Alloy Design and Processing Considerations for the Production of Light- and Heavy-Gauge Structural Plates Using Low-C, Low-Mn and Ultralow-Nb Additions

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INTRODUCTION

Carbon-Manganese commodity structural steel plates are widely used across various applications in the construction and infrastructure sectors. While these ferrite-pearlite steels are well developed and applied in the industry, recent studies have demonstrated the benefits of ultra-low niobium additions to generate notable strengthening contributions permitting a reduction of 30-40% of manganese content in the alloy. Reduction of manganese content is leading to cost savings, improved castability, reduced centerline segregation, and microstructural banding, among other advantages.¹⁻⁵

Manganese is a traditional alloying element, which has been used for strengthening via solid solution of C-Mn systems for decades. It is well accepted that manganese will tend to provide a linear increase of strength, approximately 1.00%Mn = 32 MPa towards the yield strength. This relationship has been long established and empirical equations have been developed.⁷⁻⁸ However, much has been published regarding the effect of Mn on centerline segregation, microstructural banding and sulfides.⁸⁻⁹ In addition, numerous steel specifications applied to structural applications allow C maximum levels as high as 0.26% and peritectic grades in the range of 0.11-0.16%C are quite often applied to plate products.³,⁶, ¹⁰ By using a rational alloy design of low-Mn, low-C and ultra-low-Nb additions, mechanical properties can be substantially improved with an optimum cost-effective alloy design. Addition of Nb offset the loss of yield strength by the reduction of Mn. The specific attribute of Nb at such small additions derives from its ability to significantly inhibit austenite grain coarsening during reheating and subsequent processing. The literature suggests that addition of Nb to a small extent (0.01-0.02 wt.%) supplements Mn additions by approximately 0.5 wt.%.¹⁰ The use of a low-Mn, low-C, ultra-low-Nb concept reduces overall cost per ton of the alloy, despite the additions of Nb. Lower manganese steel chemistries require less overall alloying which in turn lowers BOF turndown temperature requirements. Lowering turndown temperature provides advantages that include but are not limited to improved refractory wear, lower hot metal to scrap charge ratios and potentially shorter oxygen blow duration. Optimizing steel chemistry in a way that minimizes total alloying content has other advantages such as lowering overall annual alloying procurement requirements as well as reduces transportation, storage, and logistics of alloying materials. Grades with less alloying content, such as with lower ferromanganese alloying additions, also have better mixing during the tapping process. Better mixing during tap provides a more representative steel sample for fine-tuning chemistry in Secondary Metallurgy. In addition, the literature also states the potential weldability benefits with lower manganese.³,⁴,¹⁰

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This work focuses on the development of a new version of the traditional ASTM A36 steel using this approach. This includes not only a reduction in manganese, but also in carbon content and targeted 0.010% Nb additions. The definition of lower carbon steels in this paper is a carbon content ≥ 0.10%. This paper discusses alloy design and rolling practices. The performance of laboratory heats was compared with industrial trials. The strengthening mechanisms were examined and associated with the presence of fine nanoclusters of Nb(C) particles embedded in a non-crystalline network. Mechanical properties and microstructure of the produced plates are compared with conventional ASTM A36 plates and other alloys that employ a similar concept but with higher carbon and Nb contents.

