THE ROLE OF NIOBIUM AS AN ALLOYING ELEMENT IN HIGH-STRENGTH STEELS FOR OIL COUNTRY TUBULAR GOODS

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Abstract

The information found in this report is the result of a review of the literature and meetings with representatives of oil companies, steel producers, OCTG distributors, ferro-alloy producers and equipment manufacturers. The NACE publication, "H_2S Corrosion - A Compilation of Classic Papers", is an excellent general reference. A bibliography is not included; the references are cited only where information is presented in the text. This review deals with the present use of Niobium-bearing steels in the drilling and production of oil and gas. It also treats potential usage of such materials and suggests areas for research and development. Excluded from this paper is any significant treatment of the transmission of petroleum products through pipelines or other means. It assumes a basic understanding of the metallurgy of the alloy systems that are described and deals as much as possible with the unique role and benefits of niobium. Moreover, the technology of drilling and production are not discussed beyond the limited extent necessary to identify the need for the alloys used.

The uniquely beneficial effect of microstructural refinement as a result of very small additions is the key to the use of niobium for OCTG. The production of a finer-grained austenite whether during hot working or heat treatment is probably the most important attribute. Moreover, a finer carbide distribution is produced in both as - worked and heat treated steels. Also, the addition of niobium permits the use of higher tempering temperatures for quenched and tempered steels resulting in a more well-developed, cracking-resistant, ferritic matrix. Improved toughness, resistance to hydrogen assisted cracking, and resistance to cracking in various corrosive environments generally result. The need for superior quenched and tempered steels to access petroleum products in sour gas environments is the most important opportunity for increased usage of niobium in oil country tubular goods. Rendering normalized steels suitable vs. quenched and tempered steels is another opportunity in view of the desire to maximize heat treating capacity in many cases. Direct quenching off the seamless mill presents demands on the steel that can be met in part by the addition of niobium. This practice has benefits in energy conservation and is expected to increase in the future.

In general, niobium has not been used in either regular or heat treated seamless OCTG. This is changing, however. The relentless consumption of petroleum products and the increased cost of oil and gas from traditional sources have resulted in activity in previously non-economical strata, notably deep "sour" wells containing highly corrosive hydrogen sulfide (H_2S). Drilling and production have traditionally made extensive use of the AISI 4IXX (Cr + Mo) series of steels in the heat treated condition. These deep, sour wells require stronger steels with superior corrosion resistance versus the traditional alloys. The most desireable microstructures are generally agreed upon to be quenched and tempered with a fine prior austenite grain size, uniformly dispersed M_3C particles, and highly ductile, well-tempered ferrite grains forming the martensitic matrix.

Niobium is almost uniquely beneficial in achieving the desired microstructural modifications by small additions, i.e. .02/.05 percent. Figure 1 (1) shows the significant effect of niobium on austenite grain size. Figure 2 (1) shows that for a given strength level the carbides in the niobium-modified steel are distributed more uniformly particularly with respect to precipitation at grain boundaries. Figure 3 (1) shows the carbide structure also, but more importantly shows a lesser number of dislocations and distortion to be characteristic of the matrix of the niobium-modified steel. The above microstructural features are enhanced by high tempering temperatures and niobium does increase the tempering resistance but not to the same extent as vanadium - see Figure 4 (2). However, niobium is generally considered to be preferable to vanadium because the secondary hardening characteristic of the latter requires excessively long and/or high temperature tempering unless very-high-strength levels are required, i.e. greater than 120 KSI (827 MPa). This is significant because the present consensus is that a yield strength of 100 KSI (689 MPa) is the upper limit for safe application of high-strength steels for most sour gas applications.

