MICRONIOBIUM-LOW MANGANESE STEELMAKING APPROACH, METHODOLOGY AND PROCESS METALLURGY*

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Abstract

Recent steelmaking developments have recently successfully melted steel grades with as much as a 25% reduction in Manganese content and a MicroNiobium replacement addition of .010 to .020% for several structural and infrastructure plate, sections and long products. The result involves a steelmaking alloy raw material cost reduction, improved castability, reduced internal Manganese Sulfide centerline segregation and less microstructural banding in the hot rolled slabs yielding a more homogeneous pearlitic microstructure. The applications within the infrastructure segment are growing due to the competitive nature of this product segment.

Keywords: Castability, Manganese, MicroNiobium, Segregation.

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1 INTRODUCTION

The current global steel market has experienced increased Manganese (Mn) concentrations in several value added automotive and some pressure vessel, ship and offshore plate product segments. Especially within the automotive sector there are some excellent high strength and elongation balance hot rolled sheet grades achieved through the addition of Mn levels between 3 to 6%. However, in some automotive developments Mn levels are even higher. This FeMn situation creates a supply-demand imbalance for other product segments, affecting FeMn raw material prices, within the lower yield and tensile strength family [1]. This FeMn supply shortage has resulted in an availability situation for some steel producers in different regions of the world, especially for some structural beam, plate and long products steel segment.
The solid solution strengthening that results from a FeMn addition is well established and relied upon by many producers to meet strength requirements. However, the current Mn supply situation is significantly increasing material costs at both Basic Oxygen Furnace (BOF) and Electric Arc Furnace (EAF) steelmaking shops around the globe. One technological solution to reduce steelmaking operational cost utilizes grain refinement via a MicroNiobium addition to compensate for the reduced Mn level and still successfully achieve mechanical properties. The Nb-induced grain refinement mechanism offsets the yield strength loss from the lower Mn with finer grain size and resultant increase in strength. The technological steelmaking developmental approach reduces Mn by 0.3 to 0.5% and then makes a MicroNiobium additions of as little as 0.010 to 0.020%Nb to successfully achieve strength at reduced ferroalloy cost. This study also introduces an activity based cost approach and cost-benefit methodology to properly evaluate the improvement in slab quality via less centerline segregation at lower Mn levels and improved grain size homogeneity where the cast slabs are hot rolled into bar, plate or sheet. Specific successful industrial examples are presented across several product sectors in both long product and flat commodity grades such as S235 and S275, as well as HSLA S355 and some potential for S420. The cost benefit methodology is simple and utilized for the proper evaluation and methodology to properly analyze this MicroNiobium Low Manganese approach and significant cost reductions at both the Melt Shop and Hot Rolling mill.

2 FERROMANGANESE EFFECT ON STEEL SLAB QUALITY

Much has been published regarding the effect of Mn on centerline segregation. Delamination and cracking related to segregations are mostly observed at the centerline of hot-rolled products. The delamination is related to a heavy concentration of manganese sulfide inclusions originating from centerline segregation in slabs. In numerous customer complaints. Similar delamination or cracking is also observed at locations away from the mid-thickness plane of hot-rolled products during forming operations at customers. Even in relatively homogeneous microstructures, segregation may often lead to the rejection of materials and increased External Cost of Quality for the steel operation. Metallographic investigation reveals a segregation line with an abundance of manganese sulfide stringers at the off-center location like observations in cases of centerline defects. Centerline segregation is a well-understood phenomenon, but the presence of off-center segregation line in hot-rolled products has not been systematically studied before [2]. Intercolumnar cracks in slabs can be filled with segregated elements in addition to Mn. Through the course of this MicroNiobium-Low Manganese Approach development, the initial replacement recently initiated due to the increasing FeMn prices creating the global supply-demand imbalance. However, as this paper reports, a further analysis of the benefits is well beyond just a simple alloy cost reduction at the Melt Shop. Internal mill quality improvements, reduced steelmaking and hot rolling cost and reduced external rejects at end users are captured via Cost Benefit Methodology analysis [3].

