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IMPROVEMENT OF THE QUALITY OF FLAT STRUCTURAL STEEL PRODUCTS THROUGH PARTIAL REPLACEMENT OF MANGANESE BY NIOBIUM

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ABSTRACT

The use of manganese in structural steels has become established over time due to the numerous benefits it provides at low cost, such as the elimination of hot brittleness caused by sulfur and increased mechanical strength. On the other hand, higher levels of this element affect weldability and give rise to intensified central segregation in the core of the plates, which affects their ductility and toughness, as well hydrogen cracking. In addition, one of its main advantages, the low cost, is starting to disappear. More recently, the carbon footprint associated with manganese-based alloy designs has also become a factor of concern. A solution to this situation, from the point of view of quality, environmental impact and cost of steels, is the partial replacement of manganese by niobium, which will be detailed in this work.

Key words — HSLA Structural Steel; Niobium; Manganese; Alloy Design.

RESUMO

O uso de manganês em aços estruturais consagrou-se ao longo do tempo em função dos vários benefícios que ele proporciona a baixo custo, como a eliminação da fragilidade a quente causada pelo enxofre e aumento de resistência mecânica. Por outro lado, maiores teores desse elemento afetam a soldabilidade e dão origem à segregação central intensificada no núcleo das chapas, a qual afeta sua ductilidade e tenacidade, bem como o trincamento induzido por hidrogênio. Além disso, uma de suas principais vantagens, o baixo custo, está começando a desaparecer. Mais recentemente, também a pegada de carbono associada ao projeto de ligas contendo manganês também passou a ser um fator de preocupação. Uma solução para essa situação, do ponto de vista da qualidade, impacto ambiental e custo dos aços, está na substituição parcial do manganês pelo nióbio, a qual será detalhada neste trabalho.

Key words — Aço ARBL Estrutural, Nióbio, Manganês, Projeto de Liga.

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1. INTRODUCTION

The structural steels market is increasingly demanding higher strength steels, with yield strength increasing from 235 to 355 MPa, to reduce the weight of structures and, in this way, reducing its footprint and erection costs. The more intuitive and cheap way to achieve such increase in mechanical strength is to use a higher content of carbon. However, its content is restricted to a maximum of 0.20% in many specifications, as carbon is deleterious to ductility, toughness and weldability [1]. So, the next element of choice is manganese, as it provides an economical increase in mechanical strength due to the various hardening mechanisms it promotes, as solid solution, increase in the fraction of pearlite in the microstructure and a discrete grain size refinement, since it reduces the temperature of the transformation of austenite into ferrite (Ar_3).

On the other hand, the use of manganese brings some problems, as it tends to intensely segregate in the core of the slabs during its continuous casting, which can affect the performance of the finished product due to the massive formation of MnS inclusions in this location [2]. Other inconveniences are the increase in the degree of banding of the microstructure and reduction in weldability due to the higher value of carbon equivalent [2]. The literature reports successful experiences involving the reduction of manganese content in structural steels with the objective of minimizing costs and avoiding the mentioned problems [3,4]. More recently, even the advantage of low cost of manganese is disappearing due to an increase of its use, as the forementioned increase of Mn contents in structural steels, as shown in figure 1, plus the advent of AHSS steels with very high content of this alloy element and its use in batteries for electric cars [5]. And, last but not the least, carbon footprint must now be considered during the development of alloy designs, which eventually can be an additional disadvantage for the use of manganese [1].

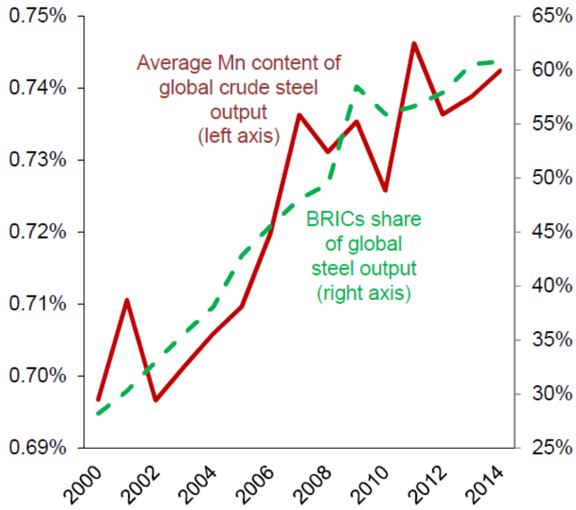


Figure 1: Evolution over time of the average Mn content and the participation of countries in the BRIC group in crude steel production [5].

