ULTRA-LOW NIOBIUM (ULNb) - ENABLING LOWER GREENHOUSE GAS EMISSIONS IN COMMODITY GRADE STRUCTURAL STEELS

BY

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SYNOPSIS

As steel makers focus their efforts towards achieving a lower / net-zero carbon footprint via step changes in steelmaking technologies (scope 1) and green energy generation or supply (scope 2) , it is equally important not to overlook what immediate savings could be captured along this journey by reducing scope 3 emissions. These are indirect greenhouse gas emissions generated as a result of activities undertaken either upstream or downstream of a steelmakers operation. The use of raw materials such as iron ore and ferro-alloys fall into this category.

When making any grade of steel, and especially commodity grade structural steels, there is a staple requirement to add ferro-alloys containing manganese and silicon. Furthermore, in some long products the use of vanadium (V) microalloying is also often employed. All additions made will contribute not only towards the ferro-alloy cost burden but also contribute towards an increase in scope 3 emissions.

Recent laboratory studies, coupled with industrial trials, have demonstrated an alternative alloying solution to making commodity grade structural steels. By using an Ultra-Low addition of Niobium (ULNb) (i.e., ≤100ppmNb) it is possible to enable cost savings in ferro-alloying expenditure coupled with a reduction in grade specific GWPe/tonne of steel produced. Furthermore, there is no significant changes required to existing operating practices and importantly a solution which can be implemented and benefited from today.

This paper summarises and presents these recent finding towards extracting greater value from existing commodity grade structural steels through Ultra-Low additions of Nb.

Keywords: Steel, Structural, Commodity, Niobium, Savings, GWPe

INTRODUCTION

Worldwide, the construction and infrastructure sectors consistently account for approximately 50% of steels produced and in 2021 this amounted to approximately 950 million tonnes (Mt) of crude steel [1]. Of this, it is estimated that 200-250Mt is in the form of hot-rolled long products (i.e., beams, sections, channels, angles, flat bar and profiles) and 300-350Mt in the form of flat-rolled products (i.e., plates, narrow-plate and strip). Most of this steel tonnage is produced as low strength, commodity grades, with yield strengths (YS) ranging from 235 to 355MPa and consequently are highly sensitive to the cost of production, namely; raw materials of iron ore and ferro-alloys, energy, scrap metal and emissions output. With respect to ferro-alloys, these basic steels rely on increasing additions of carbon (C) and manganese (Mn) to satisfy the minimum YS requirements, especially when approaching 355MPa and/or the steel product size increases (i.e., greater kg/m or thickness). However, whilst C is a cheap alloying element it has an upper limit of 0.20wt.%C in many specifications as it is detrimental to elongation, toughness, weldability and has more influence on the tensile strength (TS) due to an increased volume fraction of second phase pearlite micro-constituent.

Consequently, all steelmakers will therefore opt for increasing the Mn content to make final strengths. Mn is added to for a number of reasons, namely: (i) to combine with sulphur / act as a deoxidiser; (ii) provide solid solution strengthening, and; (iii) lowering the decomposition temperature of austenite. For many steelmakers producing commodity structural steels, Silico-Manganese is often used as the primary deoxidizer and any further requirement in Mn will be through additions of Ferro-Manganese (FeMn). It is well accepted that Mn will tend to provide a linear increase in strength by means of solid solution strengthening. As a guide, approximately 1.0%Mn = 32MPa towards the yield strength. This relationship has been long established through the study of a range of steel compositions developing the following semi-empirical relationship for the YS and TS respectively [2]:

$$\sigma_y = 53.9 + 32.34Mn + 83.2Si + 678P + 354.2N_f + 17.4d^{-1/2} \qquad \text{Eq.1}$$

$$\sigma_{TS} = = 294 + 27.7Mn + 83.2Si + 3.85Pearlite + 7.7d^{-1/2} \qquad \text{Eq.2}$$

With σ_y and σ_{TS} the measured YS and TS, the alloy content in wt.%, N_f is the 'free' nitrogen content and *d* the average ferrite grain size in mm.

From the above equations, it can be seen that Mn is in fact a weak solid solution strengthener. However, it is also an austenite stabiliser, so it will depress the austenite-to-ferrite (Ar_3) transformation temperature. Published regression equations propose approximately 1.0wt.%Mn can lead to a drop of up to 80°C in the Ar_3 temperature when combined with additional cooling, leading to a small degree of grain refinement [3].

With respect to other alloys, an addition of vanadium (via Ferro-Vanadium (FeV)) is often made to structural long products to provide that extra strengthening contribution from precipitation post-rolling. Typically, this is found when upper limits in Mn content have also been reached with respect to the grade specification, and/or, moving towards higher Mn content is resulting in the formation of larger volume fractions of undesired lower transformation temperature microstructures, such as bainite, as well as higher levels of residuals due to the increased ferro-alloy burden.

With respect to V, the level of strengthening is principally dependent on the amount added, but equally important as with all micro-alloys, the degree of strengthening will also depend on the cooling rate post-rolling, the solubility and stoichiometry of the precipitating system (i.e., governs the precipitate size and volume fraction = strengthening contribution). For most commodity structural grades, the addition can range from 0.015 to 0.030wt.%V, and whilst niobium (Nb) will perform a similar role as V here and has been shown to be twice as effective in strengthening contribution per wt.% addition [4-6], it has a tendency not to be considered as an alternative alloy due to some improper presumptions (discussed further below).