Segregation away from the centerline of continuously cast slabs occurs as well and often relates to continuous casting operational aberrations involving; 1) superheat, 2) mould level fluctuation, 3) casting speed variation and 4) sub-surface location of the thin equiaxed chill zone and columnar transition-zone (EACLZ) in the continuous cast slab during steel solidification in the mould and upper section of the caster. A laboratory-based experimental study was conducted by other researchers using a by S-printing technique to identify intercolumnar cracks [4]. The aim of this research was to evaluate the effect of intercolumnar cracks on internal quality of rolled products. This other research reports a strong correlation between intercolumnar cracks in slabs and off-center cracking in fabricated hot-rolled products [2].

There have been several instances when delamination or cracks are reported at the mid-thickness location of hot-rolled products during forming stage as shown in Figure 1. Metallographic investigations in most cases reveal a segregation band of manganese sulfide stringers along the centerline of rolled products indicating the defect to have originated from centerline segregation in slab.

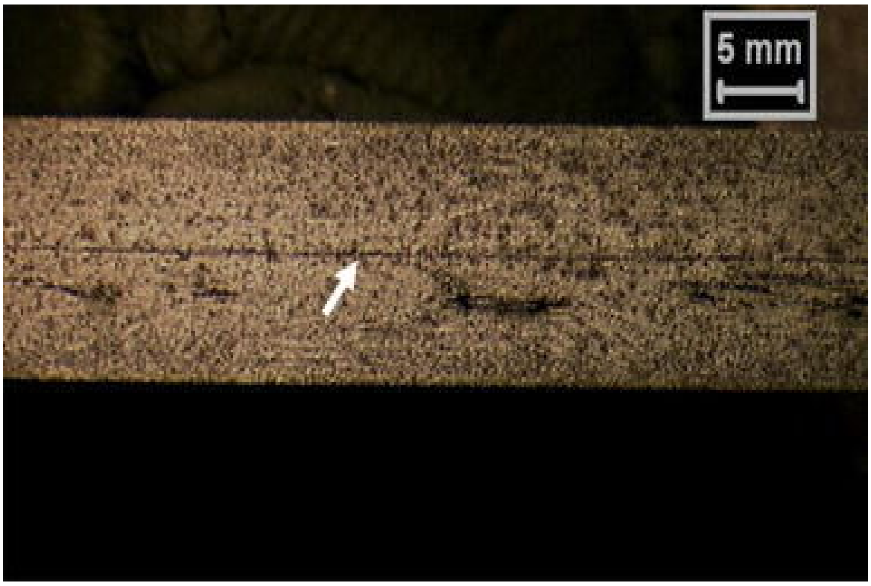

Figure 1. Crack-like defect at slab or billet centerline [2]

For example, at several end users during cold-forming operations, some customers of hot-rolled products report similar delamination or cracking at locations away from the centerline (henceforth, defined as off-center) as shown in Figure 2.

