Niobium Bearing Structural Steels
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NIOBIUM-BEARING STRUCTURAL STEELS FOR THE 21ST CENTURY

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Abstract

Value-added applications of niobium (Nb) microalloyed steels continue to be developed for commercial implementation to meet increased material demands and improved properties for 21st century structural applications. These applications demand Nb-bearing steels that deliver improved toughness, fracture and fire resistance and weldability. Such applications include medium and jumbo beam, boiler, bridge, container, heavy equipment, long product, pressure vessel, ship, storage tank and windtower applications. Steel producers are challenged to develop microalloyed steel grades that cost effectively meet end user demands for higher strength at thinner cross sections, better low temperature toughness to resist brittle fracture in building, pressure vessel and ship structures, sustain higher loads per unit area in earthquake and hurricane zone product applications, demonstrate improved fire-resistance in buildings, bridges and tunnels and provide overall improved weldability. Niobium is often a key element to achieve these results. This paper will discuss Nb market opportunities and key operational practices required to successfully melt, cast and roll these high strength steel grades. Niobium process metallurgy is important to leverage the ability of niobium to obtain ultra-fine grain, homogeneous structural steel microstructures with superior mechanical properties. In addition, with the ever-growing concern regarding the environment and resource sustainability, the application of advanced high strength Nb-bearing steels for both long product and structural applications have been shown to reduce resource usage and improve the carbon footprint. Recent Nb-microalloyed steel applications provide more efficient product design, reduce steelmaking emissions and reduce energy consumption.

Introduction

The unique metallurgical attributes that niobium provides to structural steels create the opportunity to successfully meet stringent mechanical, corrosion and elevated temperature demands. Nb-based structural steels were in limited production during the 1980's. Over the last two decades, through the numerous Nb-bearing structural steel global research and development project activities conducted by steel mills, universities, research institutions and CBMM, significant progress has been achieved. Nb-bearing structural products are now specified in a variety of applications and markets. The diverse array of Nb-structural steel markets and future potential is discussed herein. Finally, the process metallurgy required to consistently and cost effectively maximize the Nb effectiveness in the melting, casting and rolling operation is outlined.

Background

Applications of value-added Nb-bearing steels can reduce the overall material and construction costs for many advanced high strength structural and civil engineering applications. Although there are different civil engineering designs and many diverse product applications in the structural market, the Nb metallurgy and production strategy to manufacture these steels often remain the same. Cross-application of similar niobium microalloy steel grade systems are specified for different end user requirements. Today's structural steel demands properties such as: 1) improved toughness at lower temperature, 2) higher yield strengths for lower cross sectional area of structure, 3) higher elongations, 4) improved weldability to reduce construction time, 5) improved elevated temperature properties, 6) improved fracture toughness, 8) seismic-resistance and 9) improved fatigue resistance. Cross-application of Nb-bearing steels has resulted in a variety of large-scale structural designs with improved properties for diverse products from beams to storage tanks. Recently, Nb-bearing steel grades are also being applied at an accelerated pace in long products that require improved mechanical properties in more demanding applications such as automotive suspension components, microalloy forgings for power transmission, high carbon rail, wind tower supports and seismic rebar.

Market Overview

The carbon steel structural segment is by far the largest global steel segment in the world and represents over 60% of the crude steel production. Over 10 percent of the 669.9 million metric tons of structural plate and long products production in 2009 contained Nb. The major structural steel segment distribution for 2009 is shown in Figure 1.

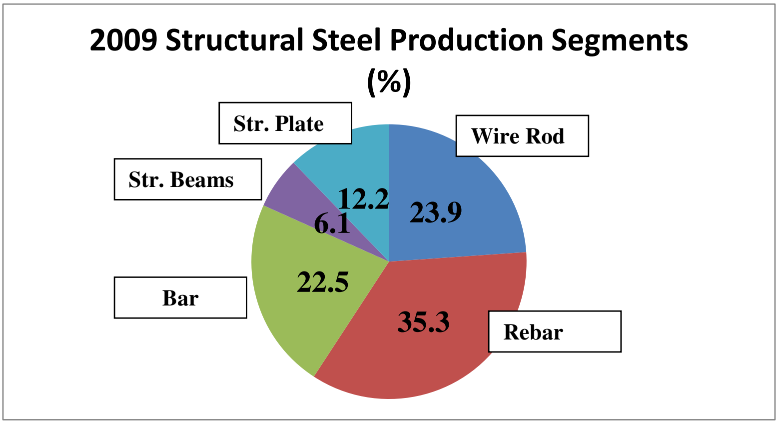

Figure 1. Global Steel Long Products & Plate Production Steel Segment Distribution

The current application of niobium in structural steels is more predominant in the structural plate and beam segment than in the long product segments such as wire rod, rebar and merchant bar. However, current and future product development activities are making technological advancements within the Nb-bearing high carbon and alloy long product segment. For example, with the increasing demand for fire resistant and seismic resistant construction materials, the S500 and S600 Nb-Mo reinforcing bar research and industrial trials support applications in reinforced-concrete bridge, building and tunnel construction. Nb-bearing structural plate, beams rod and bar find their niche and application in numerous end user segments and are entering some new product development segments as illustrated in Table 1.

Table 1. Nb-bearing end user steel application & development by structural segment

Structural Plate	Beams & Str. Shapes	Bar	Wire Rod	Structural Pipe & Tube	Rebar
Windtower supports	Light to jumbo beams	Spring steels	High carbon pre-stressed	Structural scaffolding	Seismic resistant
Bridge	Bridge	Forging quality	Engineering	Construction	Fire resistant
Pressure vessels & containers	Buildings (Freedom Tower)	Automotive suspension systems	Cold headed	Irrigation and utilities	Bridges
Railway tank cars & rail cars	Power plants	Carburized gears & shafts	High strength bolts	Boiler tubing	Buildings
Ship plate/Offshore platforms	Trailer support rails	Quench & Temper	Wire rope	Utility power plants	Tunnels
Heavy machinery	Rails				

The global structural steel market development, research and industrial implementation requires a shift in the traditional metallurgical approach. Current challenges confronting structural and long product steelmakers are identical in nature to the challenges faced by automotive steel producers in their development of advanced high strength steels last decade. Similarly, during the evolution of pipeline steel development from X-52 through X-100, similar challenges existed resulting in steelmaking and processing changes to successfully apply High Temperature Processing (HTP) to overcome these production and product quality challenges. Much of this technology can be transferred to the structural steel production of Nb-bearing steels.

The successful production of value-added structural products requires the application of melt shop and rolling mill practices that in many cases are similar to practices for value-added automotive, pipeline and structural grades. Tighter process control during the melting, casting, slab/bloom/billet heating and rolling is necessary to make improved properties. Different control strategies are required for the production of these high quality construction steels. These strategies include lower residual element levels, scrap segregation, lower sulfur and phosphorous levels, the adoption of a low carbon approach, control of nitrogen levels at the basic oxygen furnace (BOF) or electric arc furnace (EAF) and at the billet/bloom/slab caster. Such operational and metallurgical practices were once considered unnecessary in long product structural production. However, the future generation of value-added long products will demand changes in operational practices similar to the adaptive developmental progression within the plate producer community.

In the spirit of disseminating and sharing the constant evolution of Nb-technology, CBMM sponsored an automotive symposium in Araxa in December of 2005 and a pipeline symposium in January 2006 where numerous Nb-bearing steel papers were presented by customers, research institutions and universities. [1,2] This book is added to that body of knowledge to meet three objectives: 1) compile state-of-the-art Nb structural steel technology papers, 2) identify opportunities to further develop Nb in value-added structural steel and 3) provide a comprehensive Nb structural steel reference book. Numerous case examples are published within this book highlighting the process metallurgy to successfully produce the physical metallurgy in the final structural product to the end users' desired properties.

