

## **RECENT NIOBIUM DEVELOPMENTS FOR HIGH STRENGTH STEEL ENERGY APPLICATIONS**

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### **Abstract**

Niobium-containing high strength steel materials have been developed for oil and gas pipelines, offshore platforms, nuclear plants, boilers and alternative energy applications. Recent research and the commercialization of alternative energy applications such as windtower structural supports and power transmission gear components provide enhanced performance. Through the application of these Nb-bearing steels in demanding energy-related applications, the designer and end user experience improved toughness at low temperature, excellent fatigue resistance and fracture toughness and excellent weldability. These enhancements provide structural engineers the opportunity to further improve the structural design and performance. For example, through the adoption of these Nb-containing structural materials, several design-manufacturing companies are initiating new windtower designs operating at higher energy efficiency, lower cost, and improved overall material design performance.

### **Introduction**

Niobium (Nb) plays a very important role in the energy-generation sector. The application of FerroNiobium (FeNb) in carbon steels for conventional oil and gas pipelines as well as materials of construction for alternative energy generation sources such as windtowers and solar farms. Another most important sector involves NickelNiobium (NiNb) which is a key alloy addition for the production of several Inconel® superalloy applications for power generation. For example, Inconel 718, 740 and 740+ is a vital material applied to the hot section of land based turbines and aircraft engines. The value-added attribute is an improvement in both the tensile and creep resistance properties at elevated temperature.

The focus of this paper is the application FeNb in steels for energy related steel applications, such as boilers, structural steels for windtowers and power transmission components for windtowers. The evolution of Nb in carbon, ferritic and austenitic steels is leading to the development of Nb in boiler tubing. The end user continues to demand higher service temperatures, improved high temperature corrosion resistance and improved creep and fatigue performance. Within the windtower sector, the end user demands further improvements in power generation efficiency. This demand has created two material challenges which are being met in two ways: 1) construction of towers to higher elevation with Nb-bearing high strength steels that offer improved fatigue and fracture toughness concerns due to the higher

jetstream velocities and 2) improved fatigue life and reduced coefficient of friction of gearbox component materials. Also, the threat of alternative materials to substitute for steel was recently encountered, such as carbon fiber composites for the structural supports for better fatigue and fracture toughness performance compared to conventional S355 and S420 structural steels. The solution in this case is a better steel and not an alternative substitute material. The Nb-Low Carbon Low Alloy (Nb-LCLA) as rolled product was further developed and has become a viable, cost effective solution. Within the power generation sector, the application of Nb-bearing ferritic boiler steels in Ultra Super Critical (USC) power plants play a significant role in improved performance and operating efficiency.

### **Wind Tower Design Trends**

This decade will see a further increase in the height of wind towers presenting new materials and civil engineering challenges. In the past 15 years of wind energy growth, the current trends of the industry have continued to increase elevations to 80, 90 and now over 100 meter towers being introduced in Europe and North America. Turbines have increased in size to 2.0MW, 2.5MW, 3.0MW and increasing to 4.5MW. The dead load of these higher elevation structures are surpassing 2600kN (600kips). Consequently, structural dynamics, frequency response, fatigue and fracture toughness properties of materials and soil-structure interactions become increasingly important. These industry demands are high priority for the designers and fabricators. Many of these countries embrace wind energy as a sustainable, cost effective and environmentally-friendly green solution.

Windtower designs will transcend beyond the traditional pole-tube design into special shapes with improved materials, for both S355 and S420. In some cases higher strength steels that will better accommodate these higher dynamic stresses, complex loading and vibrational fatigue conditions experienced during the operation of these higher structures.

The cost-benefit considerations are higher structures that translate into higher efficiency, lower cost per MW generated and stronger structural tower capacity. Considering these increased structural steel demands, fatigue and fracture toughness structural steels were examined. CBMM, SSAB and Illinois Institute of technology decided to collaborate on a joint research fatigue and fracture toughness study comparing normalized versus as-rolled industrially-produced Grades S355 plate steels for windtower construction in the USA. [1] There has been very little published on the fatigue and fracture toughness properties of such structural steels. The data is new based upon 21<sup>st</sup> century steelmaking and hot rolling practices for very common structural steel types.