As FeMn-alloys are a fundamental addition to steelmaking and V is also applied in other industry sectors, their respective prices can fluctuate greatly depending on market demands and supply availability. This price volatility has been well documented and for steelmakers, impacts on their profit margin per tonne of steel. Figure 1 shows the price (ex-works) of high-carbon ferro-manganese (75%Mn-8%C) and ferro-vanadium (80%V) over 2020/21 (normalized). As can be seen there is reasonable volatility in the price per tonne of each alloy which provokes the question as to whether an alternative, lower cost, steel alloy composition can be employed. Furthermore, any Global Warming Potential equivalent (GWPe) savings that could be realised through more judicious use of such heavily used raw materials (i.e., FeMn) and/or alternative alloying pathways could collectively make significant contributions towards lower Scope 3 emissions for the steelmaking community across the world.

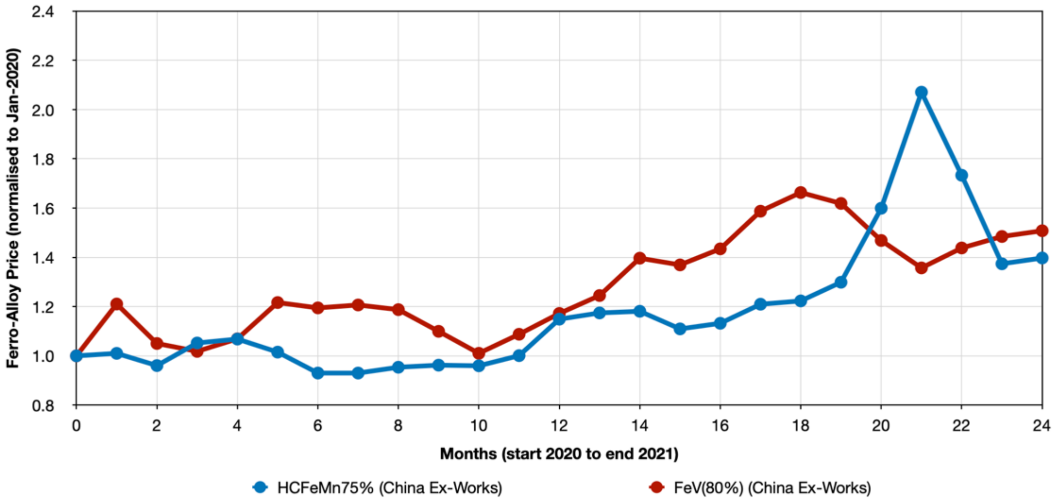


Figure 1. Historical HCFeMn(75%) and FeV(80%) prices (normalised from 2020 base)

ULTRA-LOW NIOBIUM (ULNb) PROPOSITION

Traditionally, the use of niobium has been synonymous with Thermo-Mechanical (TM) processing and High Strength Low Alloy (HSLA) steels, whereby increasing levels of solute niobium are made to sufficiently delay austenite recrystallisation during rolling. With progressive reductions, a pancaked austenite morphology is developed which, on cooling, transforms to a finer ferrite grain and thus higher yield strength and improved low temperature toughness properties [7-9]. This role of niobium (Nb) is well known, well accepted and well-practised by steelmakers across the world when producing high strength steels ≥355MPa, and for steels requiring both higher strength and low temperature impact properties. Consequently, it is reasonable to postulate that the addition of niobium has not been widely associated with commodity grade structural steels, primarily because by their very nature they are of lower strengths (i.e., 275 to 355MPa) and also have no low temperature toughness needs (i.e., they have a minimum requirement of 27J at room temperature). As an example, see Table 1, specification requirements for EN10025-2 [10].

Table 1. Mechanical properties (min) and chemical composition (max) according to EN10025-2

Grade	C	Mn	Si	CEV	TS (MPa)	YS (MPa)	CVN@20ºC
S235JR	0.17	1.40	--	0.35	360-510	235	27J
S275JR	0.21	1.50	--	0.40	410-560	275	27J
S355JR	0.24	1.60	0.55	0.45	470-630	355	27J

Figure 2 shows the seminal research work of Cuddy and the relationship between Nb content and the austenite no-recrystallisation temperature (T_{nr}) for a 0.07wt.%C steel [11]. This corresponds to the temperature where recrystallisation starts to be incomplete during the rolling process. In reality it has been shown by several authors that of more practical relevance are the temperatures whereby recrystallisation is completely absent (often set at ≤5%), i.e., the recrystallisation stop temperature (RST), and the recrystallisation limit temperature (RLT), which is the lowest temperature above which recrystallisation is complete (often defined at ≥85%). As these points are also dependent on interpass times and applied pass strain, the T_{nr} is nowadays used as an overall guide and is determined via empirically defined equations [12,13]. However, as these equations often do not account for process variables such as strain and interpass times, greater attention must be applied when determining the optimum Nb content from both a metallurgical and economic aspect.

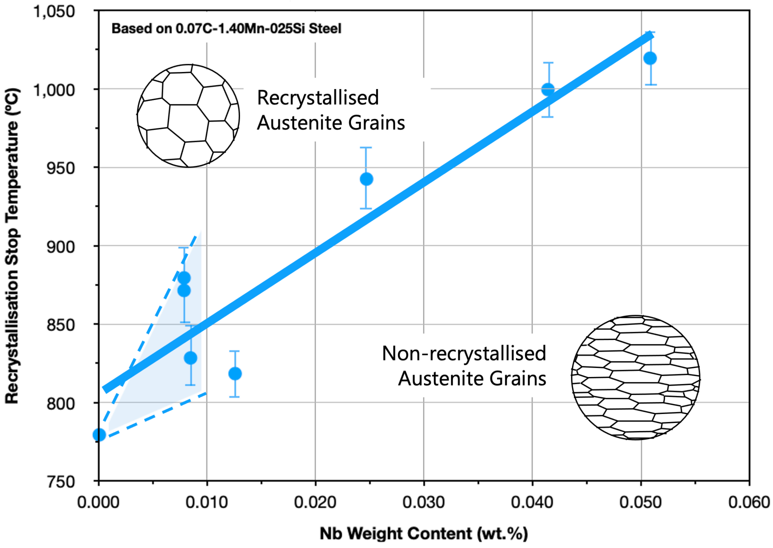


Figure 2. Effect of solute Nb on the recrystallisation-stop temperature; adapted from [11].