21st Century Nb-bearing Structural Steel Approach, Challenges, Changes and Opportunities

Different from the automotive or pipeline segment where carbon levels are typically less than 0.10%, many of the plate structural products exceed 0.15%C approaching allowable specification maximum carbon levels of 0.22%. There is a still a preponderance of structural plates and beams produced throughout the world with carbon levels greater than 0.18%C. There are various reasons for this as it relates to the process metallurgy, mill configuration and furnace reheating efficiency and performance. Some mills choose the higher carbon level approach to achieve strength, but sacrifice toughness, weldability and product performance. [3] Mills have been unable to adapt their heating and rolling operation to accommodate low carbon microalloy mechanical metallurgy practices. In these cases, the plate production approach has not taken full advantage of the Nb solution to lower carbon levels which increases yield strength, ductility, toughness and weldability. Within the long products sector, the addition of Nb in high carbon and alloy long products has been limited to date, but is increasing in popularity and application as evident in Table 1.

Structural Plate and Beams

Over 50% of the structural plate and beam sections are intermediate carbon levels from 0.15 to 0.22%. There is a gradual shift at some mills seeking participation in the value-added structural plate and beam segment to produce Nb-bearing structural grades at less than 0.10%C to make lower carbon base alloys for both plate and some long product applications. The benefits are not only improved mechanical properties and functional performance, but also the opportunity to reduce overall steelmaking cost per tonne through improved productivity, reduced diverts and improved product quality. [4]

Excellent research and development progress has resulted in the successful commercialization of lower carbon Nb-bearing microalloyed plate steel and near net shape cast and rolled beams throughout the world. Many of these progressive metallurgical accomplishments are presented within this text. With increasing raw material and energy costs, the effects of processing parameters such as reheating temperature and cooling rate after hot rolling to achieve improved mechanical properties can result in significant savings. A lower total cost of production may be achieved through a low carbon-low alloy (LCLA©) chemistry with selective accelerated cooling and better control of reheat furnace temperatures. [4]

Cost Benefit

A Cost-Benefit Analysis Methodology system will assist steel producers in the minimization of the total cost to commercialize and produce LCLA steels. [4] 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. A Cost-Benefit Methodology system captures the economic implications of operational, metallurgical and required customer specifications as they specifically apply to an individual mill.

A Nb plate steel example incorporating the Cost-Benefit Analysis Methodology is shown in Figure 3 and compares a rich alloy S500 plate steel high carbon composition with conventional cooling versus Figure 2, a LCLA composition with accelerated cooling on a percent total operating cost basis.

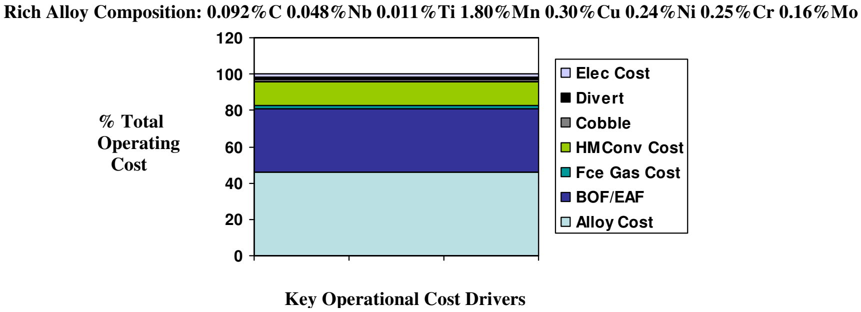

Figure 2. Rich alloy high carbon 500MPA composition with conventional cooling [5]

Note that 46% of the total operational cost is related to raw material ferroalloy cost in the rich alloy higher carbon approach versus only 18% for the LCLA grade with accelerated cooling shown below in Figure 3.

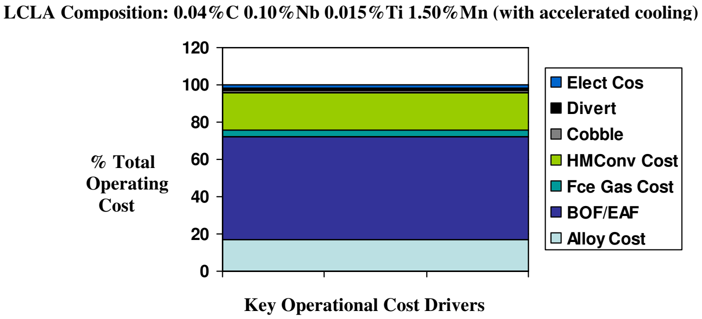

Figure 3. Low carbon lean alloy 500MPA composition with accelerated cooling [5]

Other Considerations

High strength and high toughness structural plate and some selected long product applications require a commitment to clean steel practices with sulfur levels less than 0.010%, phosphorous less than .020%, control of residual elemental levels and with preferably less than 0.10%C. World class steel companies around the world are implementing this strategy to cost effectively produce lean alloy plate with excellent toughness, weldability and yield to strength ratio balance.

It is important to differentiate between different TMCP types: thermo-mechanical rolling (TMR), accelerated cooling (and Tempering) (AC (+T), and direct quenched and tempered (DQT). The separation into these TMR types coupled with other accelerated cooling schemes results in different processes dependent upon whether the end product is ship plate, bridge, offshore structures, line pipes or other heavy plate applications. Nb is a critical element in the application of TMCP increasing its cost effectiveness and high performance characteristics at Sumitomo. [6]

Another example of the Nb LCLA design is implemented cost effectively at Voest Alpine in plate approaching strength levels of 960MPa. Excellent upper shelf energy (100J at -80°C for 10mm plates) is achieved. [7]

Nb Product Development Opportunities

Steel value-added markets require; 1) exceptional toughness and low temperature properties, 2) excellent yield strength to tensile strength balance with minimal σ_{ys} to σ_{ts} ratio variation, 3) ultra fine grain microstructure, 4) excellent weldability and 5) exceptional fatigue resistance. More consistent low sulfur and phosphorous steels with calcium shape control and restricted residual levels are required to produce the demanding toughness requirements at low temperature, reduce yield to tensile variation, improve fatigue performance and improve weldability.

These are opportunities and challenges for the adaptation of Nb technology in the following areas:

- Development of a more economical LCLA steel incorporating accelerated cooling in the rolling mill to replace some rich alloy steel grades.
- Shift more construction structural grades to less than 0.10%C incorporating TMCP and Nb technology (i.e. S355 and S460 LCLA-accelerated controlled cooling approach).
- Development activities to accelerate the application of 0.005-0.020%Nb for fine grain refinement in over 0.50%C steels (rail steels, heavy equipment, abrasion resistant plate).
- Taking advantage of the Nb-Mo nano co-precipitation synergy, a family of fire resistant and seismic resistant S500 and S600 rebar will be developed.
- Commercialization of fire resistant plate/beam construction steels.
- Grain refinement of Ni bearing pressure vessel steels with improved creep and fatigue performance.
- Adaptation of the automotive approach to reduce the mass of a vehicle for fuel economy and reduced emissions will be akin to the application of high strength low alloy steels to accommodate lighter cross sectional thicknesses in civil engineering designs resulting in less mass in the structure. This also results in reduced emissions and reduced energy consumption in the steel producing and welding operations.
- Reinforced concrete versus steel bridge design approach continues to be closely analyzed from a carbon footprint perspective considering the resource sustainability and emissions considerations.
- Using Nb grain refinement to create a finer grain microstructure in virtually all carbon steel grades translates into improved processability at the steel mill (i.e. reduced cobbles, reduced diverts, higher productivity).
- The concentration of Nb in structural applications must be carefully controlled at lower levels compared to the higher Nb levels currently used in automotive and pipeline steels.

Bridge Steels

The opportunity exists for the global steel industry to further develop value-added high performance bridge steel materials that will meet future construction and performance needs of the market. Because of increasing raw material, alloy and steelmaking cost, the civil engineering community demands bridge steels that result in faster and lower cost replacement for bridges in the USA and Europe, as well as for new bridge construction in Brazil, China, Russia and India. There is a major opportunity and demand for the development of even lower carbon-lean alloy bridge steels. Many current High Performance Steels of 490 and 700MPa compositions are rich alloy compositions resulting in high cost to the end user. Global research activity in some areas of the world is focused upon the development of a series of Nb-bearing LCLA bridge steels meeting the properties of HPS 50W, HPS 70W and HPS 100W.