EXPERIMENTAL PROCEDURE

Experimental rolling
To demonstrate that the use of a low-Mn, low-C, ultra-low-Nb concept could be effectively employed to generate enough strengthening contributions and allow for the reduction of the manganese content in the A36 plates, a series of 45kg laboratory heats with varying chemistries were processed under identical conditions. In addition to the experimental rolled material, industrial continuously cast and hot rolled steels where the Mn was reduced from conventional 1.3% to 0.7% adding 0.01% Nb were evaluated.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr+Ni+Cu+Mo</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Steel (138)</td>
<td>0.13</td>
<td>1.10</td>
<td>0.22</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>9Mn10Nb (139)</td>
<td>0.13</td>
<td>0.89</td>
<td>0.22</td>
<td>0.20</td>
<td>0.01</td>
</tr>
<tr>
<td>7Mn10Nb (140)</td>
<td>0.13</td>
<td>0.68</td>
<td>0.21</td>
<td>0.21</td>
<td>0.01</td>
</tr>
<tr>
<td>7Mn10Nb-LC (165)</td>
<td>0.10</td>
<td>0.71</td>
<td>0.23</td>
<td>0.20</td>
<td>0.01</td>
</tr>
<tr>
<td>Commercial Grade</td>
<td>&lt; 0.10</td>
<td>0.70</td>
<td>0.04</td>
<td>&lt; 0.15</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Experimental ingots were vacuum induction melted and cast according to the chemical composition shown in Table 1. The ingots were first preconditioned for hot rolling by milling the opposite surfaces. Ingots were then reheated at 1230°C and hot rolled in 10 passes according to the schedule described in Figure 1. The rolling reduction per pass reproduces the typical rolling schedule for a structural A36 plate in the mill. Most of these C-Mn structural steels are finished rolled at temperatures (FRT) above 900°C, and in this case FRT was above 1050°C for all plates. Practically, this will mean that the mill can make use of Nb without the need for conventional TMCP and FRT at lower temperatures. Under conventional TMCP the austenite is pancaked and leads to finer ferrite grains and greater strength contributions. For a recrystallized austenite grains, as in this case when FRT > 1050°C this effect is not present. However, it is expected that the development of smaller recrystallized austenitic grains during rolling will promote some ferrite refinement thus contributing to increase in strength.

In addition to this hot rolling schedule, additional ingots from alloy 7Mn10Nb-LC were rolled to 860°C FRT to explore the additional benefits of the Nb in the composition when the rolling recipe is modified.
Microstructural Characterization

Samples for microstructural characterization were sectioned from the hot rolled plates and submitted to standard metallographic preparation procedures. Samples were mounted in a 1.5" mount using a conductive Cu-powder. After abrasive grinding, and polishing using a 0.5 µm and 0.3 µm alumina suspension, samples were placed in a mechanical vibratory polisher for 12 hours using a 0.05 µm deagglomerated alumina solution. Microstructural characterization was conducted using optical microscopy (OM) and Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-Ray Spectroscopy (EDS) detector. Elemental quantitative analysis was conducted using an Electron Probe Microanalyzer (EPMA) to study centerline segregation in the microstructure. This analysis was conducted using a 10kV beam at a probe current of 100nA.

Samples were also analyzed using Electron Backscattered Diffraction (EBSD). The mapping of interest regions was performed using a 20kV electron beam with 13 nA probe current on the specimens tilted 70° towards the EBSD phosphorus screen at a 14 mm working distance. The scans were acquired at the quarter thickness location at 500x magnification, 0.5 µm step size and a 200x200 µm scan area. All EBSD scans were collected and post-processed using the TSL-OIM8 analysis software. The data was cleaned using grain dilation and confidence index (CI) standardization. A minimum grain size of 2 pixels was conditioned with a minimum 5° grain boundary misorientation and 0.3 as a minimum confidence index.

For Transmission Electron Microscopy (TEM) analysis, samples were prepared for carbon replica extraction. After vibro-polishing, samples were submitted to a carbon coating procedure. Each sample was individually coated with a thin carbon layer of ~10 nm inside a sputtering chamber under a high vacuum ($5 \times 10^{-5}$ Torr). The carbon film was deposited from a carbon rod using a working current of 45A for 2 seconds. The carbon layer was then scored into 3mm squares and placed in a 15% Nital solution. The carbon films lifted from the sample surface were transferred using a 300-mesh Cu grid from the Nital solution into deionized water. The nanoscale imaging and EDS analysis were performed using a Thermo Fisher Titan Themis G2 200Cs-corrected S/TEM set up in a high-angle annular dark-field (HAADF) STEM mode. HAADF-STEM images have the benefit of directly interpretable image contrast, primarily dependent on the atomic mass of the element and thickness of material. Heavier elements such as Nb and Mo and thicker regions will appear brighter than lighter elements such as C and O and thinner regions. The microscope is also equipped with a Super-X quad-detector (0.7 sr) EDS system, facilitating rapid, high-SNR collection.

For the mechanical properties characterization tensile tests and Charpy V-notch impact tests samples were machined transverse to rolling direction according to the ASTM E8/E8M and ASTM E23 standards. Charpy V-notch impact tests were conducted at -50°C, -40°C, -30°C, -23°C, -18°C, -12°C and 0°C.