### **Future Windtower Material and Design Performance Trends**

Windtowers are approaching 20-year service life or nearly 20 million fatigue cycles. Post-service evaluation of the materials' performance provides valuable metallographic and fractographic information about the historical material performance of these higher carbon structural steel windtowers constructed several decades ago. Today, designers are demanding steel producers and fabricators to improve structural performance requiring materials, maintenance and design for the following reasons: 1) Turbines are shutdown if wind speed exceeds 80 km/hr.; 2) Improve vibrational rotational stiffness; 3) Fatigue failures at weld and base metal; 4) Residual stresses induced by internal welds; 5) Base foundation cracking from fatigue; 6) Corrosion of foundation bolts from aggressive corrosive soils; 7) Seismic and

earthquake loading will be incorporated in design specifications; 8) Windtower structural failures in weld and base plates in older towers and 9) Gearbox component fatigue life

Some of these concerns are maintenance-related and are defined as a condition in which the tower-foundation system is not performing to its stated specifications. This situation may result in turbine performance degradation. If this condition persists, a shut-down process leads to lost revenues and increased maintenance costs which are a long term problem. The S355 structural steel fatigue and fracture generated within this study conducted by CBMM-SSAB-IIT, sets a template for future work in higher strength steels, such as S420 and S460. An accelerated application of the Nb-Low C-Nb approach for windtowers is expected universally because of improved fatigue and fracture toughness properties. Opportunities to improve windtower design also apply to the structure, foundation using the Nb-LCLA Approach and the MicroNiobium Alloy Approach for gearbox components.

### Improved Quality of Current Windtower Structural Plate

EN and ASTM specifications allow windtower plate producers to design a very wide chemistry range of carbon and manganese levels in the final product. Internal CBMM estimates are that over 75% of the global windtower structural steel supports exceed 0.15%C, and in developing countries, they may be approaching the allowable specification maximum carbon levels of 0.22%. There are a variety of reasons for this practice 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. [2] Some mills have not properly adapted their heating and rolling operation (i.e. finishing temperatures) 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, fatigue resistance, fracture toughness, weldability and quality. Another reason for the higher carbon S355 chemistries involves the normalizing heat treatment requirement in some windtower specifications. Typically a 0.15% to 0.18%C steel is applied due to the loss of strength during the normalizing heat treatment.

### **EN 10025-2 Grade S355 versus ASTM A572/A709 Grade 50 Comparison [1]**

A large segment of the global windtower plate production is specified to the EN 10025-2 Grade S355 or the ASTM A572/A709 Grade 50 Specification. Plates ordered to EN 10025-2 Grade S355 with low-temperature CVN requirements often specify a requirement for “normalized rolling” (e.g. +N delivery condition). Structural steel plates produced in the normalized rolling condition will require control of the hot rolling process such that the final deformation is accomplished over a temperature range which is intended to produce a microstructure and properties equivalent to that obtained from a normalizing heat treatment. Furthermore, steel plates supplied in the normalized rolling condition are, by definition, required to maintain the specified mechanical properties following a normalizing heat treatment. As such, peritectic higher carbon steels are applied to compensate for this loss in strength subsequent to heat treatment.

The ASTM specification does not have this normalized heat treatment conditional. Thus, when the end user specifies the ASTM A572/A709 Grade 50 specification, the Nb-LCLA (less

than 0.10%C) is applied. An evaluation was made of a typical low-carbon A572/A709 Grade 50 to comply with the normalized rolling definition of EN 10025-2 as part of the collaborative research project. Table I below illustrates the chemical composition of three steels and rolling practices and Figure 1 presents the mechanical property comparison for these industrial trials. [1]

Table I. Chemical Compositions of Nb-LCLA vs. Higher Carbon

Steel	C	Mn	P	S	Si	Cu	Ni+Cr+Mo	Nb	CE <sup>1</sup>
Low C – Nb	0.06	1.27	0.011	0.001	0.34	0.27	0.41	0.031	0.35
Med C – Nb	0.15	1.39	0.012	0.003	0.22	0.20	0.32	0.019	0.43
Med C – Nb Norm	0.15	1.32	0.011	0.003	0.21	0.22	0.23	0.014	0.42
ASTM A572-50 & A709-50 (max)	0.23	1.35	0.04	0.05	0.40	-	-	-	-
EN 10025-2 S355K2 (max)	0.23	1.70	0.035	0.035	0.60	0.60	-	-	0.45