The World Bridge Symposium assembled the civil engineering community in 2007 to present their viewpoints on current global bridge design and fabrication. [8] From a materials engineering perspective, the following list outlines requested material and fabrication demands from the civil engineering community and end users. [9] These objectives are intended for those steel producers' consideration in future bridge steel development of the next generation of bridge steels; many of which represent opportunities for Nb-bearing steels:

- Reduce weight of bridge assemblies for faster installation time.
- Civil engineering goal: two crane lifts of bridge assembly to span 6-lane highway (reducing traffic closure time).
- Improved weldability to increase productivity at fabricator and in the field erection.
- Increase use of hot forming for curved bridge beams.
- Reduce cost of High Performance Bridge steel materials.
- Fire resistive steel (rebar) for tunnel & long span bridge applications (Class II flammable truck traffic).
- Improve structural performance (i.e. deflection, expansion).

Current Status

As in Europe and the USA, China has evolved through the progression of low strength 16Mnq series (345MPa) steels which lacked grain refinement and controlled rolling to its current focus on bridge steels using high strength steels (530 and 690MPa) to sustain loads, provide seismic and corrosion resistance and improve fabrication. Currently, through the application of clean steel-low carbon Nb technology, the development of such grades as the WQ530E (14MnNbq), WNG 570 and WNQ690 has been applied in many bridges such as the construction of the Nanjing Dashengguan Yangtze River Bridge. The weathering steel grades of WNG 570 and WNQ690 are specifically designed to offer high yield strength, good toughness and excellent corrosion resistance for long span bridges. [10]

In addition to the move toward lower carbon plate steels, additional research on new types of high strength bridge steels with excellent weldability and low temperature toughness is necessary. Wuhan Iron and Steel Company has developed a series of high strength bridge steels with an ultra low carbon bainitic microstructure (WNQ570 steel and WNQ690 steel). The bainitic WNQ570 steel is successfully applied to Nanjing Dashengguan Yangtze River and the cantilever beam in an offshore drilling platform. The WNQ690 steel is successfully installed in the Floating Crane made at Shanghai Zhenhua Port Machinery Company. [10]

Some bridge steels in Europe typically contain 0.015 to 0.040% Nb. For example, Grade 460ML (EN10025) was utilized in thicknesses up to 100 mm for the construction of the Ilverich bridge near Dusseldorf airport. The special high strength pylon design was necessary due to the low flight paths with the bridge located in close proximity to the airport. Low carbon CuNiMoNb steel with a carbon equivalent CE_{IIW} of about 0.39 % was selected. The design exhibits superior toughness criterion of 27J at -80°C. [11]

The process metallurgy applied for these advanced high strength weathering bridge steels necessitate ultra low carbon acicular ferrite microstructures, strict secondary ladle metallurgy practices (i.e. less than .005%S and less than .020%P), selective scrap charge segregation to minimize residuals and incorporation of (TMCP) practices regardless of the mill configuration.

The United States bridge industry sought steels with improved weldability and higher toughness. The original development of the quench and temper (Q&T) High Performance Steel (HPS) 100W did not initially incorporate Nb. It was later changed to incorporate an addition of 0.01 to 0.03%Nb with clean steel, low carbon practices. As a result, excellent impact properties at -30°C could be realized. [12]

The progression of bridge development is similar to the development of high strength pipeline steels. This cross application of process and physical metallurgy firsts develops from a microstructure of ferrite and pearlite defined by large differences in grade composition, usually higher carbon levels and microstructure. The next development involves a bainite and ferrite microstructure in which the composition level does not vary much and carbon levels are reduced. Finally, the current plate production trend moves toward an acicular ferrite which transforms at intermediate temperatures with good uniformity of composition and microstructure. Through the progression of such process metallurgy development programs, an industrial trial may attempt to produce perhaps an X80 pipeline steel. If not successful, the material can be reapplied to a structural grade of similar dimension. In this manner, unsuccessful trials for one product may be cross applied to a prime structural plate product.

Steel vs. Reinforced Concrete Bridge Design

In any bridge design, the civil engineer makes the material decision of steel versus concrete. Ultimately, it is the overall material, labor, fabrication, welding and construction costs that drive the final decision. With the introduction of Nb-bearing high strength bridge steels, creative design can result in a lower cost bridge constructed from steel instead of pre-stressed concrete. An excellent illustration of such an application of the 460M/ML grade is evident at the Viaduct de Millau bridge in France. This bridge represents a new world record with a total height of 342m, a length of 2460m and a roadway height of 270m over the Tarn valley. Originally, the civil engineers specified a pre-stressed concrete bridge.

The new design incorporated a multiple-cable-stayed bridge consisting of a steel bridge deck and towers. The cost benefit analysis revealed a shorter construction period with steel, lighter weight (36,000mt of steel versus 120,000mt of concrete), a reduced box girder height of 4.20m, minimization of the number of inclined tension cable and less foundation work. Nearly half the structure consists of high strength fine grained S460ML structural steel in thicknesses of 10 to 120mm. [11]

Construction Steels

There is an increasing end user demand to improve the seismic, fire resistance, toughness, yield to tensile ratio consistency and/or weldability in construction steels.

A 780MPa construction steel plate grade has been developed by JFE Steel Corporation that is suitable for construction purposes. These plates exhibit microstructures of a fine M-A dispersion in the bainitic matrix. Such plates possess an excellent combination of high strength, toughness, deformability and weldability. The process metallurgy is the key technology to produce the microstructural control through on-line heat treatment immediately after accelerated cooling during the TMCP. [13]

An in-depth collaborative research study was conducted between CBMM-Reference Metals Company and a major steel beam producer in the United States. The research and development resulted in commercialization of Nb-bearing beams replacing V-bearing beams with significant toughness improvements. The ASTM992 beam (S355) study was based on industrial heats which then lead to the commercialization of low carbon Nb-bearing beam in place of a low carbon V-only bearing beam. The incorporation of Nb technology has significantly improved the beam toughness properties through grain refinement and strategic cooling practices during rolling. The Nb addition refines the grain by 2 ASTM sizes, lowers the carbon equivalent by 0.07% and improves the toughness. Near net shape cast structural beams containing only a single Nb microalloy exhibit double the impact strength at room temperature compared to a V-only microalloy system at similar sulfur, phosphorous and nitrogen levels and cooling rates as illustrated in Figure 4. [14]

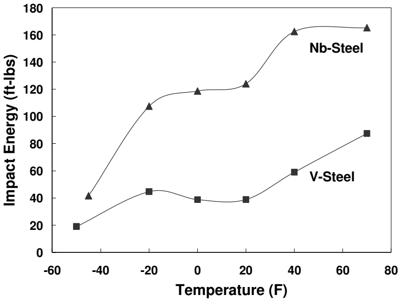

Figure 4. Charpy V-notch impact strength comparison – Nb vs. V

A second part of the study investigated a comparison of different cooling rates. Micrographic analysis revealed that the primary microstructural constituents at a low cooling rate were polygonal ferrite and pearlite. At intermediate and high cooling rates the microstructure consisted of lath-type/bainitic ferrite, and degenerated pearlite together with conventional ferrite-pearlite. With increase in cooling rate, there was an increased tendency towards formation of lath ferrite/bainitic ferrite with consequent decrease in conventional ferrite-pearlite microstructure. [15] Figure 5 illustrates the influence of Nb on the transformation to the formation of degenerated pearlite which contributes to the improved toughness. No degenerated pearlite was observed in the V-bearing steel grade.

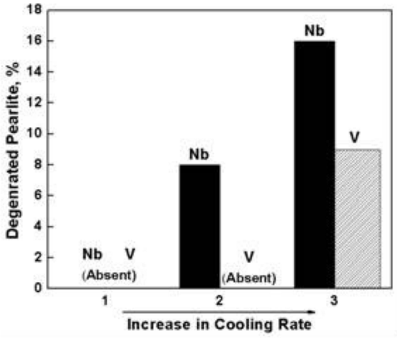

Figure 5. % degenerated pearlite of Nb- and V-microalloyed steels. [16]

Fire Resistant Plate Steels

Several papers contained herein address the current status of fire resistant (FR) plate steels. Fire resistant steels are being studied in the USA, and an ASTM specification is currently being developed. There is also a need for fire resistance in construction steels for high strength at elevated temperatures. [17] There are very limited commercially available fire resistant plates produced globally. Simultaneously, work is being performed in China at Baoshan Iron and Steel Company as a result of the increasing demand for high performance fire resistant structural steels for use in commercial building-type applications. A low Mo-Nb approach via TMCP has demonstrated acceptable high temperature strength. [18]

A huge opportunity exists for development of fire resistant beams and rebars. The goal of current research is to further develop a Nb-Mo alloy design that will retain two-thirds of its yield strength at 600°C. Figure 6 exhibits the superior elevated temperature properties of Nb-Mo plate steels compared to other ASTM A572 or ASTM A992 type construction steels.