This situation encouraged the development of new structural steels where manganese is partially replaced by other alloy elements, which have lower and more stable prices over time, such as niobium, which, moreover, can be used at contents one hundred times lower than manganese. Niobium, traditionally used in special applications and sophisticated steels, can also provide cost reduction benefits in commodity steels, without the need to modify the rolling processes or the use of controlled rolling.

2. EQUIVALENCE BETWEEN NIOBIUM AND MANGANESE IN STRUCTURAL STEELS

The proposal for partial replacement of manganese by niobium in structural steels is not exactly new [6]. According to that reference, in terms of the yield strength, a 0.30-0.40% reduction in the manganese content could be compensated by an addition of 0.010% niobium. In turn, to keep the tensile strength constant, the corresponding reduction in manganese content could be from 0.10 to 0.20%.

More recently this alloy design approach was studied with more detail for several hot rolled structural products produced in industrial scale [7-9], confirming the early findings described in [6]. This new class of structural steels with lower Mn plus very low Nb contents was appropriately named as *ULNb – Ultra Low Niobium*. Then an abacus was proposed, specifically for structural steels with a yield point lower than 355 MPa, where it is possible to determine the niobium content necessary to compensate for a given reduction in the manganese content, which is shown in Figure 2 [7]. Here the point (1) in the graph indicates the original CMn steel, with 1.50% Mn and without niobium; a reduction in this content to 1.20%, corresponding to the point (2), implies a reduction of 26 MPa in the yield strength, which can be neutralized by an addition of about 0.006% Nb to the steel – point (3).

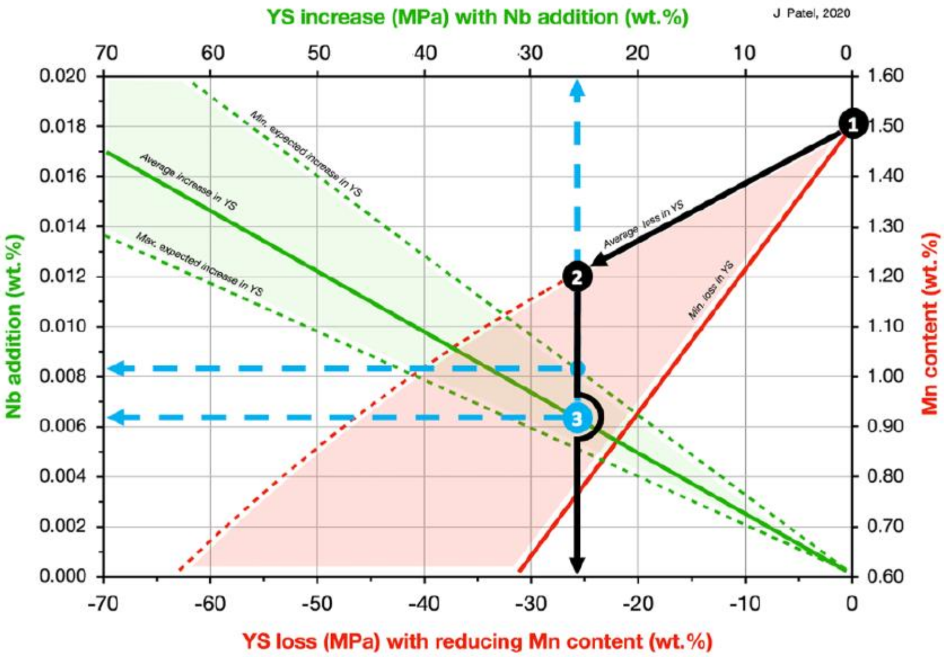


Figure 2: Abacus to determine the addition of niobium that is necessary to compensate for the loss of yield strength resulting from the reduction of the manganese content in structural steels with yield strength less than or equal to 355 MPa [7].