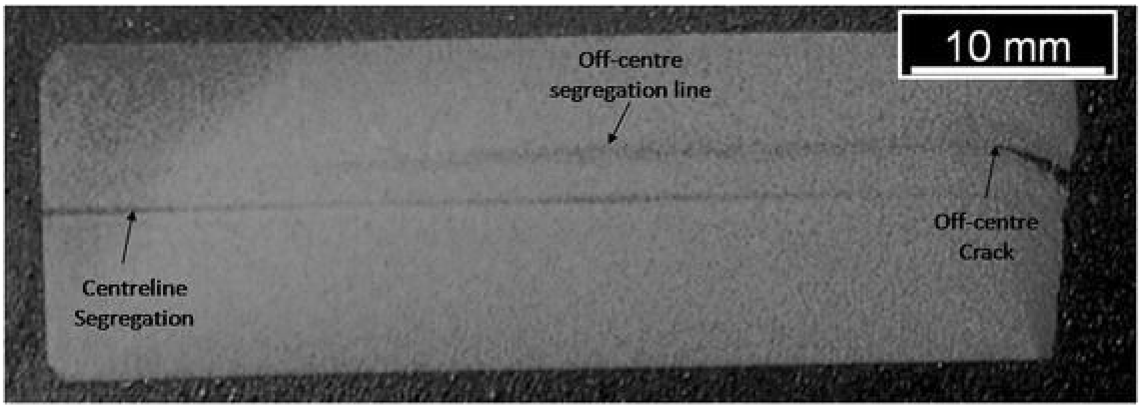

Figure 2. Transverse section of rolled product with segregation band along the crack line at off-center location after macroetching (50 vol% HCL) [2]

Metallographic investigations indicate a segregation line along the off-center crack location like that observed to occur because of centerline segregation in slabs. Optical microscopy reveals elongated stringers of manganese sulfide in the off-center segregation band as shown in Figure 3. This clearly suggests that the segregation at the off-center location of the rolled product leads to delamination or cracks during forming operations.

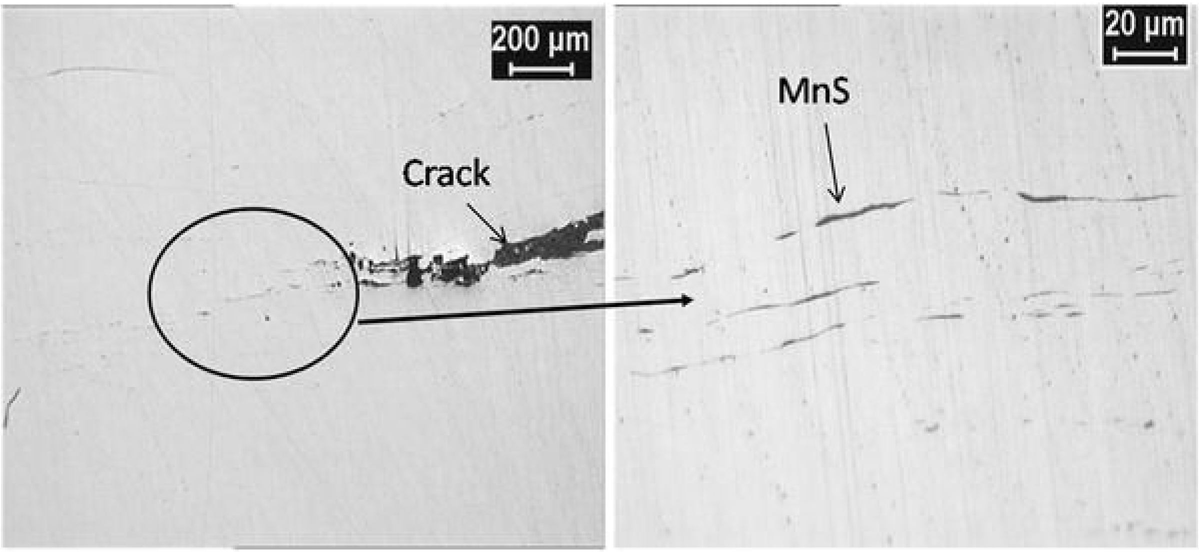

Figure 3. Optical micrographs indicating the presence of manganese sulfide stringers at the off-center crack locations [2]

Manganese is normally present in all commercial steels. It is important in the steelmaking process as Mn deoxidizes the melt and facilitates hot working of the steel by reducing the susceptibility to hot shortness. Manganese contributes to strength and hardness, but to a lesser degree than does carbon. Manganese has a strong effect on increasing the hardenability of a steel. The tendency toward macrosegregation is more than any of the other common elements Finally, Mn is a solid solution strengthener and lowers the austenite to ferrite (Ar_3) transformation temperature [5,6].

Hence, the concept of reducing Mn and compensate with a MicroNiobium addition to maintain strength. The importance of melting steel to the proper Manganese to Sulfur ratio (Mn/S) to minimize centerline segregation is fundamental to the process of achieving acceptable centerline quality. Figure 4 below references the Mannessman Demag inclusion index rating.