<sup>1</sup>CE = C+Mn/6+(Cr+Mo+V)/5+(Ni+Cu)/15

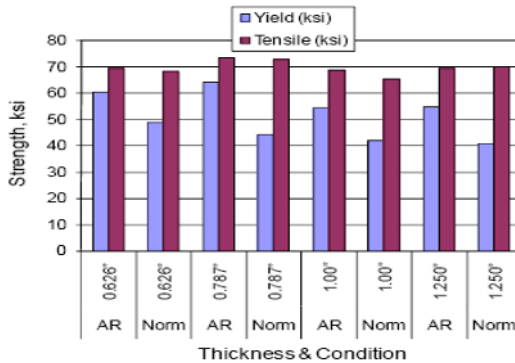


Figure 1. As-rolled low C-Nb versus normalize heat treatment comparison. [1]

The as-hot rolled Nb-bearing low-carbon HSLA steel, (with no normalize heat treatment) achieve their excellent balance of strength and toughness principally via ferrite grain refinement and a reduced carbon level. In comparison, the higher carbon process did not have sufficient capability to retain the specified tensile properties after normalizing. Based on these results and other similar studies, it was determined that in order to comply with the EN 10025-2 normalized rolling definition, a medium-carbon steel must be employed to ensure that the specified minimum as-rolled mechanical properties are retained after normalizing. The fatigue and fracture toughness performance of higher carbon normalized rolled and/or normalize-heat treated plate steels deteriorates (as shown in the next section) compared to as-rolled low carbon Nb-bearing LCLA windtower plates. As a result of the normalizing heat treatment option, higher carbon and manganese levels are necessary due to the softening effect during heat treatment. Another drawback of the higher carbon peritectic grade is increased steelmaking cost compared the Low C-Nb approach. Castability and slab surface quality is significantly improved for the Nb-LCLA composition based upon application of this approach in other structural products such

as beams and bridge steels. Improved castability is measured through increased casting speed and lower rejects for defects since the higher carbon peritectic issues are eliminated and replaced with the Nb-LCLA.

### Fatigue and Fracture Toughness Implications of As Rolled vs. Normalized

As previously introduced, this work was initiated due to the threat of substitute carbon composite materials. The outstanding improvement through improved fatigue and fracture toughness properties of the as-rolled Low C-Nb compared to the normalized rolled Medium C-Nb and Medium C-Nb heat treated are remarkable on these industrially produced heats. Table II compares the Low C to the Medium C industrial heats.

Table II. Mechanical Property Comparison [1]

Steel	YS (ksi)	UTS (ksi)	-60°F TCVN (ft-lbs)	Upper Shelf TCVN (ft-lbs)	Fracture Toughness, $K_{IC}$ (ksi $\sqrt{in}$ )	Fatigue Endurance Limit, $S_e$ (ksi)
Low C – Nb	65	76	270	280	375	44
Medium C – Nb	64	82	30	120	235	39
Medium C – Nb Normalized	57	77	80	160	250	35

There are several implications as it relates to future windtower designs involving specifications, the selected carbon level and steelmaking/rolling practices. Therefore, considering future civil engineering challenges and design trends of higher elevation windtower designs, several specification and chemistry issues need to be addressed. For example, based on these results, the implications of specifying the EN 10025 normalized rolling delivery condition are clear. The steel chemical composition constraints imposed by the EN 10025 normalized rolling requirement result in wind turbine tower plates with reduced weldability, toughness measured as Charpy Vee-Notch and  $K_{IC}$ . The second implication involves the positive benefit of a lower cost of steelmaking and welding process for the low C compared to the medium 0.15%C steel. The application of this Nb-LCLA high quality structural windtower steel has significant implications based upon the material and design performance considerations for future windtower construction.

