Microstructure and properties of low manganese and niobium containing HIC pipeline steel

S.S. Nayak, R.D.K. Misra, J. Hartmann, F. Siciliano, J.M. Gray

Center for Structural and Functional Materials and Department of Chemical Engineering, University of Louisiana at Lafayette, Lafayette, LA 70504-4130, USA
Arcelor-Mittal Steel, USA Research and Development, 3000 East Columbia Drive, East Chicago, IN 46312, USA
CBMM, Córrego da Mata, s/n (Caixa Postal 8), 38183-970 Araxá, MG, Brazil
EWI Microalloying International, 10175 Harwin Drive, Suite 107, Houston, TX 77036, USA

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ABSTRACT
The paper describes the concept of using low manganese content in pipeline steels for hydrogen-induced cracking (HIC) applications. The microstructure of thermomechanically processed pipeline steel primarily consisted of polygonal ferrite and low fraction of pearlite. The cleanliness of the steel was evident as was the absence of centerline segregation. The microstructure contained high dislocation density, sub-boundaries and dislocation substructures. Fine-scale precipitation of niobium carbides occurred on parallel array of dislocations and on random dislocations that followed \([0 0 1]_{\text{NbC}}// [0 0 1]_{\text{Fe}}\) relationship with the ferrite matrix.

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1. Introduction and background

The primary interest in the production of pipeline steels meeting the API grades is to obtain the best possible combination of strength and toughness through optimization of alloy design in conjunction with thermomechanical processing [1]. High strength is one of the pre-requisites for deep water applications and for remote regions where transmission pressures may exceed 2500 psi. Additional requirements for transmission of oil and gas through pipelines include weldability, fracture toughness [2], resistance to hydrogen-induced cracking (HIC) in sour service environment [3,4], stress corrosion cracking resistance for underground service [5–7], and fatigue resistance [8,9]. In the aforementioned regard, it is important that there is a judicious selection of alloying elements that can facilitate high strength–toughness combination to be obtained in conjunction with the above outlined additional requirements. Alloying elements commonly used for production of pipeline steels are Mn, Nb, V, Ti, Mo, Ni and Cu to obtain the desired microstructure and mechanical properties [4,5,10–12]. It is observed that high strength low alloy (HSLA) steels containing Nb and Mo exhibit superior strength and toughness combination in relation to the HSLA steels containing Nb and V [11,12]. Manganese is an important alloying element for solid solution strengthening. It is generally preferred that the Mn content in the steel is reduced to avoid the detrimental effect of centerline segregation [13].

The concept of using lower manganese steels for HIC applications has been around for many years. Conventional wisdom preaches that manganese should not exceed 1.2% for hydrogen-induced cracking resistance and this wisdom is followed in conjunction with sulfur contents that usually are restricted to between 0.001 and 0.002 wt.% maximum to prevent the formation of elongated manganese sulfides. Malcolm Gray, working as a consultant to a large diameter pipe producer, extended this concept to much lower manganese levels, aiming at about 0.3% [14,15]. After securing a number of heats at this low manganese content, with sulfur content as high as 0.006%, the success of the concept became evident. All of the experimental heats ordered to test the concept were produced and rolled at steel plants now part of the Arcelor-Mittal organization. A patent was applied for and granted to Dr. Gray based on the results of the trials [15]. The patent rights to this concept have now been granted to Arcelor-Mittal steel. This paper addresses a production order provided to a large pipe customer illustrating the mechanical properties and microstructure of the skelp product and the pipe. The cleanliness of the steel is evident as is the absence of centerline segregation. The former is the
Table 1

<table>
<thead>
<tr>
<th>Heat number</th>
<th>Yield (psi)</th>
<th>Tensile (psi)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>46,742</td>
<td>64,100</td>
<td>77,400</td>
<td>36.4</td>
</tr>
<tr>
<td>46,741</td>
<td>61,500</td>
<td>75,000</td>
<td>38.2</td>
</tr>
<tr>
<td>46,740</td>
<td>62,400</td>
<td>74,600</td>
<td>39.2</td>
</tr>
</tbody>
</table>

result of overall clean steel practices. The latter is associated with excellent casting practices, and very low C and Mn levels enable significant residence time in the high diffusivity delta ferrite region allowing equalization of carbon and manganese contents.