Closer inspection of Figure 2 shows that at very low Nb levels, *i.e., below 0.010wt.% (<100ppm),* it appears to have a greater degree of potency than that derived from evaluating the entire data set. This region, highlighted by the shaded area in Figure 2, shows that at these “ultra-low” levels, Nb is observed to potentially have a greater effect in raising the T_{nr}. At a higher carbon content, typical for commodity structural steels, this is likely to be raised further due to the lower solubility of Nb (carbo-nitrides) with increasing carbon content, as defined by the solubility product of Nb(C,N) [14]. Whilst it is acknowledged that many long products are finished rolled at temperatures (FRT) >950ºC, and thus still within the fully recrystallized austenite state, any movement closer towards the RLT should encourage a finer recrystallised austenite grain structure to be developed. In doing so, this will increase the effective austenite interfacial area (S_v) leading to a marginally finer ferrite grain, and thus strengthening [15], allowing for a small reduction in other ferro-alloying strengthening contributors. Furthermore, as the FRT remains above the RLT, the bulk of Nb should also remain in solute form and thus be available post-rolling strengthening contribution through increased hardenability and/or precipitation strengthening during and after transformation (i.e., the same strengthening mechanism when V) is used.

Practically, this would mean that producers of long products can make use of Nb without the need for conventional TM-rolling practices and finish rolling at lower temperatures. Figure 3 shows how the transformed ferrite grain size is dependent on the condition of the prior austenite grain [16]. As expected under conventional TM-rolling and Nb microalloying the austenite is deformed (pancaked) and leads to finer ferrite grains and greater strength contributions. For a recrystallized austenite grain, a lesser effect is found. Nevertheless, Figure 3 highlights that by developing even a slightly smaller recrystallized austenite grain, some ferrite refinement will still occur and thus an increase in strength.

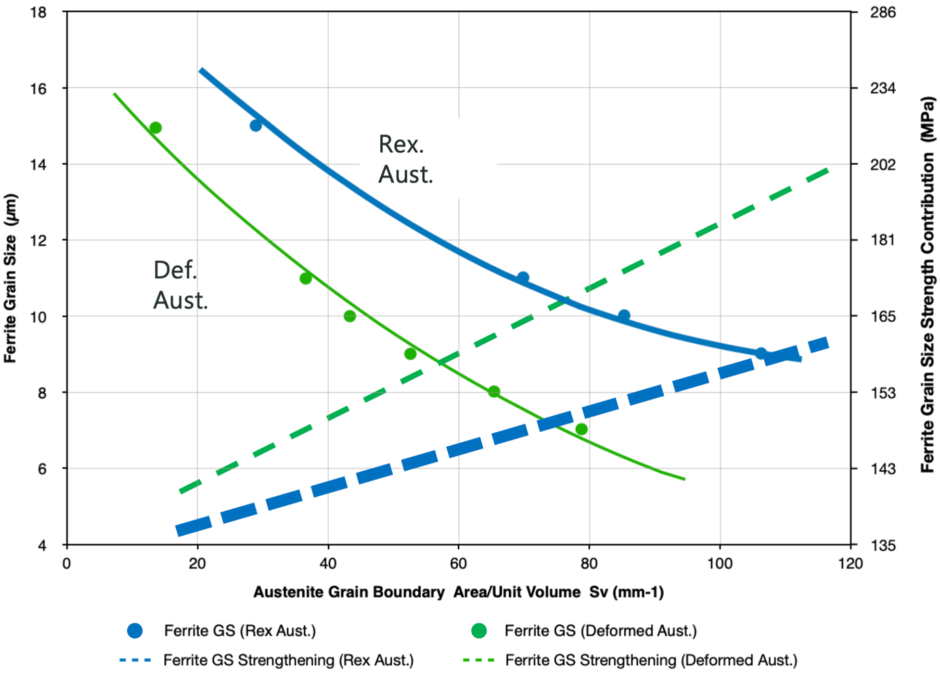


Figure 3. Effect of austenite grain boundary area on ferrite grain size and yield strength contribution; adapted from [16]

To demonstrate whether Ultra-Low levels of Nb (ULNb) could be effectively employed to generate notable strengthening contributions and thus allow for a reduction in Mn and even some cases, replacement of low levels of V, a series of controlled 100kg laboratory cast split-heats with varying chemistries were made and processed under identical conditions and tested for direct comparison. In addition, a commercially continuously cast and rolled ULNb steel with 70ppmNb was also evaluated using multi-pass torsion tests to determine the T_{nr} from the resultant mean flow stress (MFS).

EXPERIMENTAL DETAILS

A series of 100kg split heats were vacuum induction melted and cast according to the chemical compositions shown in Table 2 (in wt.%). To investigate the effects of Mn and ULNb additions, all steels were processed identically, such that a direct comparison in final mechanical properties could be made. Following casting, all ingots were homogenised at 1,200ºC for 24-hours under a protective N_2-gas atmosphere and cooled to room temperature. For each steel chemistry, two blocks sized 120x135x60mm^3 were cut for hot rolling. Each block was reheated to 1,200ºC for 2-hours in a furnace and then hot-rolled in 10-passes to a final thickness of 14mm with a FRT of 950 and 900ºC. To achieve a lower FRT, a short delay was introduced in between passes 4 and 5. Post rolling, all plates were air-cooled to room temperature. To determine the mechanical properties, three tensile specimens were taken in the rolling direction and accompanying three V-notched Charpy specimens (55x10x10mm^3) were taken and tested at 0ºC from each rolled plate. To evaluate the hot-rolled microstructure, longitudinal micro-specimens were taken in neighbouring samples to the tensile specimens. These samples were prepared for light optical metallography and etched in a solution of 2-5% Nital solution to reveal the grain structure and nature of second phase. A linear intercept method was applied to determine the average ferrite grain size.