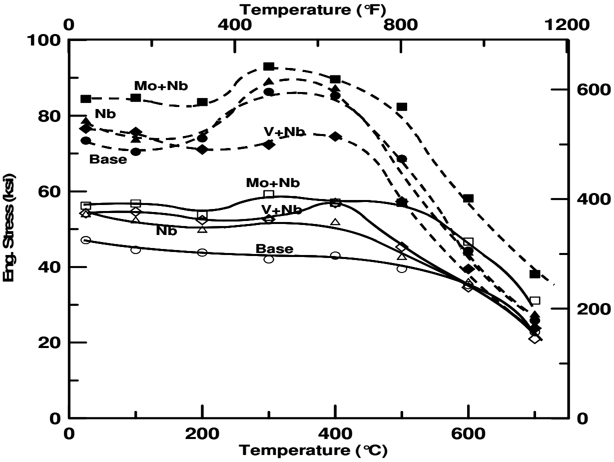

Figure 6. Elevated temperature properties [19, 20]

Research has been performed comparing the elevated temperature behavior for some experimental chemistries shown in Table 2 and elevated temperature properties shown in Figure 6. [20]

Table 2. Compositions of Experimental Fire Resistant Steels

	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	V	Nb	Al	N
Base	0.11	1.16	0.018	0.013	0.19	0.25	0.08	0.17	0.02	0.004	0.001	0.002	0.010
Nb	0.10	1.06	0.005	0.031	0.27	0.39	0.16	0.09	0.047	0.001	0.021	0.003	0.016
Mo+ Nb	0.10	0.98	0.008	0.028	0.30	0.38	0.15	0.10	0.48	-	0.017	0.004	0.010
V+Nb	0.08	1.13	0.005	0.030	0.27	0.32	0.11	0.13	0.036	0.047	0.021	0.003	-
Nippon I	0.11	1.14	0.009	0.020	0.24	-	-	-	0.52	-	0.03	-	-
Nippon II	0.10	0.64	0.009	0.050	0.10	-	-	-	0.51	-	-	-	-

Results suggest that the finish rolling at low temperatures such as 650°C can improve the elevated temperature strength of FR steel. This may be due to the presence of warm-worked ferrite generated from finish rolling at this temperature. The greater the ability to maintain strength at elevated temperature may be due to the stability of the dislocation substructure that is created during warm working of the ferrite. [21]

The constant-load test results illustrate differences between steels; with a Mo+Nb steel exhibiting better FR properties than comparative C-Mn, V, or Nb steels tested identically. [22] The good elevated temperature strength and creep properties are due to the high lattice friction stresses, which are the result of a very fine distribution of MC precipitates, Mo in solid solution, and a strong wave of secondary precipitation at approximately 650°C. It is the lattice friction stress that maintains strengths up to 600°C when grain boundary sliding initiates. [23] Nevertheless, it is observed that small additions of .017%Nb exhibit a greater elevated temperature strength offsetting the influences of significant changes in the base microstructure at these temperatures [19].

Ship Plate Steels

The shipbuilding industry is focused upon increasing productivity, reliability and quality while simultaneously improving the safety, efficiency and environmental performance at an optimal cost benefit ratio. There exists a compelling need to further improve the resistance to brittle fracture, fatigue performance and improved salt water corrosion resistance. These demands apply to a variety of ship types including oil tankers, container ships, LNG ships, bulk carriers, LPG ships, chemical tankers and automobile transport vessels. The welding of ship plate has made remarkable progress over the past few years. Welding methods have been developed which allows for the application of high heat inputs per pass on heavy thickness Nb-bearing plates so that shipbuilding productivity is more efficient.

Bainitic steels have inherently become a more popular microstructural solution characterized by high strength with high toughness and adequate weldability. Certainly, the process metallurgy practices discussed earlier involving clean steel practices, residual element restrictions, casting and thermomechanical control are of paramount importance. The clean steel and TMCP route at Dillinger is an excellent example. [24]

Value-added Nb-bearing ship plate has been successfully developed by Nippon Steel. Grade YP460MPa heavy ship plate has high toughness, excellent crack arrestability and large input weldability for hull structures of mega-container ships. [25] EH47 Nb-bearing plate and the appropriate welding technique, which have been developed for mega-container ships provide a compelling solution for three major challenges in heavy plate: 1) improved reliability of fracture toughness preventing brittle fracture and improving the ability of the base metal to arrest the brittle crack propagation, 2) improved fuel efficiency by reduced plate cross sectional area with increased size and strength of ships and 3) improved productivity in shipbuilding by welding with a large heat input. [26]

These heavy thickness steel ship plates offer an excellent balance of strength, toughness and weldability for large container ships. High strength steel plates with heavy gauges of EH36, EH40 and EH47 have been developed by POSCO through the optimization of chemical compositions and TMCP process parameters with 0.02%Nb levels in all three grades. Also, the EH36 steel plates are designed for high welding heat input rates over 550kJ/cm with the addition of TiN particles to improve HAZ toughness. [27] The strength of base plates of EH40 and EH47 significantly increased due to the synergistic effect of Nb and B, since the soluble Nb complements the effect of B on the mechanical properties. [28]

Anshan Iron and Steel Group in China has embraced the low carbon-Nb microalloying approach and optimized TMCP in the successful production of steels for shipbuilding and cross-application into offshore platforms using C levels between 0.03-0.05% in a Mn-Nb system with low alloy contents (Cr, Ni, Cu and Mo) for a family of 420MPa, 460MPa, 500MPa and 550MPa grades which provide excellent toughness down to -60°C (250J at 14mm thickness and 200J at 80mm thickness). [29] This low carbon approach allows flexibility for the steel producer to obtain a homogeneous fine grained intermediate transformation microstructure of bainite and/or acicular ferrite microstructure over a wide cooling range during the accelerated cooling of heavy gauge plate.

Pressure Vessel and Container Steels

There is a growing global pressure vessel market that demands improved performance, fabricability and cost-containment. The pressure vessel plate market is quite diverse with end market segments such as reaction vessels, heat exchanger vessels, storage containers, corrosion-resistant vessels and cylinders of multilayered clad high pressure vessels. The market for LNG and LPG pressure vessels is ever increasing with the growing global demand for natural gas and propane. Boiler plates are used in the manufacture of cylinders and shell covers for low and high pressure boilers. Within some of these product segments, specifications are some of the most stringent for any plate steel. Non-alloyed or Nb-bearing microalloyed steels with minimum 460MPa yield strength are applied in many products.

Thyssen Krupp Stahl produces high quality Nb-bearing heavy plate for several pressure vessel products. The plate thicknesses are typically between 10mm to 50mm and are characterized by: 1) high strength and toughness, 2) good cold formability, 3) high fatigue strength and 4) favorable weldability. For example, within the combination P265GH/ASTM A516 Grade 60 it is found that the minimum toughness (specified at 27J at -51°C) cannot be achieved with sufficient reliability when testing steels without Nb micro-alloying. Nb is added within the limit values in the range of up to 0.02% as specified in the standards. As a result of the grain refinement, toughness improves and the mean increase of the impact energy at -51°C is approximately 60J. [30] Micro-alloying with Nb inhibits grain growth due to the formed carbides and carbonitrides and the critical temperature for the initiation of the grain growth is shifted to higher temperatures. [31]

Pressure vessel steel production in China initiated with development of the 370MPa grade. Subsequently, improvements were made on Charpy vee-notch at -20°C, weldability and fabricability with the development of the 15MnNbR grade (570MPa) by WISCO. This grade is applied to LPG and propylene spherical pressure vessels with a maximum volume of 3000 cubic meters. [32]

Nickel-Containing Nb-Bearing Pressure Vessel Steels

The requirement of fracture toughness for pressure vessel and LPG storage tank plates is critical with respect to the crack initiation toughness of the heat-affected zone at the weld and the crack arrestability of the base plate. The combination of lowered carbon content [33] and the addition of nickel [34] improve the crack arrestability of normalized 2.5%Ni steel plate. Since the cost of nickel may be high at times and difficult to predict due to market volatility, the grain refinement developed through thermo-mechanical control with a Nb microalloy addition (0.030%Nb) can replace the more conventional normalized or quench and tempered 2.5%Ni steel plates. This chemistry adjustment will improve the crack initiation toughness of the welded joint and crack arrestability of the base plate.