The crux of the patented method incorporates low carbon as well as low manganese. By reducing the manganese to approximately one third of conventional levels, the sulfur levels need only be reduced to 40 or 50 ppm compared to the 10–20 ppm required for conventional HIC requirements. The reduced restriction on the sulfur levels allows many more of the Arcelor-Mittal steel plants to participate in the HIC markets. Thus, pipeline steels with low Mn

![Fig. 1. General microstructures of the pipeline steel recorded in a light microscope (etched in 2% nital solution). Rolling direction is indicated in below the images.](image1)

![Fig. 2. Representative of low and high magnification SEM micrographs of the pipeline steel (etched in 2% nital solution).](image2)
Fig. 3. Bright field transmission electron micrographs illustrating the general microstructures of pipeline steel: (a) polygonal ferrite and (b) polygonal ferrite-degenerated pearlite (broken pearlite colony).

Fig. 4. Bright field transmission electron micrographs at magnification higher than Fig. 3 showing (a) coarse ferrite grains with carbide precipitates (indicated by arrows) and (b) dislocations arrangement within the ferrite grains.

and C content with additional strength obtained from Nb, Cu, and Mo are preferred.

Besides alloy design, controlled thermomechanical processing is another aspect for the production of high strength pipeline steel modern API grade steels [2,10]. A number of process parameters including reheating temperature, roughing and finishing temperatures, and cooling rate play a determining role in obtaining the final microstructure and properties [10].

In thermomechanically processed pipeline steels, different combinations of microstructure including ferrite–pearlite [7], polygonal ferrite–acicular ferrite [1], acicular ferrite–bainite [10], acicular ferrite–martensite–austenite constituent (M/A) [16], a mixed microstructure [8,17–19], acicular ferrite [8,16,20,21], bainite have been obtained [3]. Acicular ferrite microstructure with martensite/austenite (M/A) islands, as a second phase exhibited optimum mechanical properties [1,10] and could be obtained by optimization of process parameters, without the need for significant concentration of alloying elements [1–2,10,22].

Thus, based on the above discussion, the objective of the study described here is to demonstrate that the demanding properties necessary for pipeline steels can be obtained in a low carbon-low manganese and niobium containing steel that is characterized by a fine-grained polygonal microstructure. This single-phase structure is preferred over the dual or multiple-phase structures for HIC applications. An accompanying objective is to illustrate the differences in the precipitation behavior between low C–Mn and relatively high C–Mn, niobium microalloyed pipeline steels.
2. Experimental

The current pipeline trials of low manganese HIC product consisted of three heats of products converted to 24 in., 0.375 in. wall (X52 grade). The nominal chemical composition range in weight% was Fe–(0.02–0.06)C–(0.30–0.50)Mn–(0.03–0.06) Nb–(0.1–0.5)Cr–(0.010–0.020)Ti–0.20–0.40 (Si)–(0.015–0.070)Al–(0.02 max.)–(0.007 max.)S. The chemistry compares to the typical HSLA grade produced for API X52 product. Standard metallographic techniques involving grinding, polishing and etching with 2% nital were used to reveal the microstructure using the light microscope. The etched samples were further examined in a JEOL 6300 field emission scanning electron microscope. Transmission electron microscopy was carried out on thin foils prepared by cutting thin wafers from the steel samples and grinding them to ∼60–70-µm thickness range. Three millimeter discs were punched from the wafers and electropolished using an electrolyte solution of 10% perchloric acid in acetic acid. Thin foils were examined by Hitachi 7600 TEM operated at 120 kV. Standard tensile tests were conducted at room temperature on longitudinal specimens machined according to ASTM E8 specification. Impact toughness was measured using standard Charpy v-notch impact test (ASTM 23) at 0 °C. The pipe properties were taken from approximately the center of the coil, on a single coil, and from each heat.