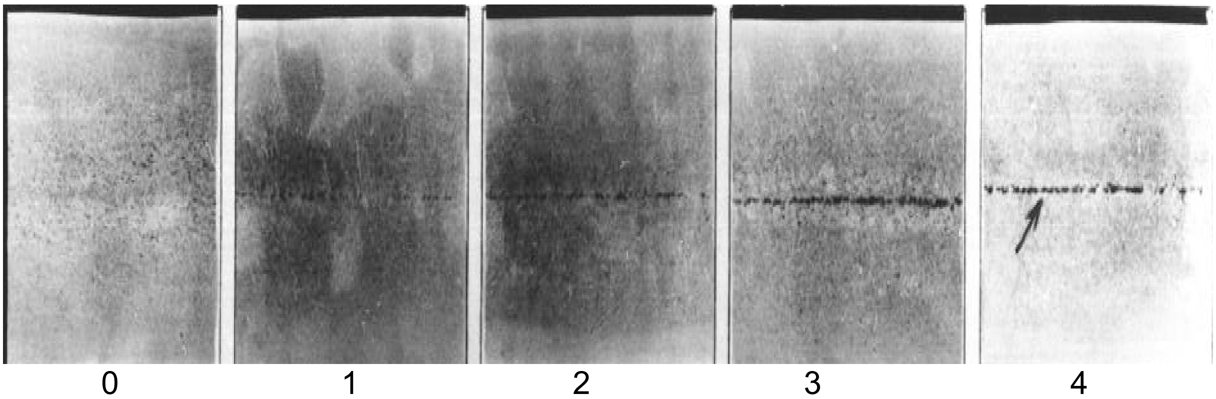

Figure 4. Mannessman Demag inclusion index rating (increasing Mn from 0 to 4 index)

The effects of segregation can be observed on the formation of these manganese sulfide inclusions shown in Figure 4, which has a detrimental effect on the reduction of area, impact upper shelf energy and transition temperature. The enrichment in the interdendritic liquid can also be responsible for the formation of coarse precipitates of microalloying elements that can act as stress concentrators and thus promote crack initiation. Figure 5 illustrates the relationship between the Mn:S ratio and the crack index and average crack length.

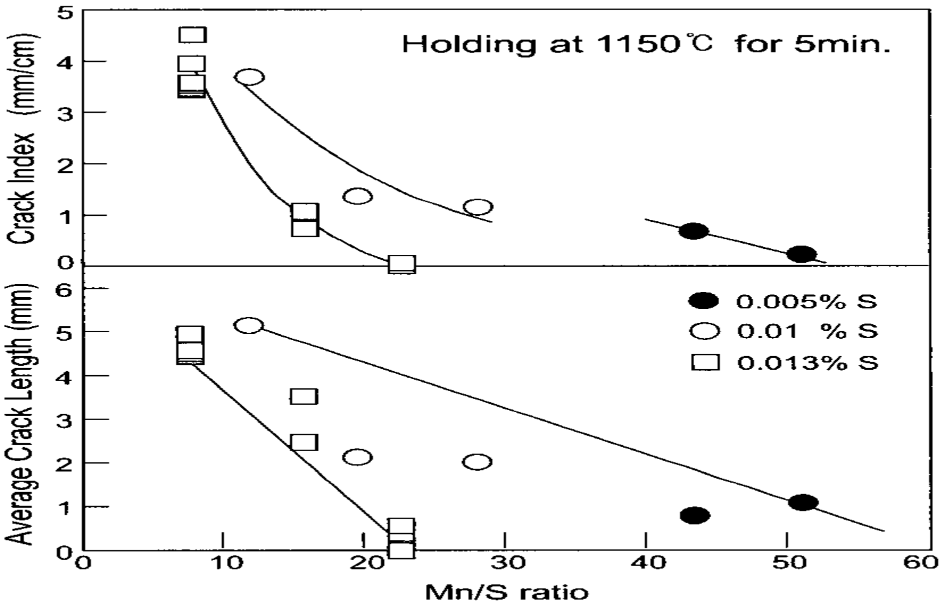

Figure 5. The effect of Mn/S ratio on the average edge crack length and edge drack index of low carbon steel held at 1150°C [7]

The MicroNiobium Low Manganese approach have successfully hot rolled with no edge cracking at a Mn/S ratio of 154 for the 0.8%Mn heat and a ratio of 241 for the

1.20%Mn heat. Even with the lower Mn/S ratio with the Mn reduction, slab and hot rolled quality was excellent at the lower Mn/S ratio.