The 9% Ni steel is increasingly applied in the inner tanks of the double shell for above ground storage tanks for liquefied natural gas. Low silicon 9%Ni plate steels with a small addition of Nb in thicknesses up to 50mm have been successfully applied to 200,000kiloliter LNG storage tanks. The lower Si and C content increase the toughness of the heat affected zone through a reduction in the volume fraction of the martensitic islands. Small additions of Nb from .005 to 0.030% will improve the strength of the base metal as well as the toughness of the heat-affected zone. Table 3 below lists the chemistry of the heats.

Table 3. Chemical compositions of LNG steels [35]

	C	**Si**	**Mn**	**P**	**S**	**Ni**	**Nb**
Heat A	0.05	0.25	0.60	0.003	0.001	9.0	-
Heat B	0.06	0.08-0.25	0.40	0.003	0.001	9.0	-
Heat C	0.06	0.16	0.40	0.003	0.001	9.0	0.03

This low Si-Nb type 9% Ni steel plate of 50mm thickness meets all requirements of JIS G3127 SL9N590 steel plate. The welded joints have sufficient toughness to prevent brittle fracture initiation. Further analysis of the effect of Nb on the toughness of the HAZ reveals improved HAZ properties through the addition of Nb in the range of 0.006 to 0.010%. Both of these applications incorporate the low carbon/clean steel/value-added Nb-microalloying approach. [35]

Nb-Ferritic Boiler Steel Development

Many global research and material development projects are currently in progress studying the development of alternative steels to improve boiler life and performance. Higher temperature materials are required with improved creep, fatigue and oxidation resistance at elevated temperatures. Consequently, Nb additions in ferritic boiler steels address these higher temperature performance requirements. The boiler steels used for ultra super-critical fossil power plants are ferritic and austenitic steels alloyed with Nb to produce desired results. [36] The Nb content in these steels is approximately 0.05%. The major precipitates found in ferritic steels after long term boiler service are MX, $M_{23}C_6$ laves phase and the Z phase. The $M_{23}C_6$ and laves phase are coarse and distributed along the grain boundary where the MX is finer, basically in nanometer scale, and distributed inside grains and along the grain boundaries. These fine MX nanometer precipitates are NbC, VC, Nb(CN) and V(C,N) and ensure the high and stable creep rupture strength of steel. Since Nb is a critical fundamental element associated with the important formation of the MX phase, it ensures the microstructural stability of boiler steels after long term boiler service at elevated temperature. [36]

Value-Added Long Product Steels

Microalloying and TMCP have traditionally been applied to plate rolling. However, there is an increasing application of TMCP rolling within long product bar mills producing higher carbon and engineering alloy grades. [37] The process/physical metallurgy design is dependent upon the cross sectional area, strength, toughness, weldability and formability requirements. Within the long products sector, carbon level can exceed 0.40% for such applications as rail, wear resistant bars, power transmission and/or engineering alloy steels. Within the forging industry, microalloying of these medium carbon steels is applied to obtain the desired metallurgical properties without additional heat treatment of forgings. [38] In these cases, niobium may be introduced as a grain refiner to improve both manufacturing processability and formability, thereby reducing operational cost.

High Carbon and Microalloyed Long Products

Niobium grain refinement enhances toughness and fatigue resistance in high carbon and alloy grades at concentrations as low as 0.01%. This niobium-technology has been applied to some degree in Japan and Europe. Current high carbon steel research is in progress to build upon the excellent research and development performed over two decades ago. [39]

Mechanical properties improve with the addition of Nb in rebar, structural shapes and automotive structural components, such as springs. For example, a North American vehicle front suspension coil spring of 0.51%C with Mo-V-N was developed and commercialized with improved mechanical properties compared to conventional springs. The improved properties are attributed to the grain refinement, microstructure, inclusion morphology and precipitate strengthening provided by Nb. [40] New long product development trends involve minor additions of Nb for grain refinement in carburized grades and opportunities to shorten heat treat cycles on quench and tempered products. As-forged microalloyed Nb steels may replace quench and temper alloy products, thereby reducing both energy and production costs. [41]

In some instances, Nb has not been the microalloy of choice in high carbon equivalent steels because of the lower solubility of the niobium carbonitrides in higher carbon steels. However, some of the Nb-high carbon microalloy metallurgical research over the last two decades incorporated much higher Nb levels than necessary. These higher Nb levels (exceeding 0.040%) were thought to be necessary in order to obtain proper grain refinement, microstructural control and strength in higher carbon equivalent steels. The higher Nb levels in high carbon steels certainly made the processing more challenging.

Over the last several years, a richer understanding of the Nb-high carbon technology, mechanisms, metallurgy and processing parameters has been achieved. This information is invaluable in the implementation process to successfully incorporate low levels of Nb in high carbon equivalent steels to improve fatigue, fracture toughness, ductility and overall product performance. Results from product applications reveal the fact that more is not always better. Based upon operational experience, the optimization of the Nb content and the proper control of the reheating furnace are critical. An optimum Nb concentration may be directly correlated to a given carbon level depending upon the reheat furnace process metallurgy parameters, heating practices and combustion conditions at a given mill. For example, the quality and consistency of reheating high carbon (>0.50%C) billets and slabs can be enhanced through the incorporation of combustion practices resulting in an air to gas ratio less than 1.00.

Nb High Carbon Opportunities to Improve Mechanical Properties

One of the most important effects of Nb in high carbon steel, such as wire rods and bars, is the prevention of austenite grain coarsening during heat treatments such as carburizing. The start temperature for grain coarsening increases with increasing Nb content. Figure 7 shows the relationship for a JIS SCr420 (0.2%C-1%Cr) steel.

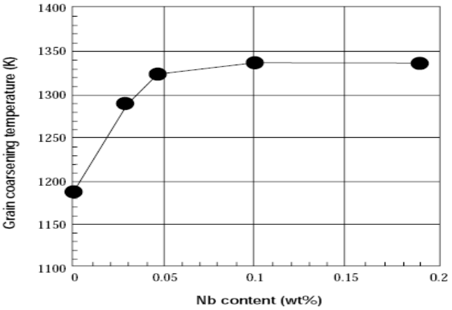

Figure 7. Nb content versus grain coarsening temperature [42]

The addition of Nb to a 1035 steel grade (0.35%C-0.3%Si-1%Mn) enhances the yield strength, tensile strength and toughness. The impact properties are markedly improved with a billet reheat temperature of 1100°C and controlled rolling practice. The process metallurgy reheat furnace control and consistency of the combustion assists greatly in achieving these excellent toughness properties. Since part of the Nb remains as a precipitate at this temperature, both grain refinement and precipitation occur and are complementary. Figure 8 illustrates this improvement in 1035 steel properties. [43]

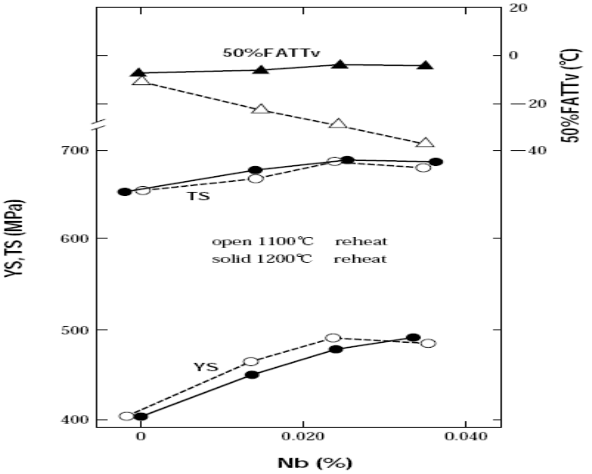

Figure 8. Effects of Nb on tensile and Charpy V notch impact properties of 1035 steel