3. Results and discussion

3.1. Mechanical properties of low carbon–manganese and niobium containing pipeline steel

The yield strength, tensile strength, % elongation and Charpy toughness for low manganese and niobium containing pipeline steel are summarized in Table 1. The yield strength and tensile strength are in the narrow range of ∼61–64 ksi (425–450 MPa) and 75–77 ksi (525–540 MPa), respectively. The Charpy v-notch impact toughness at 0 °C is in the range of 105–130 ft lb (142–176 N m). All the tests reported in Table 1 are the average of two tests for the same pipe. The variation between two test results was always less than 2 ksi (14 MPa) for the yield and tensile strength and less than 2% on the elongation.
3.2. Microstructure

Representative low and high magnification light and scanning electron micrographs are presented in Figs. 1 and 2, respectively. Figs. 1 and 2 suggest that the microstructure is characterized by a combination of fine and coarse ferrite grains with a low fraction (5%) of pearlite. The fine grains are $\sim 2-5 \mu m$ and coarse elongated polygonal ferrite grains are $\sim 5-10 \mu m$. Furthermore, the cleanliness of the steel is evident from the absence of centerline segregation and can be discussed in terms of low carbon and manganese content. The effect of lowering the carbon content is to decrease the intensity of microsegregation of substitutional solute like Mn because of the long residence time in high diffusivity delta phase field, where significant post-solidification homogenization occurs during cooling. Under well-controlled fluid flow conditions, centerline segregation due to macrosegregation of substitutional elements is suppressed by lowering carbon content. This risk is further reduced by lowering the Mn content, which is the approach adopted here to engineer a more homogeneous microstructure free of banding due to Mn and C segregation as well as suppress the formation of MnS inclusions. Thus, the improved strength and toughness properties are expected from more homogeneous microstructure from low C and low Mn design. Such a steel design offers a niche for application in sour service conditions where the prevention of HIC cracking is an essential product requirement. Experimental data on strength and toughness are in favor of low Mn design.

Representative illustration of general microstructure as imaged by TEM is presented in Figs. 3 and 4. Fig. 3a shows the polygonal ferrite and Fig. 3b shows a region containing broken pearlite colony with morphology of degenerated pearlite [23,24]. Fig. 4a shows polygonal ferrite grains with precipitates of $\sim 50-100 \text{ nm}$ (indicated by arrows) and Fig. 4b shows random and parallel array of dislocations. Colony of non-parallel and broken-up cementite platelets in ferrite matrix is characterized as degenerated pearlite [23,24]. An illustration of polygonal ferrite with fine-scale precipitation and dislocation substructure within the grains is presented in Fig. 5. Two regions 1 and 2 are identified within a ferrite grain in Fig. 5a. High magnification micrographs of these two regions are presented in Fig. 5b and c. In Fig. 5b, dislocations are presented as
parallel arrays, with extensive precipitation on dislocations, while in Fig. 5c, the dislocations are entangled and the precipitation has occurred on dislocations and randomly in the ferrite matrix. High dislocation densities are generally representative of massive ferrite grains [25,16].

The precipitation of fine carbides within the ferrite grains and on dislocations as observed in Fig. 5 is expected to contribute to strengthening. It was interesting to note that there were a number of ferrite grains that indicated the presence of parallel array of dislocations. Another illustration is presented in Fig. 6. In Fig. 6, a grain triple point region is presented. It may be added here that grain triple point region is the point where grain boundaries of three adjacent grains meet. The bottom left ferrite grain in Fig. 5a is characterized by precipitation on parallel array of dislocations and the right grain is characterized by fine-scale precipitation on parallel array of dislocations and random dislocations.