Table 1 shows examples of alloy design developments where manganese was partially replaced by niobium [8]. A36 and S355 steels were processed through hot strip rolling, while Q345 was used for heavy plate rolling. As can be seen, the mechanical properties between the two alloy designs for each standard were always remarkably similar. The addition of 0.010% Nb allowed to reduce the manganese content between 0.25% and 0.50%; this decrease was proportional to the original content of this last element. Besides that, the carbon equivalent of the new steels was reduced between 20 and 25% comparing with the conventional alloy design, which represents a potential improvement in weldability. And, in the specific case of steel for the Q345 standard, the reduction in the Mn content was effectively beneficial in terms of reducing the central segregation and banding in the plate, as well as greater uniformity of the microstructure of the final product, as shown in Figure 3, potentially improving its toughness and ductility performance. It must be also considered the potential reduction in the amount of residual elements and non-metallic inclusions due to the decrease of FeMn addition to the liquid steel.

Table 1: Comparison between industrially rolled flat products with conventional alloy design or with Mn partially replaced by Nb [8].

Standard	Thickness [mm]	Alloy Design	C [%]	Mn [%]	Nb [%]	CEq	LE [MPa]	LR [MPa]	A [%]	CVN @0°C [J]
ASTM A36	2,3	CMn	0.07	0.80	-	0.20	301	435	35.4	-
		ULNb	0.07	0.50	0.012	0.15	321	420	34.8	-
EN S355	12,0	CMn	0.15	1.20	-	0.35	356	499	26.0	-
		ULNb	0.15	0.80	0.010	0.28	359	481	27.0	-
Q345	≤ 30	CMn	0.16	1.40	-	0.39	383	525	27	164
		ULNb	0.16	0.90	0.010	0.31	387	514	26	170

Another particularly important feature to be considered when processing ULNb steels is its lower carbon footprint as compared with conventional alloy designs with higher manganese contents [7]. The Global Warming Potential (GWP, for a time horizon of one hundred years) were calculated for conventional and ULNb structural steels. It must be observed that the values obtained depend on a myriad of factors, including the manufacturing route of each plant and its energy sources. A life cycle analysis based on the ISO 10144 technical standard was adopted in that work, using the GaBi 6.0 program and databases such as IDEMAT and Ecoinvent 2.2. The ULNb steels allowed an average reduction of 34 kg of CO_2 equivalents per ton of product when compared with the CMn alloy design, a not negligible bonus considering the pressure being put on the steel industry to reduce its carbon footprint [7]. Considering that a typical passenger car emits about 4.6 tons of CO_2 per year (or 12.60 kg per day), the reduction in the CO_2 footprint due to the partial replacement of Mn by Nb compensates 2.7 days of car use for each rolled ton of steel [10].