RESULTS AND DISCUSSION

Microstructure

Optical microscopy was used to evaluate the overall microstructures obtained after rolling. The optical micrograph of a conventional high manganese A36 steel is presented in Figure 2. Conventional steel has a heavily banded ferrite-pearlite microstructure. In contrast the alloys with low Mn and ultra-low additions of Nb contain nearly no banding in the microstructure. The presence of banding has been proven critical in pearlitic steels, leading to higher levels of anisotropy and overall lower mechanical properties, such impact toughness and ductility. The absence of microstructural banding in the low Mn alloys is expected to result in an improved impact toughness.$^{10}$

![Figure 2. Microstructure at quarter thickness location showing microstructural banding in the industrially rolled A36 steel (Reference) in comparison with a low manganese with ultra-low addition of niobium experimental steel.](image-url)
Figure 3. Microstructure of the experimental steels in comparison with the standard reference material (2% Nital etching) with the average of pearlite fraction and grain size.

Figure 3 presents the as-rolled microstructure of each sample, along with details of the pearlite fraction and the ferrite grain size. Although a very small refinement of the ferrite grain size is observed, presence of substructure in the low Mn alloys is evident by the optical micrographs. On the other hand, the fraction of pearlite decreases as a function of the Mn content in the steel. The Mn causes the eutectoid composition to occur at lower carbon contents, which increases the total pearlite fraction.

**Electron Probe Micro Analyzer (EPMA)**

Optical microscopy and EPMA analysis were conducted to show the difference in centerline segregation between the reference A36 sample with high Mn (138) and the low Mn sample 7Mn10Nb-LC. The quantitative distribution of elements C, Mn, Al, and Cu along pearlite regions (shaded areas) and the matrix are presented in Figures 4 and 5.

Figure 4. EPMA results for the reference sample 138 (high Mn) with the content of respective alloying elements. The highlighted shaded areas in the graphs correspond to the Pearlitic regions.
The results from the OM and EPMA analysis clearly demonstrate the effect of higher Mn content in terms of centerline segregation and alloying segregation. For the reference sample, with higher Mn content, there is a stronger segregation of C and Mn in the pearlitic regions, while in sample 7Mn10Nb-LC the Mn content in the pearlitic regions is very similar to that in the matrix. Figure 6 shows the difference between the average composition of the alloying elements observed in each region for both steels. These results support the well-known effect that higher Mn contents leads to segregation effects and show the benefits of the lower manganese alloys.

**Figure 6. Average content of the alloying elements in the microstructure (weight %) for the Reference A36 sample with high Mn and the low Mn alloy with Nb additions.**

**Electron Backscattered Diffraction (EBSD)**

EBSD-IQ analysis was used to investigate the microstructural differences between the samples. Different maps were acquired detailing the overall microstructural characteristics of the studied steels. Figure 7 shows the inverse pole figure (IPF) maps, representing samples with random crystallographic orientation, with no preferred orientation. These results were expected since all the steels were rolled above the $T_{NR}$ temperature with FRT $\geq 1050^\circ$C.
Figure 7: Inverse Pole Figure (IPF) maps acquired for all samples. The color represents crystallographic orientation.

Figure 8 shows the recrystallization behavior of the ferrite grains after transformation in terms of the grain boundary character distribution (GBCD) plots. The final microstructure of all samples showed large fraction of high angle grain boundaries (HAGB) (>15°), indicating effects of recrystallization and grain growth during processing. The smaller fraction of low angle grain boundaries (LAGB) (<15°) shows effects of partial recrystallization and strain effects associated with the high temperature deformation and transformation behavior, creating small number of sub-grains inside the ferritic grains.

The EBSD-IQ data can also be used to deconvolute the present phases of the material. This process is performed using polynomial functions based on the Image Quality (IQ) values obtained from EBSD. All scans were acquired using Iron-alpha (ferrite) phase as the standard. When the area consists of iron-alpha, a high IQ value is observed, while when the phases present a different crystal structure (e.g., Cementite) the IQ values will be lower, allowing the phase identification and quantification in the material. The phase balance plots and values for these alloys are shown in Figure 9.

Figure 8: Grain Boundary Character Distribution (GBCD) maps. The numerical fraction of each boundary type is shown in captions. The high angle grain boundaries (HAGB) are represented in blue.