The fine-scale, needle-shaped precipitation on dislocations was further confirmed by selected area diffraction analysis in association with the dark field micrograph. Fig. 7a and b are the bright field and dark field micrographs depicting predominantly fine-scale precipitation on dislocations. Fig. 7c is the selected area diffraction pattern corresponding to the region in Fig. 7a. Analysis of diffraction pattern suggested that the precipitates are NbC as indexed in Fig. 7c. Twin selected area diffraction (SAD) patterns for the [0 0 1] ferrite and NbC zone axes is presented (Fig. 7c). The dark field micrograph was obtained using the (1 3 1) diffraction spot for NbC. The NbC precipitates on dislocations exhibit an orientation relationship of [001]_{NbC}/[001]_{\alpha-Fe} with the ferrite matrix. This irrational orientation relationship presumably implies that the precipitates formed during austenite to ferrite transformation. Occasionally, grain boundary precipitation of cementite was observed (Fig. 8).

We now compare the general microstructure and the precipitation behavior of the low carbon–manganese steel investigated here with relatively high carbon–manganese pipeline steel [26,27]. The considerable dominance of strain-induced precipitation on dislocations (Figs. 5–7) is an important strengthening mechanism in the investigated steel. The precipitation of microalloying elements occurs during various stages of thermomechanical processing of steels. At the soaking temperatures, the microalloying elements are taken into solution depending on the limitation imposed by the solubility product. For carbide and nitride forming elements, the solubility in austenite at any given temperature depends on C and N content of the steel. When the temperature is lowered during cooling, supersaturation of these solute elements increases and precipitation begins at favorable kinetic conditions. Deformation of austenite introduces lattice defects such as dislocations and vacancies which assist in the diffusional process and controls the kinetics of precipitation. As a consequence, strain-induced precipitation occurs at the prior austenite grain boundaries or at lattice defects.

In microalloyed steels precipitation may occur randomly in the austenite or ferrite grain boundaries, sub-boundaries, lattice defects such as dislocations or at interphase boundaries during the transformation of austenite to ferrite. There are two possibilities of such an observation. The precipitation may have occurred in austenite immediately before the austenite to ferrite transforma-
Interphase precipitation of NbC in addition to regular precipitation is an interesting observation in this study. The interface precipitation occurred in some part of the grain starting at transformation temperature and did not undergo completion such that the general precipitation occurred in the remaining part of the grain at lower temperatures. If interphase precipitation occurred throughout the grain, then there is limited thermodynamic potential in the same grain for general precipitation to occur. Since these precipitates are known to be stable and do not coarsen on temperature cycling because of low surface energy, these observations in production coils obtained in low Mn, Nb microalloyed steel is of significance. For example interphase precipitation will be very effective in preventing grain coarsening in HAZ region during thermal cycling of base plate in welding operation involved in pipe making.

The steel in the present study exhibited yield strength of 61–64 ksi (425–450 MPa), even though the carbon and manganese contents were low compared to conventional microalloyed steels. Microalloyed steels derive their high strength from precipitation hardening and grain size. The grain size of the steel is bimodal distribution, with small fine grains ~2–5 μm and coarse grains ~5–10 μm.

4. Conclusions

1. The general microstructure of low C–Mn and Nb-containing pipeline steel primarily consisted of polygonal ferrite with small fraction of pearlite.

2. Microstructure indicated cleanliness of the steel and absence of centerline segregation.

3. The steel exhibits yield strength and tensile strength of 61–64 ksi (425–450 MPa) and 75–77 ksi (525–540 MPa), respectively with elongation of 36–39%. Excellent toughness of 105–130 ft lb (142–176 N m) at 0 °C was obtained.

4. Strain-induced precipitation occurred on dislocations and in the ferrite matrix along with precipitation at interface boundaries.

5. The selected area diffraction pattern analysis suggested that the fine precipitates on dislocations and inside the ferrite matrix were MC type niobium carbides with orientation relationship of [001]_{NbC}//[001]_{Fe}.

References

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