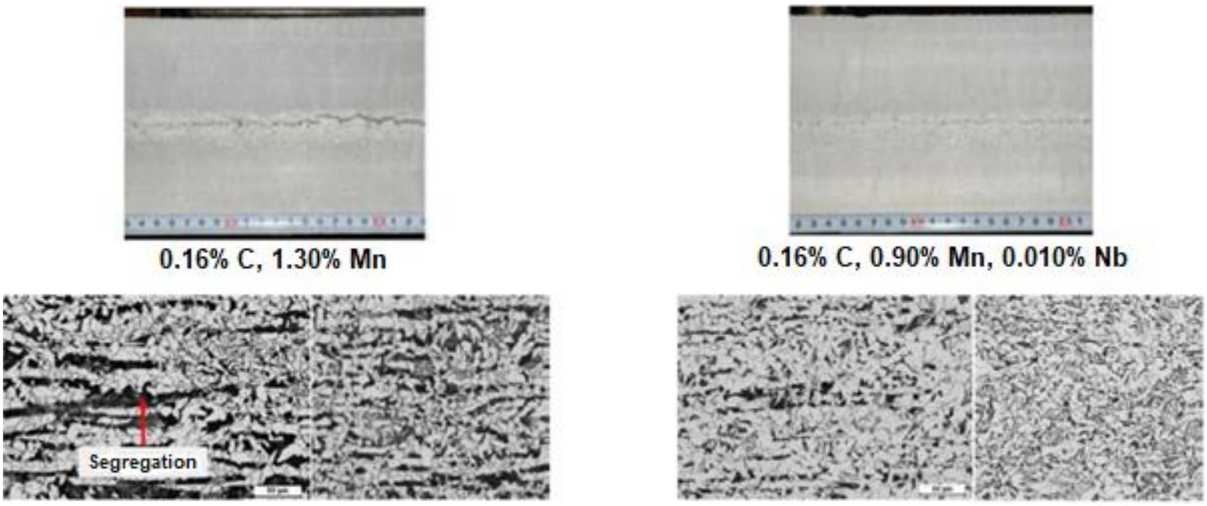


Figure 3: Effect of reducing manganese content in Q345 steel: (a) original Mn content; (b) reduced Mn, showing minimization of central segregation and greater uniformity of the microstructure of the final product [8].

The ULNb concept is already being extensively used in China. It is being processed in 14 rolling mill lines; 997.000 tons of Q345 and Q355 grade plates were processed by the end of 2021, with thickness range between 12 and 60 mm; the average manganese content reduction was about 0.3%.

3. A SYSTEMATIC STUDY ABOUT ULNB STEELS

The former studies about ULNb steel were developed in industrial scale, so it was necessary a more systematic analysis of this alloy design. So, several chemical compositions were cast in laboratory, with 0.18% C, variable Mn amounts (0.40%, 0.80% and 1.20%, approximately) and approximately 0.008% Nb. Two groups of steels were melted, Group A without Nb (CMn steels) and Group B with Nb (ULNb steels) [1].

Figure 4 shows that both yield and tensile strength increases with increasing amount of Mn, addition of Nb and reduction of finish rolling temperature (FRT) from 950 to 900°C [1]. For the CMn steels, the effect of this last parameter was decreased as Mn amount increased, reaching a maximum increase of yield strength of 20 MPa for 0.40% Mn and becoming virtually null for 1.15% Mn. Tensile strength showed similar trend, but the increase due to reduction of FRT was lower at 0.40% Mn. The mean yield strength contribution of Mn was approximately 69 MPa/%Mn, due to ferrite grain refinement and solid solution strength. The addition of Nb promoted a relative yield strength increase of 50 MPa/0.010%Nb. The mean yield strength contribution of Mn in the ULNb steels was about 68 MPa/%Mn, virtually identical to the value observed in the CMn steels. This clearly indicates that the hardening contribution of Nb is independent and overlaps the contribution of Mn. An analysis of the microstructures shown at Figure 5 allows to verify that even the very small addition of Nb was enough to promote some refinement of grain size, which contributes for the higher level of mechanical strength observed for ULNb steels, except in the case of 1.20% Mn steels, when both group of alloys showed a similar value of grain size. Finally, figure 6 shows that the addition of Nb was always favorable for toughness, except for the case of steels with 1.20% Mn and FRT of 950°C [11]. However, toughness performance was the same for CMn and ULNb steels with 1.20% Mn and FRT of 900°C.