At a given strength level, however, quenched and tempered steels containing niobium, vanadium or niobium + vanadium have essentially the same stress corrosion resistance see Figure 5 (2) which is substantially improved over the standard grade - Figure 6 (3). The above discussion of the beneficial effect of niobium on hydrogen stress cracking resistance is consistent with the observations of Craig and Krauss *(4)*. They explain the beneficial effect of increased molybdenum over standard AISI 4130 in terms of finer carbides at a given strength level resulting in increased carbide/ferrite interface area per unit volume of carbide which increases the time required to accumulate

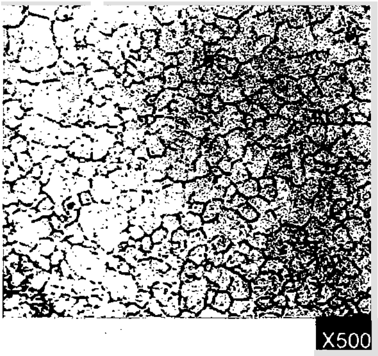


Figure 1(a). Mo-Nb-Modified AISI 4130 Steel. ASTM G.S. No. 9.5.

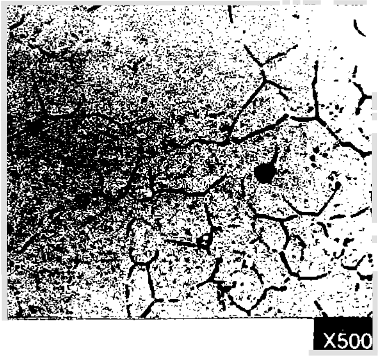


Figure 1(b). Standard AISI 4130 Steel. ASTM G.S. No. 5.5.

Figure 1. Steels Etched to Reveal Prior Austenite Grain Boundaries (1).

sufficient hydrogen to cause cracking. Therefore, since niobium further restricts the size of the carbides for a given tempering treatment, it follows that it should have a similarly beneficial effect.

At the present time, there are only two products, special L-80 and C-90, currently available from the North American steel producers (primarily Republic Steel and Algoma Steel) made especially for sour gas environments. None of these steels contain niobium. However, the Japanese steel industry presently uses niobium in high performance OCTG. Therefore, it is instructive to examine Table I which gives Sumitomo's and Kawasaki's C-90 compositions. Both producers are seen to have utilized lower carbon content and higher alloy content than the more standard AISI 4130 in combination with microalloying by niobium-addition and (apparently) boron treatment. All of the above are consistent with the development of the best sulfide cracking resistance according to current understanding of the role of microstructure for quenched and tempered steels.

The use of inhibitors has permitted the successful application of low-alloy steels in sour gas environments up to certain limits of temperature (~200°C or ~ 392°F), atmosphere (CO_2 + H_2S constitute a very bad combination), and depth (~ 6000m or ~ 19,500 ft.). The combination of natural pas with CO_2 and H_2S at the high temperatures and pressures characteristic of these very deep wells is a particularly demanding situation. Therefore, refer to Table II for Sumitomo's special CO_2 resistant L-80 containing 9 percent chromium plus niobium. Once again, structural refinement by niobium-addition is important in this grade with enhanced corrosion resistance.

Other Japanese producers also have special corrosion resistant grades currently available. For example, NKK has AC-80, AC-85, AC-95, AC-85S, AC-90S and AC-95S. The upper limit of yield strength currently available for corrosion resistant applications is 95,000 psi (655 MPa). The consensus is that OD/ID quenching is a necessity to achieve the degree of uniformity required in these products. Most U.S. producers currently do not have this capability but several have recently let contracts to purchase the necessary equipment and technology. Furthermore, the opinion is expressed by most that