The chemical composition (in wt.%) of the steel studied for torsion testing was 0.23C-0.30Si-1.28Mn-0.0050N-0.0070Nb and the sample was taken from a commercially rolled H-beam. Tests were carried out using a computer-controlled torsion machine using a specimen gauge length of 17mm with a diameter of 7.5mm. An induction furnace was used to heat the specimens to 1,150ºC where they were held at temperature for 20 minutes. Specimens were then deformed under multi-pass torsion tests at decreasing temperatures in the range 1,140 to 700°C, at intervals of 20°C. Two tests were carried out with a fixed pass-strain of 0.3, a pass strain-rate of 1s^{-1} and inter-pass times of 5 and 20 seconds respectively. The T_{nr} has been determined by using the method proposed by Jonas and co-workers [13,17].

Table 2. Chemical composition of the steels investigated (in wt.%)

Steel	C	Mn	Si	N	V	Nb
Group A	0.18	0.40 0.77 1.16	0.20	0.0050	---	---
Group B	0.18	0.38 0.77 1.14	0.19	0.0050	---	0.0063 0.0072 0.0081
Industrial ULNb	0.23	1.28	0.30	0.0050	---	0.0070

RESULTS AND DISCUSSION

The effect of Ultra-Low Nb additions on a CMn steel

From Table 2, Group B steels (i.e., ULNb) did unintentionally have a very small range of between 0.0063 to 0.0081wt.%Nb against an aim of 0.0080wt.% (i.e., 80ppm), but nevertheless well within the definition of ULNb levels. On average, this was 0.0073wt.%Nb. Apart from this minor deviation, there was no difference between the reference CMn steels (i.e., Group A) with varying Mn content and Group B steels respectively, thereby, permitting a direct comparison to be made. Figure 4a and 4b shows the effect of increasing Mn content on YS and TS for steel Groups A and B, and the FRT.

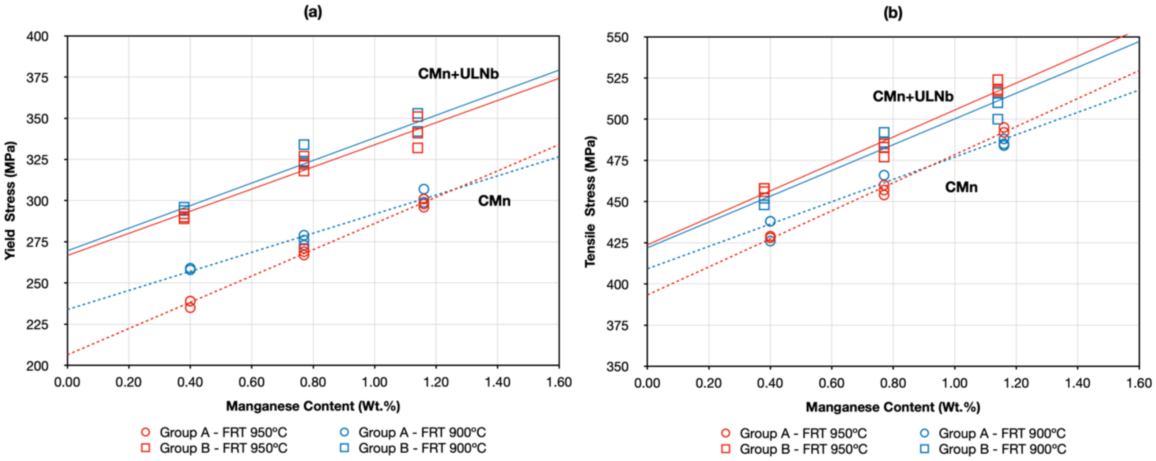


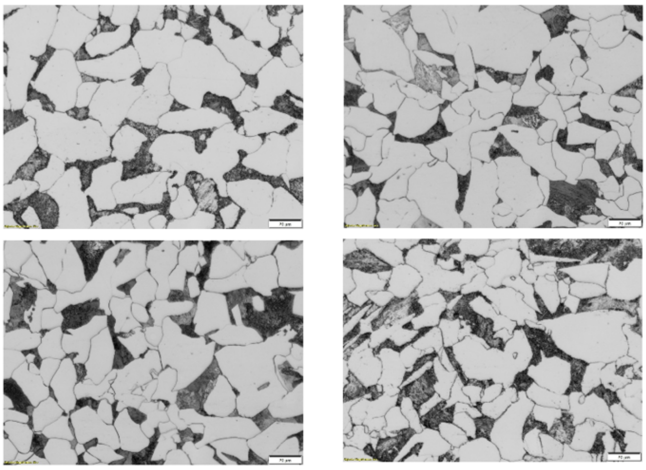
Figure 4a and 4b. The effect of increasing Mn content on the (a) yield stress and (b) tensile stress for Group A and B steels with respect to finish rolling temperatures of 950ºC and 900ºC

As expected, Group A steels exhibited a steady increase in strength with greater Mn content. As Mn is an austenite stabiliser, it will depress the Ar_3 transformation temperature by partitioning into the austenite phase during transformation. This this has a marked effect on the kinetics of the ferrite reaction which will support refinement of ferrite grains via greater nucleation sites and thus, an increase in YS [3]. Figure 4a and 4b indicates that as Mn increases from 0.40 to 1.16wt.% the effect of FRT is decreased. At the very lowest 0.40wt.%Mn content, maintaining a lower FRT of 900ºC is observed to result in a higher YS of +20MPa in comparison to a FRT of 950ºC. This is likely due to the reduced temperature gap (and thus time) of 76ºC between the FRT and the Ar_3 at 900ºC versus 126ºC at 950ºC and thus allowing for less recovery and growth of the austenite grain post rolling. At the higher Mn content, the effect of FRTs is less pronounced. This is likely due the significantly longer time to reach the Ar_3, even with a 50ºC starting temperature difference, allowing the austenite grains to reach similar state prior to transformation.