Rail steels and pre-stressed wire rod are produced from similar high carbon compositions (approximately 0.80%C). Figure 9 below shows the effect of the pearlitic block size and reduction in area of patented 2%Cr versus 2%Cr-Nb steel wire rods. [44]

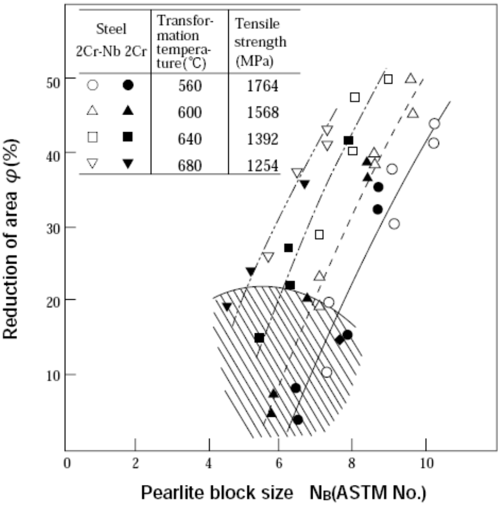

Figure 9. 2Cr-Nb vs. 2Cr wire rod reduction of area (%) comparison

The reduction in area will increase with the increase in pearlite block size number (which is a decrease in the pearlite block size). The addition of 0.02%Nb reduces the pearlite block size by reducing the austenite grain size. As a result, ductility measured in % reduction in area is improved.

The increase in demand for high speed rail systems and improved rail performance has initiated research into Nb-modified rail steels. Improved rail performance is measured by the following attributes: 1) wear resistance, 2) rolling contact fatigue resistance, 3) ductility and 4) weldability. The finer pearlitic microstructures in Nb-bearing 1080 steels result in better wear resistance than martensitic and ferrite-spheroidized cementite microstructure at similar hardness levels. Only 0.02%Nb is needed to refine the pearlitic colony size in rail steels. [45]

Reinforcing Bar for Earthquake Zone Steel Development

With the projected increased intensity and frequency of hurricanes, earthquakes and cyclones, there is a market demand to develop and then consistently produce S500 and S600 rebars with elongations of 25 to 30%. Civil engineers are requesting steelmakers to produce reinforcing bar at elongation levels approaching 30%. Microalloying with Nb and Mo offers the possibility to achieve 600MPa with elongations of 25 to 30% and an ultimate tensile strength to yield strength (UTS/YS) ratio of 1.28-1.30. [46] The S500 Nb grade with a 700°C self temper has a 1.24 tensile to yield ratio compared to a 1.18 ratio for a Nb-V chemistry. Specifications need to include a tensile to yield ratio similar to ASTM A706 in North America for seismic applications. In addition to a Nb or Nb/Mo chemistry, customized and disciplined quenching practices are of critical importance in order to successfully meet the properties of this demanding application.

The S500 and S600 rebar alloy design strategy involves: (i) lower carbon equivalent to improve weldability, (ii) improved ductility and toughness, and (iii) achievement of good yield point elongation. Niobium is added at the 0.020 to 0.035% level to effect precipitation strengthening, improve grain refinement and enhance hardenability to compensate for the strength loss due to the reduced carbon and manganese levels. Additions of Mo in the 0.05 to 0.10% range will enhance hardenability in order to meet stringent earthquake applications and improve fire resistance, achieving elongations exceeding 25% and approaching 30% consistently. Nb and Mo have a synergistic effect to achieve a ferrite and bainite core in place of the conventional ferrite and pearlite core with Tempcore. An alloying combination of Mo+Nb+Cr+Ni < 0.30%, C between 0.10-0.20% and Mn between 0.60-1.20% with specially designed coiling cooling conditions and low sulfur/low phosphorous should consistently meet S500, and with further adjustments to rolling temperature and cooling, meet S600. This is an area of continuing research. [47]

Niobium and Molybdenum have a synergistic precipitation effect creating nano-precipitates (5 to 10 nanometers in size) uniformly distributed throughout the matrix. The combination of grain refinement and nanoprecipitation are significant to achieve a finer ferrite and bainite core in place of the conventional ferrite and pearlite core with Tempcore. [46] The future seismic rebar recipe is an alloying combination of Mo+Nb, C between 0.10-0.20%, restriction of the Mn to less than 1.00%, utilization of specially designed coiling cooling practices and incorporation of low sulfur (less than .007%) and/low phosphorous levels (less than .020% if possible). Such practices will significantly improve a given mills' capability to consistently meet S500 property requirements, and with further adjustments to rolling temperature and cooling, meet S600 product requirements. As there has been limited published research on the impact and toughness properties of rebar, some fundamental process metallurgy considerations should be incorporated into the production scheme to effectively manufacture S420, S500 and S600 seismic rebars. Three key elements that require strict control to improve ductility are illustrated in Figure 10.

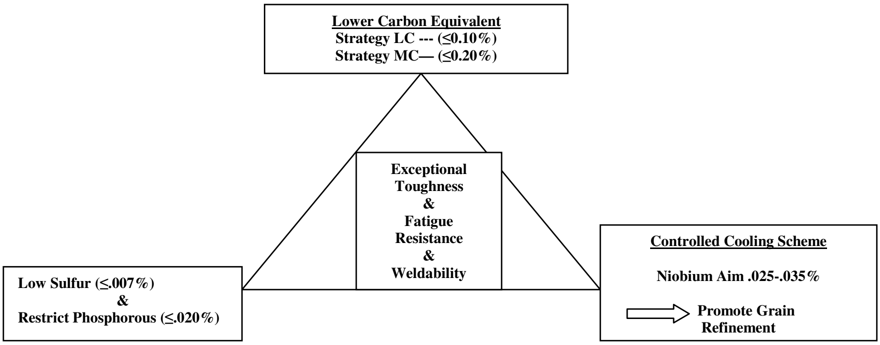

Figure 10. Ultra tough seismic rebar approach [48]

A lower total cost of production may be achieved through a low carbon-Nb alloy design incorporating the selective accelerated cooling approach in conjunction with better control of reheat furnace temperatures. For example, in comparing a Nb chemistry rebar with a V chemistry rebar, the Nb chemistry exhibits the most consistent elongation between 1100 and 1150°C which is the optimal soak zone temperature for both ductility and efficient lower cost energy consumption (i.e. mmbtu per tonne). Less yield-to-tensile strength ratio variation is experienced as well with Nb-bearing versus V-bearing rebar when rolled to these thermal practices which offers quality improvements and reduced external cost of quality [49].

It is recommended those steel producers considering development of seismic (and perhaps fire resistant) reinforcing bar apply the following factors and metallurgical parameters [48]:

A) Rebar and long product producers should consider the successful process strategies exercised today in high strength and high toughness automotive, pipeline and other critical structural applications, such as beams forging quality bars, ship plate and pressure vessels. Cross application of these grade designs and process metallurgy is extremely valuable when applied to the manufacture of high quality, high strength seismic rebar.

B) High strength and high toughness seismic rebar applications require clean steel practices controlling sulfur levels less than 0.010%, phosphorous less than .020%, control residual elemental levels and should consider either a less than 0.10%C approach or a 0.10 to 0.20%C approach.

C) Mills that adopt disciplined melting and hot rolling thermal practices will be successful in producing S500 & S600 rebar. Sulfur levels need to be below .007%S and P levels below .020% in order to participate in seismic product applications.

D) The current fire resistant Nb-containing plate research provides a valuable foundation for the development of a family of Nb-Mo chemistries which can be cross-applied to fire resistant and seismic rebar research and grade development.

E) Seismic and fire resistant grades with Nb and Mo exhibit opportunities to increase toughness and maintain 2/3 of its yield strength at 600°C. Further research and development activities are needed to cross apply into the S500 and S600 value-added rebar sector globally.

Additionally, the civil engineering and materials engineering communities need to collaborate more effectively to optimize structural design, tensile to yield ratio criterion and Nb-bearing steel rebar materials selection.