M_3C Carbides in the Mo-Cb-Modified AISI 4130 Steel

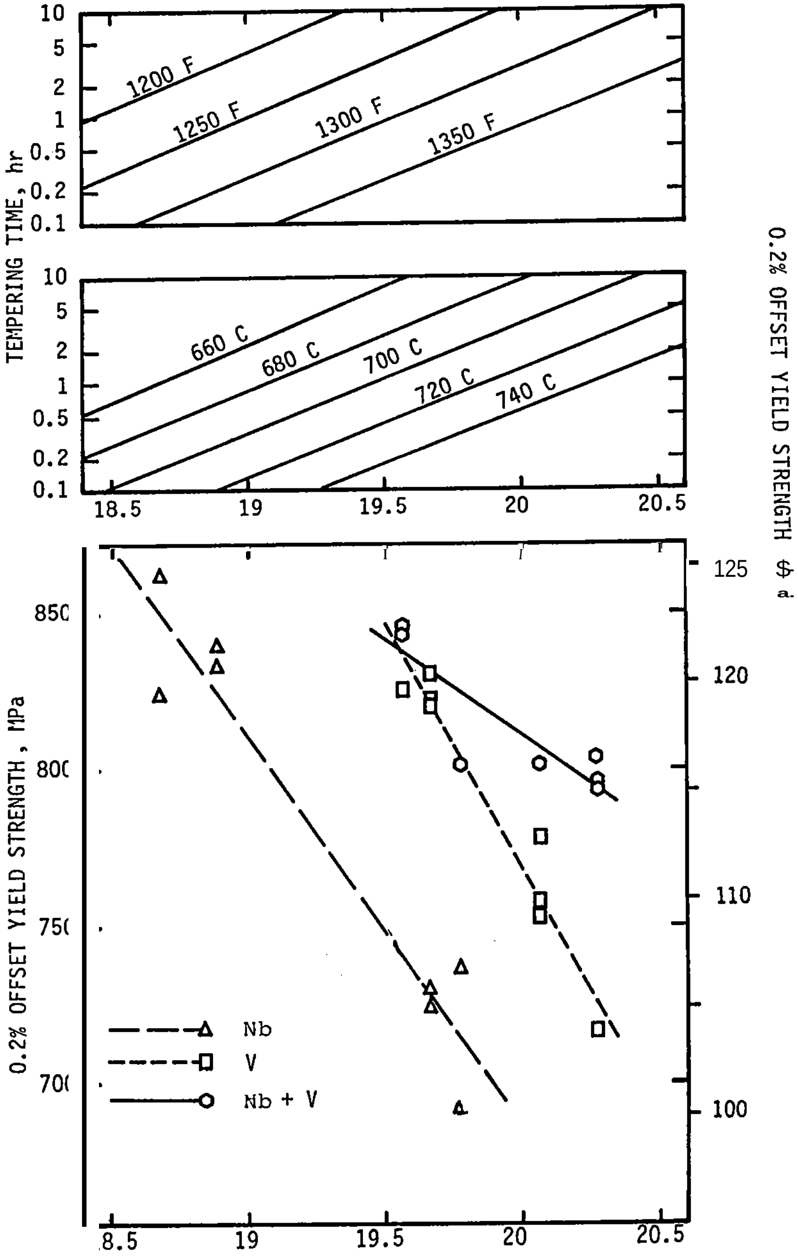
M_3C Carbides in the Standard AISI 4130 Steel

Figure 2. Extraction Replicas, Original Magnification 15,000 x, Reduced 80% in Reproduction.