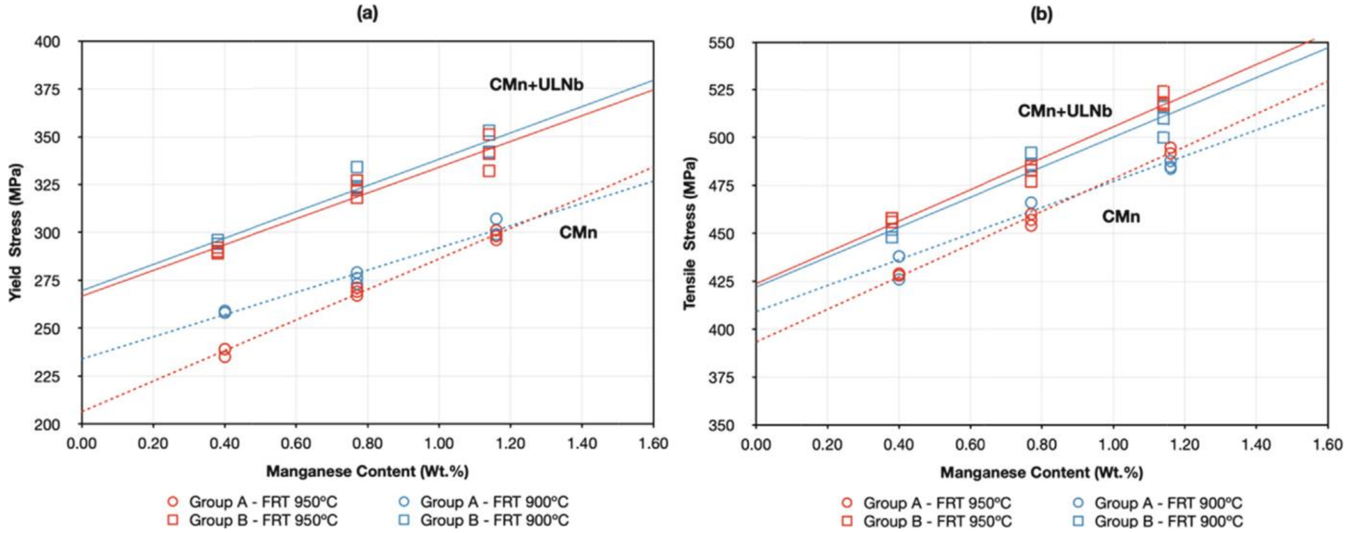
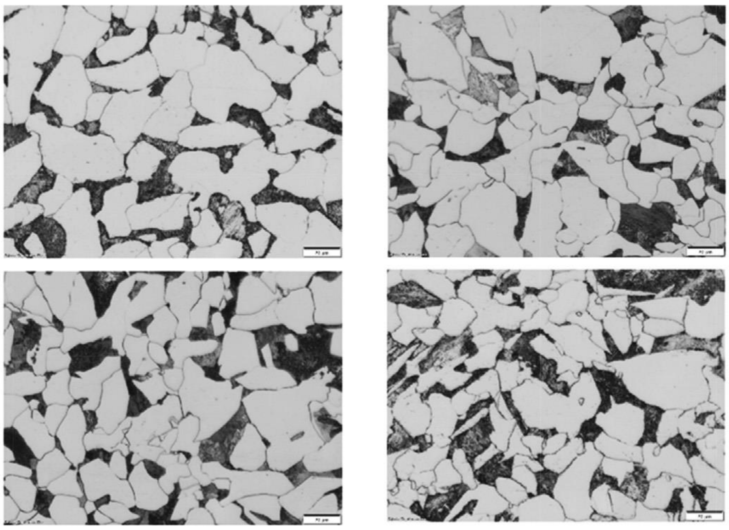


Figure 4: Effect of manganese content on (a) yield stress and (b) tensile stress) for CMn (Group A) and ULNb (Group B) steels, considering finish rolling temperatures of 950°C and 900°C [1].

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

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



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

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

Figure 5: Comparison of the microstructures for the CMn (at left) and ULNb (at right) steels with 0.77 and 1.14% Mn at FRT of 950°C [1].