Performing a simple linear regression analysis on all YS results, the contribution of Mn is found to be 69MPa per 1wt.%Mn which is due to strengthening contributions from ferrite grain refinement and solid solution strengthening.

For Group B steels, the effect of an ULNb addition (63 to 81ppmNb) is very clear to see on both the YS and TS. As with Group A steels, there is a progressive increase in strength with higher Mn content, but remarkably the YS is notably by 40 to 57MPa higher due to the addition of 63-81ppmNb. Furthermore, the influence of the FRTs appears to be minimal, with a marginal higher YS at the lower 950ºC FRT. Taking the YS difference at the higher Mn content, the contribution of ULNb is found to be in the region of 5,000MPa/wt.%Nb, which is considerably higher than that typically found for conventional Nb additions (e.g. 0.020wt.%Nb) and provides prima facie evidence that Nb is making a greater contribution to the YS at these ultra-low levels. Taking the average of the YS for Group B steels and performing a simple linear regression analysis, the Mn contribution to the YS is found to be 68MPa per 1wt.%Mn which is almost identical to that found for Group A steels (69MPa per 1wt.%Mn), therefore, adding confidence to the derived strengthening contribution from ULNb to the overall mechanical properties.

Figure 5 shows an example of the final as-rolled microstructures for Group A and Group B steels at 0.77wt.% and 1.16wt.%Mn along with details of the final mechanical properties. As can be seen, even at 72-81ppmNb addition and with a high FRT of 950ºC, a very small refinement of the ferrite grain size is observed. This lends weight to the earlier described strategy of ferrite grain refinement via the development of a finer recrystallized austenite grain.



0.18C-0.77Mn-0.19Si
18.2µm; 20% Pearlite
YS = 269 MPa
TS = 457 MPa
TS/YS = 1.70
CVN@0ºC = 217J

0.18C-0.77Mn-0.19Si+72ppmNb
15.2µm; 15% Pearlite
YS = 322 MPa
TS = 482 MPa
TS/YS = 1.50
CVN@0ºC = 190J

0.18C-1.16Mn-0.20Si
13.3µm; 25% Pearlite
YS = 298 MPa
TS = 493 MPa
TS/YS = 1.65
CVN@0ºC = 235J

0.18C-1.14Mn-0.20Si+81ppmNb
12.8µm; 20% Pearlite
YS = 341 MPa
TS = 520 MPa
TS/YS = 1.53
CVN@0ºC = 227J

Figure 5. Comparison microstructures for Group A (CMn) and B (ULNb) steels with 0.77 and 1.16wt.%Mn at FRT of 950ºC

STRUCTURE-PROPERTY RELATIONSHIPS

To better understand the various metallurgical strengthening contributions to the YS, the established structure-property relationship equation developed by Pickering for ferrite-pearlite microstructure steels was applied (see Eq.1). As the starting nitrogen content is 0.0050wt.%N, any 'free' nitrogen that may exist will have a negligible contribution to the YS and so was omitted from the calculation. The outcome of applying of Eq.1 to Group A steels is shown in Figure 6a. Interestingly, subtracting the expected YS according to Eq.1 from the actual YS gave a remaining 'surplus' of +36MPa (irrespective of Mn content) for an FRT at 950ºC and +47MPa at 900ºC. For now, this is assumed to be a fixed contribution due to dislocation + secondary hardening not fully captured by Eq. 1.

The breakdown of strengthening mechanisms is also shown in Figure 6a. The relationship between the Mn content and the ferrite grain size strengthening contribution, which is found to hold a linear relationship for all Group A steels at 34MPa per 1.0wt.%Mn addition (see Figure 6b). Using this semi-empirically derived value, and the earlier YS results of 69MPa strengthening contribution from 1wt.%Mn, it can be approximated that this comprises of: 35MPa from solid solutional and 34MPa from ferrite grain refinement for the steels investigated.

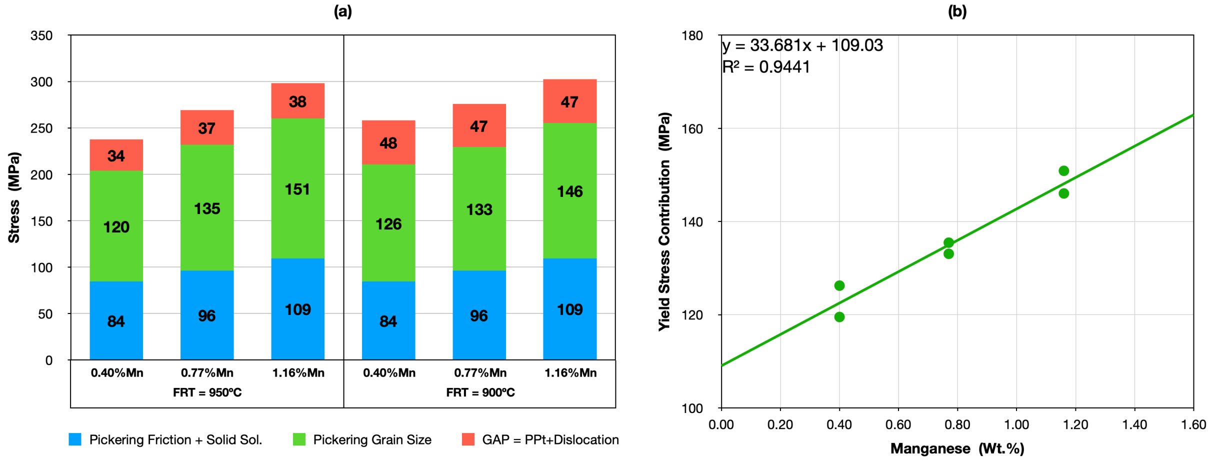


Figure 6(a). Breakdown of individual strengthening components for Group A steels and (b) Mn content on ferrite grain size contribution to yield stress