Internal Structure of the Mo-Cb-Modified AISI 4130 Steel

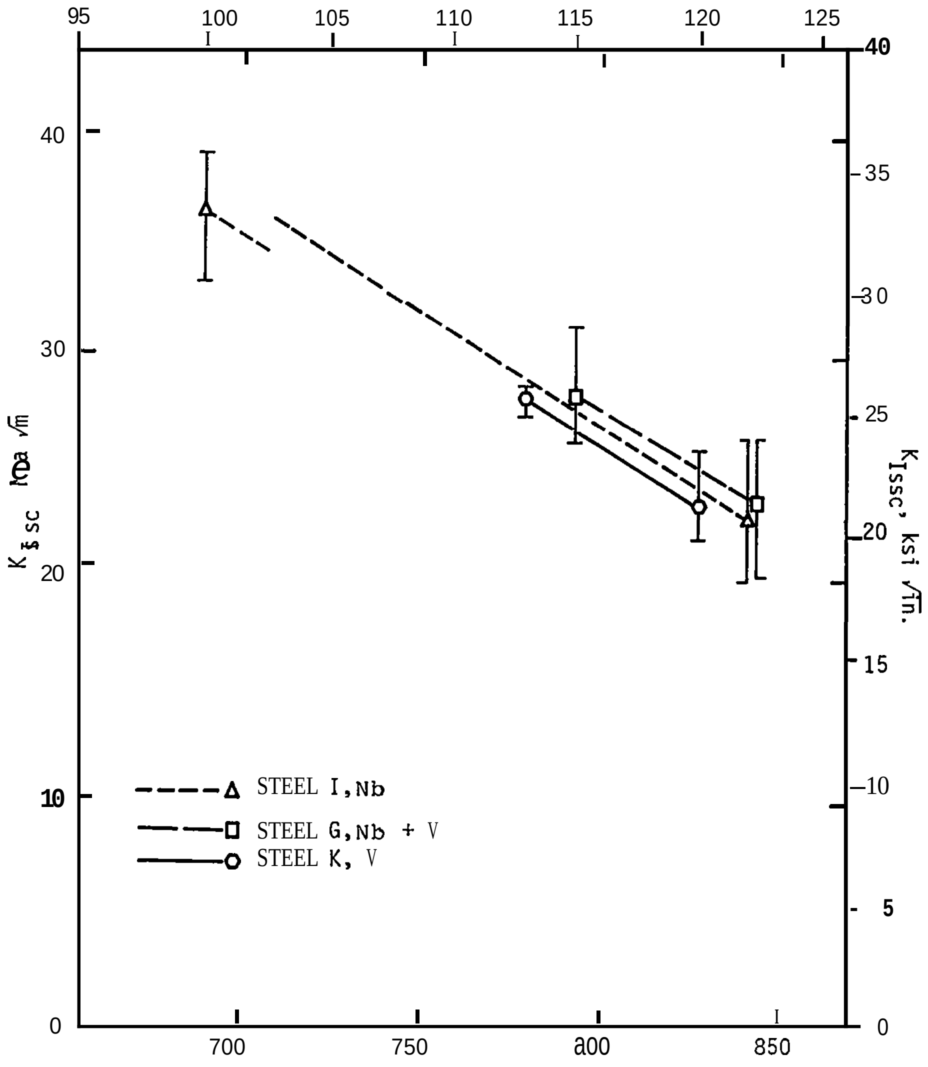
Internal Structure of the Standard AISI 4130 Steel

Figure 3. Transmission Electron Photomicrographs, Original Magnification 75,000 x, Reduced 80% in Reproduction.



$P_T = T(20 + \log t) \times 10^{-3}$

Figure 4. Effect of Tempering Parameter P_T on the Yield Strength of Heat Treated Steels. Base Composition: .3% C, .25% Mn, 1.5% Cr (2).