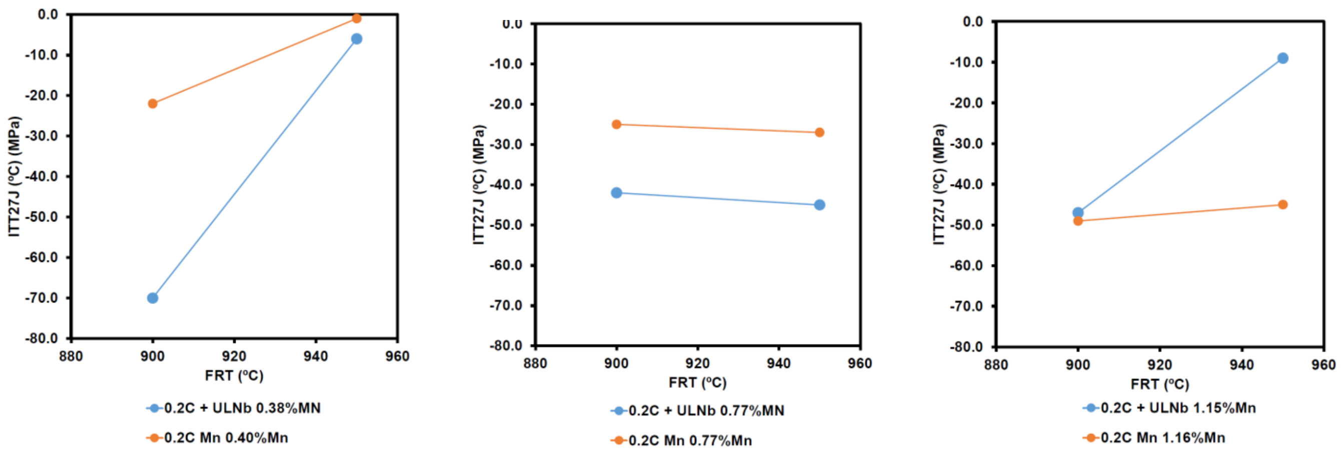


Figure 6: Effect of finish rolling temperature on impact transition temperature at 27 J for CMn (Group A) and ULNb (Group B) steels [11].

Finally, figure 7 shows the breaking down of the strengthening mechanisms for all steels and FRT values [1]. From these graphics, it is possible to verify that the contribution of grain refining was greater for ULNb steels with 0.4 and 0.8% Mn, especially when FRT was equal to 900°C. However, this effect practically disappeared in the 1.2% Mn steel, probably due to the lowering of Ar_3 induced by this element. The contribution of dislocation hardening was equal for both steel groups, A and B, and increased for the lower FRT values.