3 NIOBIUM GRAIN REFINEMENT EFFECT ON SLAB AND HOT ROLLED STEEL QUALITY

Nb microalloying in combination with TMCP has been applied to produce a wide range of fine-grained steels for numerous applications. For example, compared to Ti, since Ti will form TiN at high temperature there is a toughness deterioration, especially at lower temperature, while V has little influence on the recrystallization behavior of austenite in solute condition during rolling process [8,9]. Therefore, by using much lower Nb content the same strength level can be achieved with much finer microstructure and improved steel properties even at reduced Mn levels. The fundamentals of grain refinement through Nb microalloying are principally based on four important effects throughout TMCP process:

1) Pinning of the austenite grain boundaries from abnormal growth in reheat furnace
2) Reducing austenite grain size during TMCP rolling
3) Retarding phase transformation to lower temperature during cooling
4) Preventing grain coarsening during coiling

These grain refinement attributes are a function of both the Nb and C levels in the steel, but fundamentally even at MicroNiobium concentrations each mechanistic attribute may play a role. In the Mn substitution work performed to date, the mechanical properties of these MicroNiobium additions at lower Mn levels have been achieved and validated meeting the mechanical properties for a given customer's specification. HSLA steels are microalloyed low carbon steels which have been widely used in mechanical engineering, automotive segment, pipe line and structural applications in both hot and cold rolled conditions. [8] At a low carbon content (generally less than 0.08% and excellent weldability at lower Mn) the strength of HSLA steels is dominantly attributed to grain refinement and precipitation hardening in the typical ferritic-pearlitic or bainitic microstructure provided by Nb or Nb-Ti microalloying. By reducing the grain size of ferrite and perlite or bainite and precipitation hardening the yield strength can be significantly increased up to 700MPa and at the same time the Ductile to Brittle Transition Temperature (DBTT) significantly decreases. Among all strengthening mechanisms in the steel, grain refinement is the only one that will increase both strength and toughness simultaneously, as shown in Figure 5.

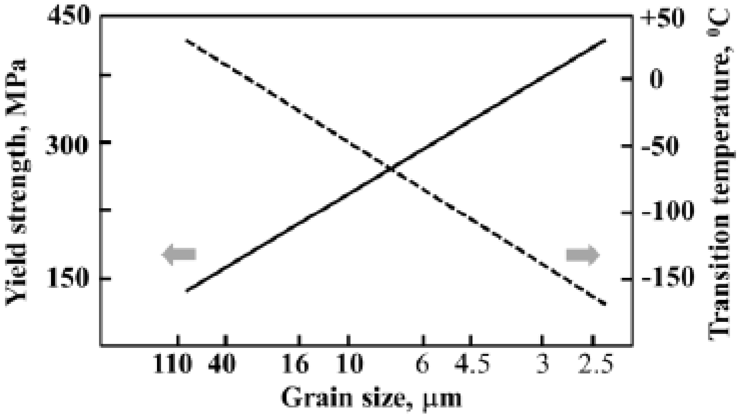

Figure 5. Ferrite grain size relationship to yield strength and Ductile to Brittle Transition Temperature