Figure 9: Ferrite and Pearlite phase distribution based on EBSD image quality (IQ) analysis.
As expected, all samples show similar phase distribution, with over 90% ferrite and remaining being pearlite. All the samples were subjected to similar rolling practices and cooling path. Another important information extracted from the EBSD scans was the Geometrically Necessary Dislocation (GND) density, that represents the number of dislocations present in the material. All samples show similarly lower values due to recrystallization effect. These values are used in the theoretical calculation of strengthening. Figure 10 shows the calculated GND density values.

![Figure 10: GND density quantification.](image)

**Transmission Electron Microscopy (TEM)**

All samples were examined on TEM to evaluate the precipitation formation and distribution. Given the chemical composition and processing of the investigated steels, it was expected that the reference would exhibit negligible precipitation, while in the samples with Nb additions a small fraction of niobium carbides (NbC) was predicted.

![Figure 11: Characteristics of the precipitation behavior in the samples with ultra low additions of niobium (a) 9Mn10Nb, (b) 7Mn10Nb and (c) 7Mn10Nb-LC. The NbC precipitates are indicated with yellow arrows. Example observed nanocluster of fine Nb particles (above) and the corresponding EDS spectrum (below) showing strong Nb peaks.](image)
Consistent with the solubility product calculations, the reference sample displayed no significant precipitates due to the absence of Nb in the composition. Sample 9Mn10Nb showed a modest number of precipitates, primarily consisting of Nb-enriched particles surrounded by regions rich in Al and Si. Sample 7Mn10Nb exhibited extremely fine particles dispersed within the matrix forming nanoclusters. These clusters are characterized by multiple nanoparticles close to each other, and occasionally embedded in a non-crystalline network. Sample 7Mn10Nb-LC exhibited similar precipitation behavior, which featured nanoclusters with multiple precipitates. Figure 11 illustrates the observed precipitate types along with a typical Energy Disperse Spectroscopy (EDS) spectrum, highlighting the Nb peaks. Also, Figure 11 provides a higher magnification TEM image showing the characteristic atomic organization of the particles.

The TEM analysis showed the effect of the ultra-low additions of Nb in the precipitation, revealing the formation of nanoclusters where Nb(C) particles are embedded in a non-crystalline network.

The precipitates average size and volume fraction are critical factors in the material’s strengthening mechanisms. A combination of high number of precipitates and fine average size could significantly enhance the mechanical properties of the alloys. Based on the TEM results, samples 7Mn10Nb and 7Mn10Nb-LC are predicted to exhibit higher yield strength, in contrast to sample 9Mn10Nb which is expected to show lower values. In general, all samples with Nb additions presented very fine precipitate sizes averaging less than 10 nm. Sample 9Mn10Nb presented relatively coarser precipitates, averaging around 6 nm, whereas samples 7Mn10Nb and 7Mn10Nb-LC contained finer precipitates, with average sizes of approximately 3 nm and less than 2 nm respectively. The calculated volume fractions for all samples were estimated to be around 0.009% and 0.008%. Figure 12 depicts the precipitate’s average size and volume fractions for the samples with Nb additions.

Figure 12: (a) Average size and number of measured precipitates. (b) Volume Fraction of precipitates.

**Mechanical properties**

The results of the tensile tests for each of the experimental alloys are shown in Figure 13. The small additions of Nb, even when there was a reduction of Mn and C, lead to an improvement of yield and tensile strength. The 0.01% of Nb addition allows the reduction of Mn in the conventional steel up to 40%.

From the information obtained from the microstructural characterization it was possible to use the empirical calculations to determine the effects of different strengthening mechanisms towards the overall yield strength of the alloys. The results of the calculations and the breakdown of the strengthening mechanisms for each alloy are presented in Figure 14. The most important contribution was the impact of the precipitation in the overall strength. The particle size for the samples with Nb additions is very fine, which appears as nanoclusters of NbC. The presence of nanoclusters of NbC compensates for the loss of strength by solid solution strengthening mechanism when the Mn content decreases from 1.1% to 0.68%. The calculated yield strength values were very close to the actual mechanical tests results.
A set of industrial trials were conducted to establish a new composition using the low Mn, low C, ultra-low Nb addition concept for 12mm thickness light gauge material. For the trials, no changes in the rolling conditions were made except FRT to 880°C and standard operating practices were maintained. The chemical composition of the industrial heats is listed in Table 2. The chemical composition of the first heat aimed to the lower end of the Mn range at 0.65%Mn, while the second heat aimed to the higher end of the Mn at 0.80%. The objective was to identify if the final properties vary with these differences in Mn. For both trials 0.01%Nb was added and the carbon content also remained constant. A third trial was conducted for assessment of the properties with the most probable expected Mn content during production. Although the Nb was aimed at ≤0.01%, the Nb content for the third trial was 0.013%.
Table 2. Chemical composition of the industrial trials (wt.%)  