### MicroNiobium Approach for Windtower Gearbox

With the evolution of the MicroNiobium Alloy Approach<sup>®</sup> in higher carbon steels and engineering alloy steels, the opportunity exists for its application in the gearbox of the windtowers. Another technology is the MicroNiobium Alloy Approach [3] which has been more widely applied in other power transmission components, but is now making entry into windtower gearbox components. This long product development trend involves micro additions of Nb for grain refinement for improved fatigue and fracture toughness resistance, even in carburized grades. As-forged microalloyed Nb steels may replace quench and temper alloy products, thereby reducing both energy and production costs for power transmission and gearbox applications. [4]

## Nb-Bearing Ferritic Boiler Steels in Ultra Super Critical (USC) Power Plants

The importance of improvement in plant boiler steel performance, efficiency and steam production parameters through materials engineering and design changes and enhancements directly influence the worldwide energy consumption, carbon footprint and volume of emissions. Niobium is mechanically enhancing boiler steel performance. Developmental research projects have been performed, and continue to be studied, involving improvements in ferritic boiler steel materials performance in China, Europe, Japan, Korea and the USA. Work relates to the chemistry design and optimization of these steels, the effect of heat treatment on properties, experimental simulation of hot deformation processes and creep rupture testing to determine the creep rupture strength. Although Nb has been more universally applied to ferritic steels, it has begun to show some potential in selected austenitic boiler tube steels.

### Evolution of Ferritic Boiler Steels

Compared to austenitic boiler steels, ferritic boiler steels are of better heat transfer efficiency, lower thermal expansion, higher cost savings and better weldability. In the past sixty years, the application temperature of ferritic boiler steel grades available are SAVE12, NF12, 9Cr-3W-3Co(NIMS) and 15Cr-6W-3Co as well as maraging steels, used for 650°C steam temperature. Table III illustrates this evolution of materials over the past 60 years

Table III. Evolution of Typical 9-12% Cr Ferritic Boiler Steels.

Generation	Year	Major alloying elements	Typical steel grades	Highest Temp °C
1 <sup>st</sup>	1960-70	Adding Mo or Nb, V	EM12, HCM9M, HT9, F9, HT91	565
2 <sup>nd</sup>	1970-85	Optimizing C, Nb and V	T91, HCM12, HCM2S	593
3 <sup>rd</sup>	1985-95	Replacing Mo with W	HCM12A(T/P122), NF616 (T/P92) , E911(T/P911)	620
4 <sup>th</sup>	1995-	Optimizing C, N, increasing W and adding Co	NF12, SAVE12, 9Cr-3W-3Co	650

The mechanism of multi-element strengthening was successfully applied in this low alloy boiler steel, which opens an opportunity to develop higher creep rupture strength ferritic boiler steels.

### Chemistry Design and Optimization of Ferritic Boiler Steels

Boiler steels operate in an environment of elevated temperature, high pressure and corrosion. Two of the most important metallurgical properties of boiler steels are creep rupture strength and corrosion-resistance. Thus, the chemistry design and optimization of boiler steel chemistries is critical in order to achieve these requirements. Long time creep rupture testing data is imperative not only for creep rupture strength, but for corrosion-resistance. Fundamental materials design research for the chemistry design and optimization of boiler steels is performed with the goal of accumulating data and analyzing experiences. Table IV shows the typical chemical compositions of major ferritic boiler steels.

Table IV. Chemical Compositons of Typical 9-12%Cr Ferritic Boiler Steels (wt%)

Steel grade	C	Si	Mn	Cr	Ni	Mo	W	Nb	V	N	B	Cu	Co	Fe
G102	0.08-0.15	0.45-0.75	0.45-0.65	1.6-2.1	-	0.5-0.65	0.3-0.55	-	0.18-0.28		<0.008	-	-	Ti: 0.08-0.18
T/P91	0.08-0.12	0.20-0.50	0.30-0.60	8.0-9.5	≤0.40	0.85-1.50	-	0.06-0.10	0.18-0.25	0.03-0.07	-	-	-	Bal
T/P92	0.07	≤0.50	0.30-0.60	8.5-9.0	≤0.40	0.30-0.60	1.50-2.00	0.04-0.09	0.15-0.25	0.03-0.07	0.001-0.006	-	-	Bal
T/P122	0.07-0.14	≤0.50	≤0.70	10.0-12.5	≤0.50	0.25-0.60	1.50-2.50	0.04-0.10	0.15-0.30	0.04-0.10	0.0005-0.005	0.30-1.70	-	Bal
T/P911	0.09-0.13	0.10-0.50	0.30-0.60	8.5-9.5	≤0.40	0.90-1.10	0.90-1.10	0.06-0.10	0.18-0.25	0.05-0.09	-	-	-	Bal
NF12	0.08	0.2	0.5	11	-	0.2	2.6	0.07	0.2	0.05	0.004	-	2.5	Bal
SAVE12	0.10	0.3	0.2	11	-	-	3.0	0.07	0.2	0.04	0.07Ta 0.04Nd	-	3.0	Bal
<sup>9</sup> Cr-3W-3Co	0.08	0.3	0.5	9.0	-	-	3.0	0.05	0.19	0.004	0.014	-	3.0	Bal