4 MECHANICAL PROPERTY RESULTS FROM INDUSTRIAL MICRONIOBIUM LOW MANGANESE PRODUCTION

Numerous papers in the literature from 20 to 30 years ago over-focused on the solubility issues with Nb and are disproven in recent years. The realization of the proper reheat time at temperature and kinetics of the given situation in actual industrial operations assisted greatly in gaining a richer understanding of niobium's true solubility behavior in actual production. It is fundamentally higher than in laboratory conditions. For example, in a thin slab caster operation producing heavy gauge sheet structural products, the excellent solubility was exhibited [10]. It also is apparent in the new generation low strength Nb structural steels that a ratio of 75%Nb in solution and 25%Nb in precipitation is acceptable and provides a twofold strengthening mechanism, (i.e. grain refinement being the most important as Nb slows down the diffusion of carbon, thereby delaying the pearlite transformation and precipitation strengthening.) Figure 7 below illustrated the calculated NbC solubility at different reheat temperature.

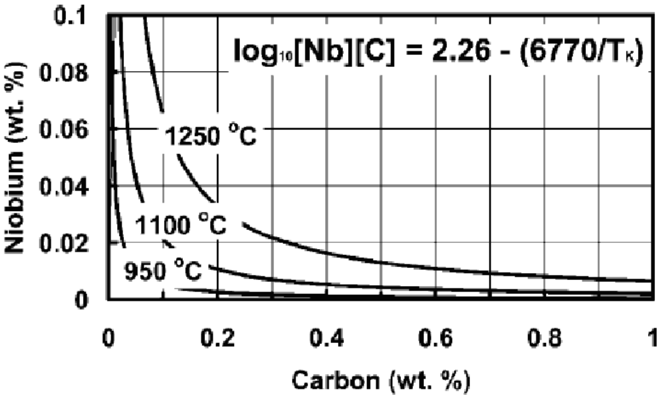

FIGURE 7. Calculated NbC solubility at selected temeprature [10]

During the hot rolling of these low carbon-manganese-MicroNb steels, delay of the pearlite transformation leads to a finer interlammelar spacing and finer grain size due to a shorter transformation time and thereby contributing to a strength increase even at lower Mn and C concentrations. Some of the other beneficial effects besides reducing alloy cost from the lowering of the Mn content by as much as 0.40%Mn are:

- Lower amount of cold additions to liquid steel (possible saving of energy)
- Lower P contamination from FeMn alloy
- Lower Mn centerline segregation in the slab/plate
- Reduced banding in hot roll microstructure
- Lower carbon equivalent (better weldability).
- Improved robustness and less YS and TS scatter
- Finer and more homogeneous grain size through thickness and across width
- Improved toughness and lower DBTT (ductile to brittle transition temperature)

The low Mn-low Nb construction steels research and development has recently been commercialized. The approach involves the application of quite simple conventional rolling schedules and reheat and hot rolling practices. Implementation is quite seamless and feasible in industrial operations. In the past, there was limited research into such products for two primary reasons. First, when secondary and tertiary processes such as hot forging, drawing and cold forging were applied to medium and high carbon steels, some think that the effects of controlled rolling may be lost through the process. Secondly, Nb has a lower solubility in austenite in comparison with low carbon steels at the same temperature. However, these trials have exhibited excellent results even in medium carbon peritectic S355 structural steels applied to offshore platforms and other structural supports at very economical cost as shown below in Table 1.

Table 1. Medium C-Low Mn MicroNiobium mechanical properties*

Sample	**Yield Strength(MPa)**	**Tensile Strength(MPa)**	**Elongation (%)**	**Impact Strength-20°C**	**Impact Strength 0°C**	**Impact Strength +20°C**
Aim	345	470	21.0	-	>34	-
II-16mm	405	525	28.5	150	170	160
III-16mm	410	535	33.0	150	170	160
IV-40mm	455	615	22.0	100	155	180

* Mn level reduced from Standard 1.45 to 1.15%Mn and 0.010%Nb at 0.16%C (peritectic) and Mn/S is reduced from 181 to 144.