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr+Ni+Cu+Mo</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Steel (138)</td>
<td>0.13</td>
<td>1.10</td>
<td>0.22</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>Industrial Heat # 1</td>
<td>0.65</td>
<td>&lt; 0.10</td>
<td>0.65</td>
<td>&lt; 0.15</td>
<td>0.010</td>
</tr>
<tr>
<td>Industrial Heat # 2</td>
<td>0.80</td>
<td>&lt; 0.10</td>
<td>0.80</td>
<td>&lt; 0.15</td>
<td>0.010</td>
</tr>
<tr>
<td>Industrial heat # 3</td>
<td>0.72</td>
<td>&lt; 0.10</td>
<td>0.72</td>
<td>&lt; 0.15</td>
<td>0.013</td>
</tr>
</tbody>
</table>

The microstructures of the industrial rolled material are shown in Figure 15 at quarter thickness and mid-thickness locations. The microstructures revealed a very fine-grained structure predominantly ferritic with pearlite and carbides. There is no banding or centerline segregation present in the microstructures at the mid-thickness location, which was anticipated with the reduction of Mn content in the alloy. Figure 16 presents the results of the grain size analysis determined by EBSD. The grain size in all cases was more refined in comparison with the reference A36 steel, which was anticipated due to the retarding action of the Nb over recrystallization and grain growth. The homogeneity of the grain size distribution was determined through the ratio between Dc20% and Dm, where Dc20% is the critical grain size obtained at 80% of accumulated area fraction and Dm is the mean grain size obtained at 50% of accumulated area fraction. The calculated ratio tends to 1.0 when the grain size is more homogeneously distributed. Smaller Dc20% /Dm ratio were obtained as the Mn content in the alloy decreased, for the 0.01-0.013% range of Nb additions.

Figure 15. Optical and SEM microstructures at quarter thickness location of the industrial rolled material, showing the phase balance calculated using EBSD data.
Figure 16. Comparison of the grains size distribution for the industrial rolled material.

The results of tensile tests from the material produced in the trials are shown in Table 3. The values of the mechanical properties specified by the ASTM A36 standard were satisfied in all cases. Figure 17 shows the transverse Charpy impact energies obtained at various test temperatures. Not only excellent impact energies were obtained at all test temperatures, but the improvement on toughness was significant in comparison with the reference A36 material.

The industrial trials confirmed the results from the experimental alloys in which the Nb additions enabled a reduction of 40% Mn of the steel without making any changes to existing processing routes. The Nb additions not only contributed to improving the tensile properties, but also the overall toughness of the steel.

Table 3. Tensile properties of 9 and 12mm light gauge industrial trials.

<table>
<thead>
<tr>
<th>Industrial Heat</th>
<th>Yield Strength (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65%Mn – 0.010%Nb</td>
<td>359</td>
<td>445</td>
<td>39</td>
</tr>
<tr>
<td>0.80%Mn – 0.010%Nb</td>
<td>369</td>
<td>452</td>
<td>40</td>
</tr>
<tr>
<td>0.72%Mn – 0.013%Nb</td>
<td>383</td>
<td>462</td>
<td>41</td>
</tr>
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</table>
CONCLUSIONS

The laboratory study and industrial trials have demonstrated the possibility to use a lower cost alternative solution to produce ASTM A36 structural steel without any changes to existing processing routes. The reduction of 40% Mn content in the alloy was possible by small additions of Nb which led to a reduced Mn segregation and banding effect, improving the homogeneity of the as-rolled product with a more refined microstructure. The values of the mechanical properties specified by the ASTM A36 standard were satisfied in all cases. More importantly yield, tensile strength and overall impact toughness were improved in comparison with the conventional high C-Mn A36 alloy.

ACKNOWLEDGEMENTS

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