Stainless Steel Construction

The use of stainless steel reinforcing bars and associated products has increased significantly over the past several years. Stainless steel rebars extend service life of concrete structures in corrosive environments, thereby reducing the frequency of structural inspection and maintenance and rebuild. Stainless steel rebar is applied in bridges, barrier walls and decking construction to extend the life of critical areas of roadways and marine structures. Nb is added in the ferritic grades combining with the C to reduce the susceptibility to intergranular corrosion. Nb has a twofold purpose in ferritic steels: 1) grain refinement and 2) promote formation of ferrite, thereby leaving the Cr unaffected by oxidation and minimizing deleterious formation of Cr_2O_3 scale.

Environmental and Cost Considerations

The application of Nb-microalloyed structural steels offer the opportunity to reduce the total weight of a given structure, such as a bridge, compared to a non-microalloy steel construction. Generally, one considers the cost savings associated with less material and lower construction costs associated with construction which translates into significant cost savings. The intangible benefit is the reduction in emissions and energy consumption from the fact that less steel is produced.

The following study illustrates the significant reduction in emissions (pounds of CO_2) and energy consumption (mmbtu) comparing a bridge constructed from 10,000 tons of S235 steel versus a 9,000 ton S355 Nb-bearing HSLA steel bridge at 0.03%Nb. The 10% weight savings is a conservative estimate considering bridge design stiffness, specification requirements and design considerations. The results of the analysis are shown in Table 4 (CO_2 emission reduction) and Table 5 (mmbtu savings) compares steel plates and beams melted via the BOF versus the EAF route. [50]

Table 4. CO_2 Emission savings – BOF vs. EAF comparison

Factor	**BOF (pounds CO_2 per ton of steel)**	**Emission Reduction (x 10^5 pounds CO_2)**	**EAF (pounds CO_2 per ton of steel)**	**Emission Reduction (x 10^5 pounds CO_2)**
Coke savings	102	1.02	0	-
Blast Furnace	2000	20.0	0	-
BOF	490	4.9	0	-
EAF	0	-	1012	10.12
V Degas/Ladle Met	78	0.78	141	1.41
Cont Cast	39	0.39	39	0.39
Hot Rolling	376	3.76	282	2.82
Pickling	155	1.55	85	0.85
CO2 Reduced Emissions	**-**	**32.40**	**-**	**15.59**
Reduced CO_2 Emissions 1,620 tons from BOF & 779.5 from EAF				

Table 5. Energy savings – BOF vs. EAF comparison

Factor	**BOF (mmbtu per ton of steel)**	**Energy Reduction (x 10^9 btu)**	**EAF (mmbtu per ton of steel)**	**Energy Reduction (x 10^9 btu)**
Coke savings	**3.35**	**3.35**	**0**	**0**
Blast Furnace	**10.73**	**10.73**	**0**	**0**
BOF	**0.88**	**0.88**	**0**	**0**
EAF	**-**	**-**	**5.25**	**5.25**
V Degas/Ladle Met	**0.62**	**0.62**	**1.07**	**1.07**
Cont Cast	**0.29**	**0.29**	**0.29**	**0.29**
Hot Rolling	**2.30**	**2.30**	**3.53**	**3.53**
Pickling	**1.21**	**1.21**	**0.68**	**0.68**
BTU Reduced Energy Consumption (x10^9)	**-**	**19.38**	**-**	**10.82**
Reduced Energy Consumption 19,380MMBTU - BOF & 10,820MMBTU - EAF				

Metallurgical Operational Integration (MOI) ©

The process metallurgy, physical metallurgy and resultant properties are significantly determined by mill capabilities, mill practices, operational understanding and the culture of the steel mill. The optimal combination and implementation aspects that are unique to each mill we call metallurgical operational integration (MOI). MOI is the bridge that links the product requirements to mill capability and process implementation. Product research and development from the laboratory to the mill production floor requires a disciplined transfer of technology from research to the mill. Fully appreciating a given mill's melting and heating strategy by steel grade, rolling mill horsepower limitations, reheat furnace practices and resultant thermal profiles throughout the rolling operation are key. [4] Even with all that, unless the leadership of a steel mill takes initiative and remains committed, the development of newer, more challenging grades may not happen.

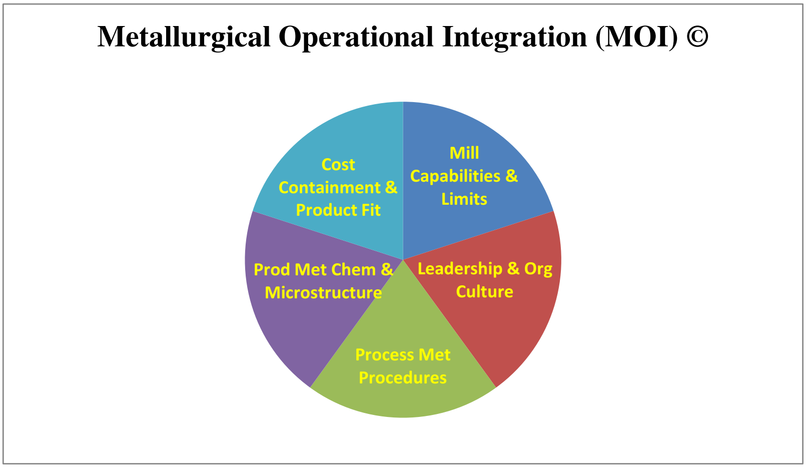

Figure 11. Metallurgical Operational Integration

Process metallurgy to use Nb specifically relates to a few critical parameters which can significantly affect product property quality and variability: 1) melting practices and controlled residual elements, 2) clean steel, 3) continuous casting quality, 4) homogeneous heating of slabs, billets and blooms, 5) consistent thermomechanical rolling practices, 6) consistent quenching to minimize property variation and 7) possible incorporation of accelerated cooling. The physical metallurgy includes: 1) microstructural control through grain refinement, 2) controlled phase transformations, 3) fine precipitate distributions, 4) minimization of carbon levels on plate grades and 5) through thickness microstructural/grain size consistency. The mechanical property attribute relates to: 1) consistent yield to tensile ratio balance, 2) toughness and low temperature performance, 3) weldability, 4) corrosion, 5) fire and seismic resistance and 6) improved manufacturability at the mill and end user. Every mill is different, and a particular new product may or may not fit as cost effectively from one mill compared to another. This makes a significant difference in margin maximization and mill productivity.

Experience indicates that laboratory simulations or models do not exactly represent actual mill melting and rolling operations. Although many times the results are close, often they are not good enough for the first trial so more than one industrial trial may be necessary to successfully execute new product development. The MOI analysis increases the probability of success. Data from trials of the process and physical metallurgy parameters previously discussed must be examined closely to correlate process parameters with resulting properties to develop Standard Operating Practices (SOP's). Since each mill is unique, there is no universal solution regarding the chemical composition, melting practice, reheat furnace soak temperature, and hot rolling regime. Carefully controlled mill trials should integrate the actual melting, casting, furnace and rolling mill operational parameters and variations of the process into the final analysis to refine standard practices to achieve desired mechanical and high-temperature properties.

Very importantly, there is a leadership and organization cultural aspect that contributes to higher success rates for new product development. These characteristics include initiative and commitment. This is another reason why some mills will be more successful than others in the development of new products.

In summary, MOI encompasses the process/physical metallurgy and specific mill culture and capabilities to achieve desired results for new product development. This integration necessitates a thorough understanding of melting, secondary metallurgy, reheat furnace combustion, hot rolling and quenching mill capabilities, along with a mill's cost drivers, culture and commitment to achieve success. A sophisticated understanding of how Nb can be used to achieve desired properties for steel in 21st century structural markets promises to yield exciting opportunities and lucrative results for steelmakers who are dedicated to doing so.

References

1. International Symposium on Niobium Microalloyed Sheet for Automotive Applications, TMS, Araxa, Minas Gerais, Brazil, December 5-8, 2005.

2. International Symposium on Microalloyed Steels for the Oil and Gas Industry, TMS, Araxa, Minas Gerais, Brazil, January 23-26, 2006.

3. S. Jansto, "Niobium Market and Technical Development for Civil Engineering Structural Applications," International Symposium of HSLA Steels for the Construction Industry, Tianjin, China October 22-23, 2007.