The intent of this work is to study existing carbon (peritectic) compositions and replace the vanadium with niobium and make a significant reduction in the manganese level for these 345MPa grades. The next step is to consider a similar reduction in Mn strategy even for lower strength steels such as 235MPa and 275MPa as a cost reduction opportunity. The knowledge gained from this work is illustrating the possibility of making Mn reductions and significant cost savings. There have been situations where the aim is to produce S275 and the mill actually produced S420MPa structural grades with improved toughness and less microstructural banding.

The solid solution strengthening equation is shown below in equation 1 and 2 per Gladman and Pickering: [11]

$$\text{Yield Strength (MPa)} = 53.9 + 32.3\%\text{Mn} + 83.2\%\text{Si} + 354\%\text{Nf} + 17.4\text{d}-1/2 \quad (1)$$

$$\text{Tensile Strength (MPa)} = 294 + 27.7\%\text{Mn} + 83.2\%\text{Si} + 3.85\%\text{Pearlite} + 7.7\text{d}-1/2 \quad (2)$$

Table 2 illustrates the solid solution strengthening effect at various Mn concentrations.

Table 2. Solid solution strengthening effect of Manganese

%Mn	Contribution to Yield Strength(MPa)	Contribution to Tensile Strength(MPa)
0.30	10	8
0.60	16	14
1.00	32	28

A second major step previously discussed is the transition from these medium carbon peritectic structural steels to less than 0.10%C grades. It is becoming apparent in S355 and S420 grades that very low manganese levels with proper reheat furnace operations and rolling practices result in easily achieving yield and tensile levels with excellent low temperature toughness as exhibited in Table 1. The process metallurgy positively contributes to the increased strength typically expected from the additions of higher carbon and higher manganese levels. These reduced manganese and carbon levels also result in reduced alloy and processing costs and improved weldability via the Cost-Benefits Activity Based Cost Approach.

5 COST BENEFIT ANALYSIS METHODOLOGY

A Cost Benefit Analysis Methodology system is presented to assist steel producers in the minimization of the total cost to commercialize and produce low-carbon lean alloy (LCLA) steels [3]. The entire supply chain is integrally connected from raw materials to the finished component. The accuracy of such drivers as the actual incremental cost of raw materials, substitute materials, product mix changes, the productivity/quality indices, operational and indirect costs are key components of this system. The Cost Benefit Methodology system is designed to capture the economic implications of operational performance, chemistry and fundamental customer specifications [12].

The primary drivers of the total operating cost per ton of steel are comprised of the following cost components: 1) alloy, 2) BOF/EAF conversion, 3) reheat furnace gas consumption, 4) plate mill/hot strip mill conversion, 5) cobbles, 6) diverts and 7) electrical energy consumption. The BOF/EAF costs are linked to the charge model which will calculate forecasted cost and then make an adjustment based upon an actual operating data variance report resulting in an adjusted cost/tonne. The natural gas cost (mmbtu per tonne) is the actual consumption of the given plate order. The cobbles and diverts are easily measured for the S500 plate schedule. The electrical cost is measured (horsepower per tonne) for the actual rolling. Reduced diverts for cracking and/or segregation is captured in the HM conversion cost. The plate steel example incorporating the Cost Benefit Analysis Methodology is shown below in Figure 6.