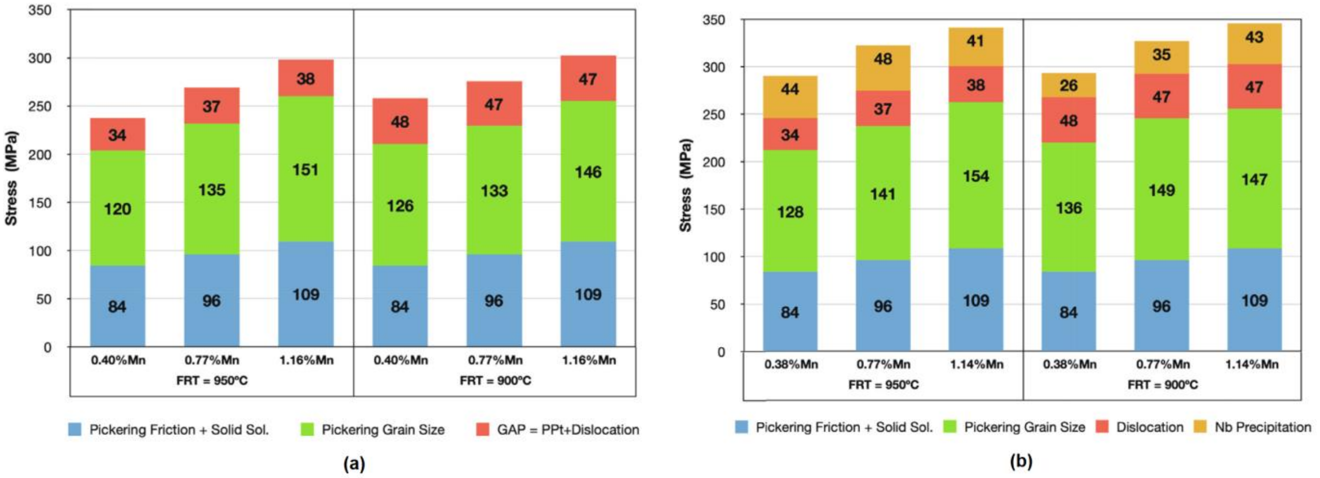


Figure 7: Breakdown of individual strengthening components for (a) Group A and (b) Group B steels [1].

Some extra hardening observed in the ULNb steels was caused by precipitation hardening, which curiously was lower for the 0.4% Mn and 0.8% Mn steels and FRT of 900°C, probably due to a lower amount of soluble niobium available at this condition.

4. LOW MANGANESE STEEL PLATES FOR PIPES USED IN SOUR SERVICE

The reduction of manganese content in steels for sour service pipes, compensated by an increase of niobium and other alloy elements, promotes even greater benefits for the quality of the product. Steels for pipes intended for use in sour service are generally microalloyed with niobium, titanium and/or vanadium. The manganese contents used in this application typically range from 0.90 to 1.20%. These values are relatively high in relation to the extremely low levels of sulfur that are required for this application, which are less than 0.001%. This leads to the formation of elongated MnS inclusions, which increase the susceptibility to hydrogen cracking of steel. The classic solution to this problem is the treatment of liquid steel with calcium, which leads to the formation of globular inclusions of calcium oxysulfide. However, this treatment is expensive and can give rise to operational problems, such as steel projections, excessive smoke generation, reoxidation and intensified presence of inclusions [12].

On the other hand, the reduction of the manganese content in the steel leads to an increase in the solubility of sulfur in the austenite, preventing its precipitation in the form of inclusions, as shown in Figure 8 [12]. Another beneficial aspect of reduced Mn contents in steel is the decrease of the intensity of its segregation in the center of the slab thickness produced by continuous casting, as shown in figure 9 [12]. All this ends up causing the steel's susceptibility to hydrogen cracking to decrease as its manganese content is reduced, as shown in figure 10 [12].

Based on these findings, a new concept of alloy design for steel was proposed for the manufacture of thick plates for sour service according to the guidelines below [12]:

- Minimization of central segregation through:
  - . Reduction of manganese content;
  - . Adoption of carbon contents below 0.06% and addition of chromium to promote solidification in the delta ferrite region, where there is greater homogenization of the segregation of alloying elements due to their higher diffusion rate;
  - . Low casting speeds;

. Use of soft reduction during continuous casting of the slabs.

- Increase in MnS solubility due to the reduction of manganese and sulfur contents;
- Reduction of MnS plasticity by reducing the value of the Mn:S ratio;
- Compensation of the reduction in the manganese content by the supplementary addition of niobium and chromium to maintain the levels of mechanical strength.

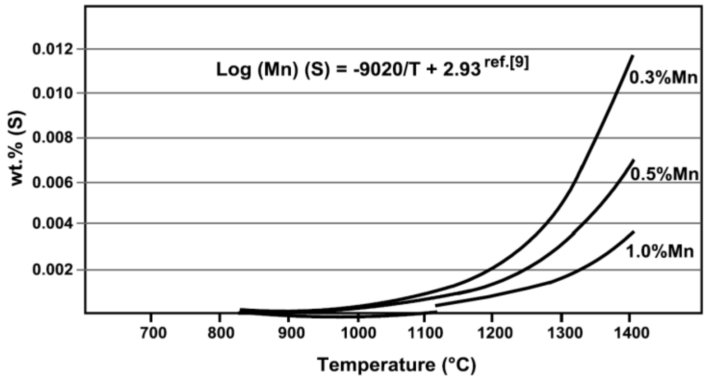


Figure 8: Sulphur solubility curves in austenite as a function of temperature and Mn content [12].