4. S. Jansto, "Cost Effective Microalloy Structural Steel Balance of Process Metallurgy and Materials Engineering," MS&T, Pittsburgh, PA, October 2008.

5. S. Jansto, "Cost Benefit Methodology Analysis," presented at HIPERC meeting, San Sebastian, Spain, January 17-18, 2008.

6. S. Suzuki, "Niobium in Structural Steels," see this book.

7. R. Grill, "The Role of Niobium in the Production of Heavy Plate at Voestalpine Grobblech GmbH with Special Emphasis on High Strength Steel Grades," see this book.

8. World Bridge Symposium 2007, New Orleans, Louisiana.

9. S. Jansto, "World Bridge Symposium Perspective & Relevance to Steel Industry," presented at American Iron & Steel Institute, March 26, 2008, Washington, D.C.

10. A. Guo and LunxiongYi, “Development and Application of Steels for Bridges and Buildings in China,” see this book.

11. Fluess, R. Valentin, V. Schwinn, F. Hanus “Application of Nb in TMCP structural Steel Plates with Thicknesses up to 120mm,” see this book.

12. A.D. Wilson, J.H. Gross, R.D. Stout, R.L. Asfahani, and S.J. Manganello, “Development of an Improved HPS 100W Steel for Bridge Applications,” International Symposium on Microalloyed Steels, ASM International, 2002.

13. S. Suzuki, K. Ueda “Development of Nb Bearing High Strength Steel for Buildings by Microstructural Control Through the On-Line Heating Process,” see this book.

14. D. Misra, S. Shanmugam, T. Mannering, D. Panda, and S. Jansto, “Some Process and Physical Metallurgy Aspects of Niobium Microalloyed Steels for Heavy Structural Beams,” International Conference on New Developments in Long Products, 2006, pp. 179-187.

15. D. Misra, T. Mannering, D. Panda and S. Jansto, “Physical Metallurgy of Nb-Microalloyed Steels for Heavy Structural Beams,” see this book.

16. S. Shanmugam, R.D.K. Misra, T. Mannering, D. Panda and S.G. Jansto, Materials Science and Engineering A, Vol 437**,** 2006, p436-445; and Vol 460-461**,** 2007, pp. 335-343.

17. J.G. Speer, S. Jansto, J. Cross, M. Walp, D.K. Matlock, “Elevated Temperature Properties of Niobium-Microalloyed Steels for Fire-Resistant Applications,” 2005 HSLA Conference, Sanyun, China.

18. D. Wen, Z. Li and J.Cui, “Development of Fire-Resistant Weathering Steel for Buildings in Baosteel,” see this book.

19. J.G. Speer, S. Jansto, J. Cross, M. Walp, D.K. Matlock, “Elevated Temperature Properties of Niobium-Microalloyed Steels for Fire-Resistant Applications,” 2005 HSLA Conference, Sanyun, China.

20. J. G. Speer, R. W. Regier, D. K. Matlock, and S. G. Jansto, “Elevated Temperature Properties of Nb-Microalloyed Fire Resistant Constructional Steels,” International Symposium on New Developments: Metallurgy & Applications of High Strength Steels, May 26-28, 2008, Buenos Aires Hotel, Argentina.

21. R. Regier, J. Speer, S. Jansto, A. Bailey and D. Matlock, “Thermomechanical Processing Effects on the Elevated Temperature Behavior of Niobium Bearing Fire-Resistant Steel,” Materials Science & Technology Conference, Detroit, Michigan, Sept. 16-20, 2007 {AIST 2008 Hunt-Kelly Award Paper}

22. J. Speer and S. Jansto, “Nb Microalloyed Fire Resistant Steel,” see this book.

23. W. Sha, F.S. Kelly, and Z.X. Guo, "Microstructure and Properties of Nippon Fire-Resistant Steels," Journal of Materials Engineering and Performance, Volume 8 (5), October 1999.

24. Fluess, R. Valentin, V. Schwinn, F. Hanus "Application of Nb in TMCP structural Steel Plates with Thicknesses up to 120mm," see this book.

25. A. Yoshie, "Recent Developments of Nb-Bearing Structural Steels for Ships and Infrastructure at Nippon Steel," see this book.

26. S.Sasaki et al., "Development of Two-Electrode Electro-Gas Arc Welding Process," Nippon Steel Tech. Report, 380(2004), p. 57.

27. O. Kwon, C. Lee, S. Kim and K. UM, "Niobium Thick Steel Plates for Large Container Shipbuilding," see this book.

28. Ph. Maitrepierre, J. Rofes-Vernis and D. Thivellier, Hardenability of Boron-Treated Low Carbon Low Alloy Steels, *Proc, Int. Symp. On Boron Steels*, TMS-AIME, Milwaukee, 1979, pp 1-18.

29. W. Hua and, "Microstructure and Mechanical Properties of 420-550MPa Grade Heavy Gauge Offshore Platform Steel," see this book.

30. J. Gottlieb, A. Kern, U. Schriever and G. Steinbeck, "High Performance Steels for Pressure Vessels," Thyssen Krupp Steel AG, see this book.

31. A. Kern, W. Reif: Steel Research 57 (1985), Nr. 7, pp. 321-331.

32. Q. Xu, "Present Status and Future Developments in Pressure Vessels and Steels in China," see this book.

33. O. Furukimi, Y. Nakano and S. Ueda, Proceedings of the Conference on the Transport and Storage of LPG and LNG, II, Royal Flemish Society of Engineering, Antwerpen, (1984), p.1.

34. S. Hasebe and Y. Kawaguchi, Tetsu-to-Hagane, 61 (1975), p. 101.

35. T. Kubo, A. Ohnori and O. Tanigawa, "Properties of High Toughness 9% Ni Heavy Section Steel Plate and Its Applicability to 200,000kL LNG Storage Tanks," Kawasaki Technical Report, No. 40, 1999.

36. Z.D. Liu, S.C. Cheng, G. Yang, Y. Gan, "Investigation and Application of Ferritic Boiler Steels in Ultra-Super-Critical - USC Power Plants," see this book.

37. J. Speer, D. Matlock and G. Krauss, Recent Developments in the Physical Metallurgy of Ferrous Long Products," Transactions Indian Institute of Metallurgy, Vol.59 no. 5, October 2006, p.756.

38. N. Fonstein, “Effects of Nb, V and Ti on the Evolution of Structure of Medium Carbon Steels during Various Hot Forging Steps,” see this book.

39. T. Wada, K. Fukuda and T. Taira, Tetsu-to-Hagané, 70 (1984), S511.

40. M. Head, T. King and A. Radulescu, “Development of New Microalloy Steel Grades for Lightweight Suspension Systems,” presented at AISI Great Designs in Steel Seminar, 2005, Livonia, Michigan.

41. J. Speer, D. Matlock and G. Krauss, Materials Science Forum, 500-501 2005, p.87.

42. Y. Kurebayashi: Denki Seiko, 67 (1996), 26 (D)*

43. T. Sampei, T. Abe, H. Osuzu and I. Kozasu: HSLA Steels Technology & Applications, 1984, p.1063.

44. T. Takahashi, M. Naguma and Y. Asano, Journal Japan Society of Technological Plasticity, v19, 1978, p.726.

45. Y. Tamura, M. Ueda, T. Irie, T. Ide, J. Fukukawa and M. Muraki, NKK Technical Report, No. 79, 1978, p. 335.

46. S. Jansto, “Niobium-bearing Steel Development for Weldable Structural Steel Applications,” International Roundtable on Yield to Tensile Ratio, Beijing, China, June 17-18, 2008.

47. V. Kumar, R. Datta, S. Kumar, A. Deva et al., “Development of Earthquake Resistant TMT Rebars,” Steel Scenario, Vol.15, Q3-2006, pp. 76-77.

48. S. Jansto, “Production and Application of High Strength Earthquake Resistant Nb-Bearing Reinforcement Bar,” Seminar on Niobium Bearing Structural Steels, New Delhi and Mumbai, India, March, 2010.

49. S. Jansto, “Production and Niobium Application in High Strength and Earthquake Resistant Reinforcing Bar,” International Reinforcing Bar Symposium, Beijing, China, May 18-20, 2009.

50. S. Jansto, “Bridge Sustainability Study,” CBMM internal study, December 2008.