Using the same methodology, the extra strengthening for ferrite-pearlite microstructures from the addition of ultra-low levels of Nb can then be determined for Group B steels, by subtracting the additional strengthening component of ‘dislocation + secondary hardening’ established for the equivalent CMn reference, Group A steels. Using this technique, the average contribution of precipitation strengthening for Group B steels from ULNb addition was found to be 40MPa, which equates to approximately 5,500MPa/wt.%Nb when both FRTs are considered and is in line with the earlier findings. Analyzed individually, and as shown in Figure 7a, steels with a higher FRT of 950ºC tended to show a higher precipitation strengthening contribution than those with a FRT of 900ºC. Without a more detailed investigation, this is assumed to be due the presence of slightly less solute Nb at the lower FRT.

Figure 7b highlights that at higher Mn content, the effect of FRTs is less pronounced in the final transformed ferrite grain size. This is similar to Group A steels; likely due the significantly longer time to reach the Ar_3, even with a 50ºC starting temperature difference, allowing the austenite grains to reach similar state prior to transformation.

Overall, results from a semi-empirical approach are very much in line with that of mechanical results shown in Figures 4a and 4b, and clearly define that an ULNb addition of 80ppmNb can contribute 40MPa increase in YS under identical rolling conditions for an equivalent CMn steel. Based on the earlier findings of Group A steels (CMn), this 40MPa would be comparable to 0.50wt.%Mn and therefore indicates that ULNb can be employed to reduce the Mn content in commodity grade structural steels without the need to modify hot-rolling conditions. Furthermore, as the Nb content is so low, the reheating temperature required to bring all the Nb into solution prior to hot rolling is calculated to be below 1,060ºC for a 0.18wt.%C steel (using the Nb-solubility product defined by Irvine et al. [14]) and therefore well within the capabilities of all rolling mills.

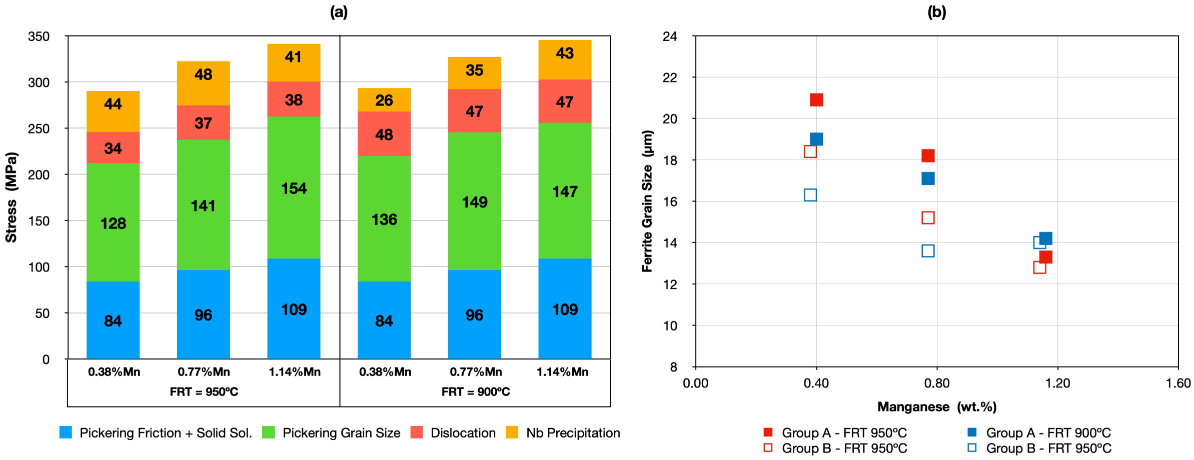


Figure 7(a). Breakdown of individual strengthening components for Group B steels and (b) Mn content on final ferrite grain size

TORSION TESTING OF ULNb STEEL

The result of multi-pass torsion test undertaken on a commercially cast and rolled steel with ULNb additions is shown in Figure 8. The chemical composition of the steel can be found in Table 2. This has been derived from the mean flow stress (MFS, defined as the area under each stress-strain curve divided by the pass strain) corresponding to each pass (calculated by numerical integration) and is plotted against the inverse absolute temperature. Three different regions can be clearly distinguished: Region I, where it is supposed that complete recrystallization between passes takes place and the stress increase from pass to pass is only due to the temperature drop; Region II, where recrystallization between passes is inhibited, and; Region III where ferrite transformation starts and consequently there is some degree of softening.

The value of T_{nr} was determined from the intersection between the regression lines of the points corresponding to regions I and II in Figure 8, following standard procedures [13,17]. From this figure a value of T_{nr} = 968ºC and 934ºC was derived with inter-pass times of 5 and 20 seconds respectively. In addition to composition, the non-recrystallization temperature depends also on deformation parameters, mainly pass-strain and interpass time. As can be observed, longer interpass times lead to lowering of the T_{nr}. This is due to a greater degree of static softening of the austenite grain in-between deformation passes [18]. On a practical level this would indicate that a slightly higher T_{nr} can be reached using ULNb in continuous rolling mills where interpass times are relatively short and finishing rolling temperatures are often high.

Based on the findings from Figure 8, in respect to the rolled plates for Group B steels which have a slightly lower carbon content, the effect of applying a FRT of 950 and 900ºC on the final mechanical properties can be considered. Whereby, the lower FRT would have developed a marginally higher effective austenite grain boundary area (S_v) and thus a marginally smaller transformed ferrite grain size. This is seen from Figure 7(b), however, at the higher Mn content this effect is diminished probably due to the lower Ar_3 transformation temperature.