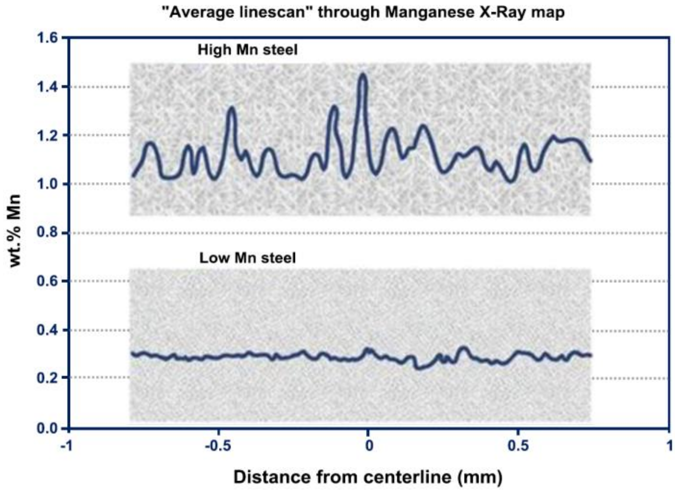


Figure 9: Segregation intensities for steels with high (top chart) and low (bottom chart) manganese contents [12].

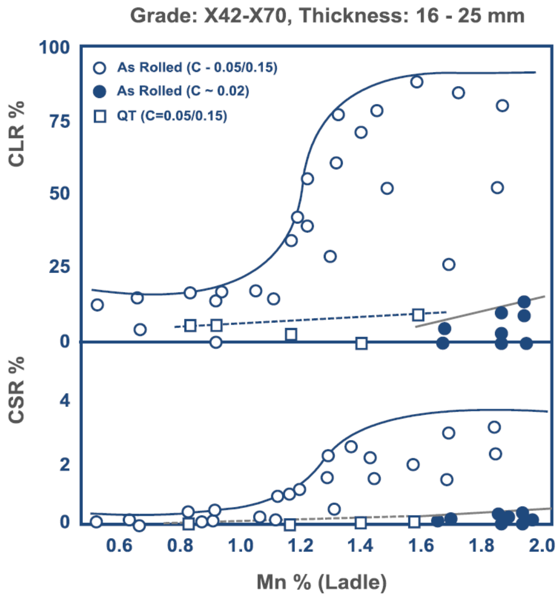


Figure 10: Effect of manganese content in steel on its susceptibility to hydrogen cracking, expressed in terms of crack length ratio (top graph) and crack sensitivity ratio (bottom graph) [12].

This new steel concept has a relatively high niobium content, around 0.10%, which fits it into the so-called HTP class (High Temperature Processing, that is, for processing at high temperature). It has been tested by several plants around the world.

5. CONCLUSIONS

In recent decades, the robust growth of world steel production has led to the continuous search for profitability and even for the survival of companies involved in the steel segment. The impressive expansion of the Chinese steel industry only added more volatility to this scenario. This situation is changing the price relationships between ferroalloy prices and several cost reduction initiatives are being developed, as exemplified in this work for the case of partial replacement of manganese through small additions of niobium. More than ever, it is necessary to “think outside the box” and seek competitiveness in creative solutions, which are not always evident at a first glance. It is about decreasing contents in the order of 0.30 to 0.50% of manganese, an alloying element traditionally used in structural steel alloy designs, by adding 0.010% of niobium, an element used until then in the case of steels of high performance. In addition, new projects for structural steels with lower manganese content and the addition of niobium have lower Global Warming Potential, a not negligible bonus when the watchword in the steel industry is to minimize the emission of gases that promote the so-called greenhouse effect. New metallurgical tools, such as the MicroSim®, are allowing the optimization of thermomechanical treatments and, in this way, extract the maximum effect from niobium and other alloying elements from steels. The optimization of alloy steel designs will progressively require deeper knowledge in metallurgy and the boldness to experiment innovative approaches.

6. ACKNOWLEDGEMENTS

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