. Rev.*, **35** (1990), 1.
- 22) H. Inagaki, K. Kurihara and I. Kozasu: *Trans. Iron Steel Inst. Jpn.*, **17** (1977), 75.
- 23) R. Glodowski: *Int. J. Metall. Eng.*, **2** (2013), No. 1, 56.