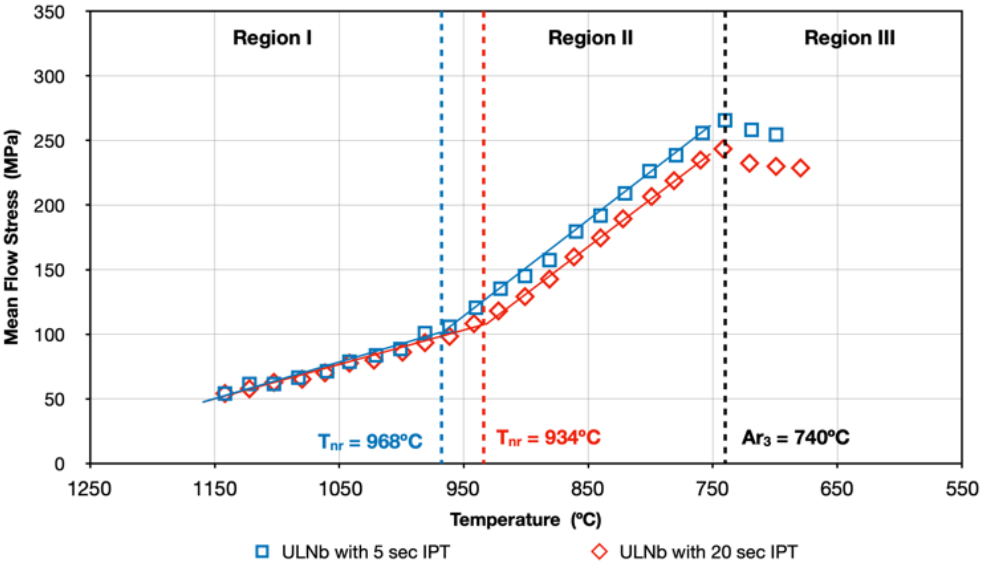


Figure 8. Mean Flow Stress (MFS) against deformation temperature for Group B steels at interpass times of 5 and 20 seconds

INDUSTRIAL TRIALS

To test the concept of applying ULNb addition to partially replace Mn and/or small additions of V, a set of industrial trials were undertaken at two separate H-Beam producers making commodity structural steel grade S275JR and S355JR respectively. Importantly, no changes in casting, reheating or rolling conditions were made (i.e., their standard operating practices were maintained). Both H-beam producers operate a modern universal beam mill set-up (i.e., a breakdown stand and a universal finishing stand) and the rolled products are air-cooled to room temperature. Additionally, the same starting beam-blank size was also used and, fortuitously, both producers rolled to the same final product dimensions (300x300x10x15mm – 95kg/m).

Table 3. Chemical composition and mechanical properties of S275 and S355 industrial trials (300x300x10x15mm)

Grade	C	Mn	V	Nb	TS(MPa)	YS(MPa)	CVN@20°C
S2755JR	0.20	0.70	--	---	Ave: 485	Ave: 345	---
S275JR+ULNb	0.20	0.70	--	0.0095	Ave: 505	Ave: 380	---
S355JR	0.20	1.45	0.0120	---	550	375	Ave: 70J
S355JR+ULNb	0.20	1.45	---	0.0080	580	400-425	Ave: 160J

For the first product trial, an average of 0.0095wt.%Nb was purposely added to the existing S275JR steel grade composition to determine what increase in YS could be realistically achieved under routine industrial steelmaking and rolling operations. Based on the result, this would then allow stepped reductions in Mn content to be made for future heats, whilst ensuring a sellable end-product (without the risk of product downgrade). The results are shown in Table 3, where the addition of ULNb (95ppmNb) was found to increase the YS by an average of 35MPa and the TS by

20MPa. Furthermore, the distribution in YS was reduced by 10-15MPa, thereby indicating a more homogeneous microstructure. Based on the results received, the average strengthening contribution of ULNb is found to be 3,685MPa/wt.%Nb. This is seen to be lower than proposed earlier at 5,000 to 5,500MPa/wt.%Nb, however, it should be noted that these values were based on controlled laboratory heats and rolling conditions. Nevertheless, the industrial results successfully demonstrated to the steel-producer that 95ppmNb generated an additional YS contribution of 35MPa and based on the findings of Group A steels (under laboratory conditions), this would enable a reduction of at least 0.40wt.%Mn.

For the S355JR product trial, 0.0080wt.%Nb was used to replace an average 0.0120wt.%V, so an addition ratio of 1.5V:1.0Nb. The initial results are also shown in Table 3. For the ULNb steel, a YS ranging 400-425MPa was achieved, well above the product specification minimum of 355MPa and above the existing average YS of 375MPa for the 0.012wt.%V alloyed steel. Thus, indicating that in fact the addition ratio is much closer to 2V:1Nb due to a higher YS demonstrated from the trial. Furthermore, the low temperature toughness at the 1/3 flange position also showed a marked improvement at the required minimum 27J at 20˚C, reaching 140J at 20ºC and 70J at -40ºC (in comparison, the original V-steel alloy averaging 70J at 20˚C). The improvement in impact energy values clearly indicating that the transformed microstructure retained a finer ferrite grain size (examination of the microstructure revealed an average size of 16μm±0.5). Consequently, comparing both steels, the ULNb steel not only contributed more to the YS but is thought to have changed the balance of strengthening contribution more towards ferrite-grain size and slightly away from precipitation strengthening and/or hardening. This is considered because of the well-established relationship between the ferrite grain size and impact transition temperature (ITT) [19], whereby grain refinement is the only mechanism to further lower the ITT (and thus improved low temperature impact properties); in addition to improving the YS. Based on the results achieved, i.e., a 'surplus' YS, a small reduction in Mn content is also feasible thereby further reducing the ferro-alloy cost burden.