W-Mo solid solution strengthening and V-Ti precipitation hardening were used for the G102 steel designed in the 1960s. Boron was added to further increase creep rupture strength. As a result of the low content of alloying elements of G102 steel, its highest application temperature is about 600°C. The G102 steel development was of significant importance as it laid the foundation for the successful development of T/P91. The successful development of T/P91 steel in 1978 then significantly influenced the chemistries for future ferritic boiler steels. Since then, several unique steel grades have been developed with optimization of alloying elements such as Nb in the range of 0.06-0.10%Nb. The creep rupture strengths of these current ferritic boiler grade steels are enhanced as illustrated below in Figure 2.

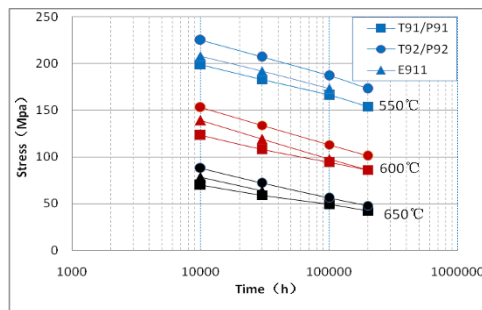


Figure 2. Creep rupture strength of typical ferritic boiler steels

These new grades further increase creep rupture strength and improve the high temperature corrosion resistance. Carbon content of these steels is 0.10% or less to ensure lower carbon equivalent. Higher chrome content enhances corrosion-resistance. However, it also increases

chrome equivalent at the same time. The higher chrome equivalent may lead to the occurrence of  $\delta$ -ferrite, resulting in the decrease of the creep rupture strength.

### Effect of Niobium in the Boiler Steels

The boiler steels used for ultra super-critical fossil power plants can be mainly divided into two categories: ferritic and austenitic boiler steels. The niobium element is one of the major alloying elements in both classes of boiler steels. The niobium content in the steels is basically controlled to be about 0.05% and the vanadium content is generally added in about 0.20%. The V to Nb stoichiometric ratio is closely controlled at 4:1. The major precipitates found in ferritic boiler steels after long term service are MX,  $M_{23}C_6$  laves phase and the Z phase. In general,  $M_{23}C_6$  and laves phase are coarse and distributed along the grain boundaries. MX is finer, basically in nanometer scale, and distributed inside grains and along the grain boundaries. Experimental investigation showed that nanometer fine MX precipitates existed in typical ferritic boiler steels, such as NbC, VC, Nb(CN), and V(CN). [5] The wing-shaped MX precipitates in T91 enhances creep rupture strength greatly. In addition, the precipitates contribute to very good stability which ensures both high and stable creep rupture strength of the steel. During actual boiler operation, it is critical to maintain stability of the microstructure and also control the growth of precipitates. The niobium element is one of most important chemical elements to ensure microstructure stability of boiler steels after long term service (see Figure 3).

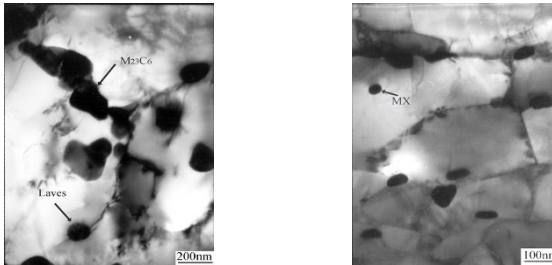


Figure 3. Morphologies of precipitates of T122 after long-term aging. [5]

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