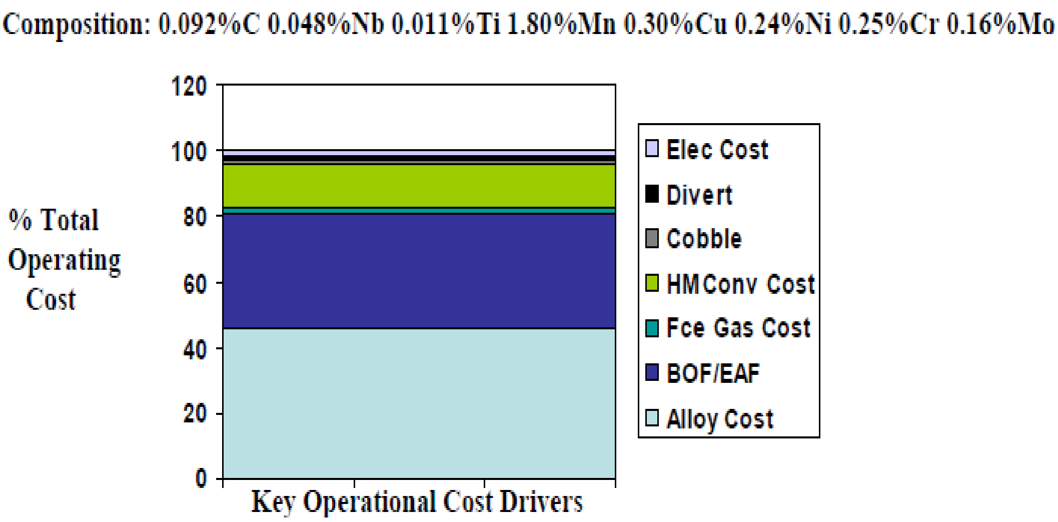

Figure 6. Rich alloy 500Mpa compostion with conventional cooling [12]

The MicroNiobium Low Managanese cost benefit analysis needs to incorporate not only the reduced alloy cost, but also the direct cost effect methodology at both the caster and hot rolling mill. Twenty to thirty percent reductions in Mn will lead to less internal segregation defects and reject cost. Also, the rollability and more homogeneous microstructure should translate into reduced total operating costs illustrated in Figure 6 within the HM conversion cost bar, cobble reduction and divert reductions.

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For example, in Table 2 if the Mn is reduced from 1.00 to 0.60%, which results in a significant alloy cost reduction in the several hundreds of thousands of dollars for the Melt Shop, the yield strength decreases only 16 MPa. This decrease of 16MPa is easily recovered with a 0.015%Nb addition primarily from a finer grain improvement from ASTM 6 to 8 (and in some cases ASTM 9 depending on finishing temperature) easily recovers the 16MPa loss in yield strength as shown below in Figure 7.

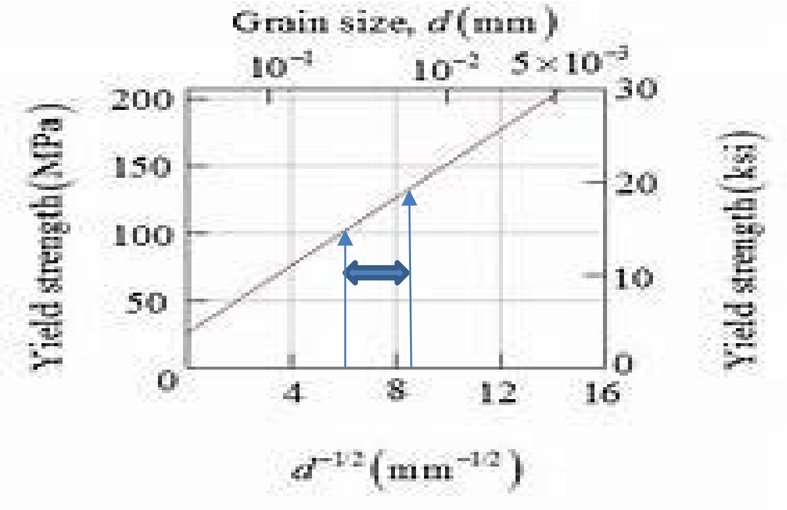

Figure 7. Grain size effect on yield strength [13]

3 CONCLUSION

This new generation of value-added low carbon-low manganese-niobium microalloyed structural steels for both low and high yield strength and energy absorption, is being implemented and the future low cost, economic and quality choice. Reductions of 20 to 30% in Mn and replacement with a MicroNiobium addition of 0.010-.020%Nb results in achievement of specified yield/tensile strength, elongation and energy absorption (toughness). The process metallurgy of reducing carbon and avoidance of peritectic structural grades further improves the steel robustness coupled with the MicroNb addition for grain refinement to better serve the increasing demands of the infrastructure sector. The reduced Mn levels result in less centerline segregation, microstructural banding and edge cracking during the fabrication as the end user customer.

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