In summary, both industrial trial results confirmed the earlier findings, in that ULNb additions enables a reduction in overall ferro-alloying addition of Mn, and even reducing or eliminating small additions of V, in commodity grade structural steels (i.e., ≤355MPa YS).

SAVINGS IN FERRO-ALLOY COSTS AND GWPe

Based on the above laboratory experimental results, industrial findings and reference to the ferro-alloy price as highlighted earlier in Figure 1 (using average of prices Q2-2022 Ex-Works China), together with a market reference price of FeNb(65%), the potential ferro-alloy cost savings can be determined. The results are shown below in Table 4 when making the following assumptions: (i) 1.0wt.%Mn ≈ 70MPa in YS; (ii) 1.0wt.%ULNb ≈ 4,000MPa, and; (iii) V:Nb substitution ratio is 2:1.

Using the reference prices shown as shown in Table 4, ferro-alloy cost savings for S275JR and S355JR would amount to US$3.95/t and US$6.77/t of steel produced. As these savings are a direct consequence of reduced consumption in raw materials, there will also be an accompanying saving in Scope 2 Global Warming Potential (GWP) equivalent emissions (i.e. emissions a steel producer makes indirectly): to make 1 tonne of steel with a composition containing 0.0080wt.%Nb (i.e. 80ppmNb) will require a physical addition of 0.13kg of FeNb(65%) to be made. As shown in Table 4, 0.008wt.%Nb replaces 0.30wt.%Mn, this would equate to 4.71kg of HCFeMn(75%) physical addition. Using published data for each of these ferro-alloys it is possible to approximate how much saving in GWPe (for the time horizon of 100 years) is possible by optimising the alloy design through ULNb.

Table 4. Cost and GWPe savings in S275 and S355 with ULNb optimum solution

Grade	C	Mn	V	Nb	TS (MPa)	YS (MPa)	Savings (US$/t)	Saving GWPe (kg.CO2e/t steel)
S275JR	0.20	0.70	--	--	Ave: 485	Ave: 345	---	---
S275JR+ULNb	0.20	0.40	--	0.0080	Est: 490	Est: 355	3.95	13.03
S355JR	0.20	1.45	0.0120	0.0080	550	375	---	---
S355JR+ULNb	0.20	1.25	---	0.0080	>560	>390	6.77	13.69

Alloying recovery rates during steelmaking: HCFeMn75%=85%; FeV80%=95% and FeNb65%=95%.
Ferro-alloy reference prices used: HCFeMn75%=US$1.69/kg; FeV80%= US$43.33/kg and FeNb65%= US$47.55/kg.
GWPe (kg.CO2e/kg): FeMn65%=2.91; FeV80%=33.10 and FeNb65%=5.1 (Sources: CBMM, GaBi database [20-22])

The results are also summarised in Table 4. Whilst it is acknowledged that there is no unique value of GWP (environmental impact) and life cycle assessment (LCA) for each ferro-alloy, as this is dependent on a multitude of factors ranging from the process route applied by each producer through to the source of energy used etc., the figures used in calculating have been sourced from published sources applying an LVA methodology based on the ISO 14044 standard, which uses GaBi 6.0 software and databases such as IDEMAT and Ecoinvent 2.2 and the value for FeNb [20-22]. The output shows that through this alloy design optimisation approach using an ULNb solution, savings in GWP are found in S275JR and S355JR of 4.72kg and 9.81kg CO2e per tonne of steel for each respective tonne for the above examples.

Lastly, besides lower ferro-alloying costs and reduced GWPe per tonne of steel produced, a reduction in Mn content would also lead to: (i) less cold-ferro alloy addition into the ladle during steelmaking and thereby reducing a drop in the liquid temperature and saving on energy and ladle electrode; (ii) a reduction in secondary impurities arising from the addition of less ferro-alloy; (iii) reduced Mn segregation and banding effect and thereby improve the homogeneity of the cast and as-rolled product; (iv) improvement in weldability due to a lower carbon equivalent value (Mn/6), and; (v) overall less use, transportation and internal handling of raw materials from suppliers.

CONCLUSIONS

Laboratory scale studies together with industrial trials have demonstrated a lower cost alternative solution when making commodity grade structural steels with yield strengths 275-355MPa, without any changes to existing process routes. By using Ultra-Low Niobium (ULNb) additions (≤100ppm) it is possible to enable an overall saving in ferro-alloying expenditure of US$3.95/t and US$6.77/t (based on current published ferro-alloy prices) and a reduction in GWPe of 13.03kg and 13.69kg CO2e per tonne of steel for grades S275JR and S355JR.

This is possible because when ultra-low levels of Nb are applied, its strengthening contribution (MPa/wt.%) has been found to be greater than that established at higher levels (i.e., ≥0.020wt.%Nb) where TM-rolling is typically practised. This study shows that ULNb can provide approximately 40-45MPa in yield strength which is the equivalent to up to 0.50wt.%Mn (i.e., 1.0wt.%Mn ≈ 70MPa in YS, and up to 100ppmNb can be used to replace up to 0.020wt.%V.

Finally for guidance, it should be noted that for all first attempts in adopting an ULNb solution for commodity structural steels, it is highly recommended that an upper addition aim of 90-100ppmNb is first made to the pre-existing steel grade to establish how much of the other ferro-alloys can be gradually reduced. As individual steelmakers equipment capabilities are different, adopting this approach will mitigate any potential risks in not meeting final product specification. Furthermore, when undertaking trials, it is advisable that a statistically relevant number of as-rolled final product steel samples are tested to fully define the distribution in mechanical properties under commercial rolling conditions. This should then be compared to the existing production grade of similar final product dimensions (e.g., 300x300x10x15mm, 25mm flat bar, 150x150x12 equal angle etc.) as a means to calibrate how much of a reduction in Mn and/or V content can safely be made.

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