95
100
105
110
115
120
125
40
35
30
25
20
15
10
5
0
40
30
20
10
0
700
750
850
STEEL I,Nb
STEEL G,Nb + V
STEEL K, V

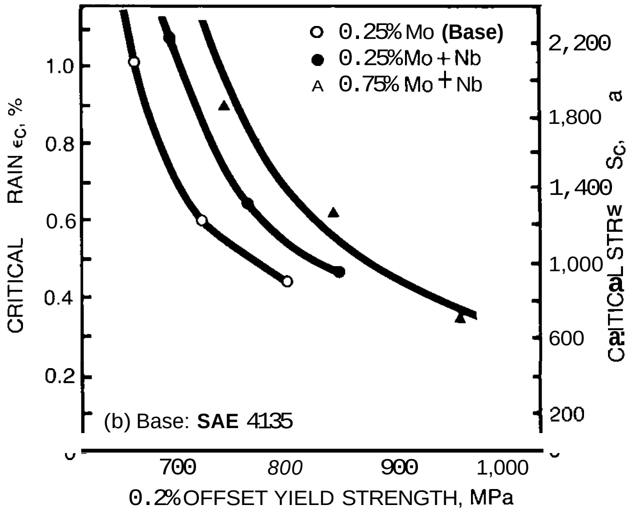


Figure 6. Optimum Combination for Sour Gas Applications: AISI 4135 Modified by the Addition of 0.75% Mo+Nb (3).

a C-100 grade will become available within the next several years and that it will probably contain niobium. For example, Climax Molybdenum Corp. has promoted AISI 4130 plus .75 molybdenum percent and .035 percent niobium as an alloy suitable for C-100 applications (3, 5, 6). Large amounts of data based upon laboratory heats have been very encouraging, but results from commercial scale heats have been erratic. The effects of impurities may be critical. In any event, at the present time 100,000 psi (689 Mpa) is felt to be the practical limit for high-strength steels in corrosive environments. Inert (nickel base) alloys will be necessary for the more demanding applications. However, improved toughness via niobium is an important consideration for higher strength (> 100 KSI) quenched and tempered OCTG used in less corrosive applications, and other heat treated OCTG - see for example, Table III (3).

As a means of energy conservation as well as production efficiency, Japanese steelmakers have pioneered continuous processing with the present achievement of direct quenching off the seamless mill and with the goal of never letting the steel get cold from casting through heat treating. This development began with in-line pipe quenching (7, 8). With this scheme, certain alloy modifications are required. In order to minimize susceptibility to hydrogen cracking (flaking) and quench cracking, the carbon-content is lowered to about .20 percent, boron is added to compensate for hardenability lost due to the lowered carbon, and niobium at about the .02 percent level can be added for grain refinement both of the wrought structure and that resultant in the product after heat treatment. The benefits of niobium for

Table I. Typical Chemical Composition of Sumitomo's C-90: SM90SS and Kawasaki's KO-90SS

	% C	% Mn	% Si	% P	% S	% Cr
SM 90SS	0.26	0.53	0.30	.010	.004	1.00
KO-90SS	.15/.35	1.00	0.35	0.30	.015	.80/1.60

	% Mo	% Ti	% Sol. Al	% B	% Nb
SM 90SS	0.49	009*	.072*	-	0.03
KO-90SS	.15/1.10	-	-	0.004	0.05

* Levels of these elements suggest this steel may also have been treated with B.

Table II. Typical Chemical Compositions of Sumitomo's 9% Cr, L-80 for CO_2 Resistance.

% C	% Mn	% Si	% P	% S	% Cr
.041	0.41	0.38	0.011	0.006	9.49

% Sol. Al	% Nb
.042	0.42

Table III. Suggested Steels and Conditions of Heat Treatment for Applications with Various Yield Strength Requirements (3).

Applications	Steel Type	Heat Treatment	MPa
Sucker Rods, Upset Casing, Tubing	AISI 4130/ SAE 4135 modified with up to 0.75% Mo + 0.03% Nb	Normalized and Tempered	725
Casing, Tubing Drill Pipe	AISI 4120/4130 modified with up to 0.75% Mo + 0.03% Nb	Quenched and Tempered	795
Drill Pipe Tool Joints, Drill Collars, Reamers	SAE 4135 modified with up to 0.75% Mo + 0.03% Nb	Quenched and Tempered	

precipitation strengthening can also be realized with direct quenching because the high temperatures used during heating for rolling puts NbC into solution provided the overall thermal-mechanical treatment and heat treatment are properly controlled.

At the present time, the demand for heat treated, seamless OCTG far exceeds existing capacity. However, significant additional facilities are planned by U.S. Steel, Armco, J & L, CF & I, etc. as well as new entries in the marketplace such as Tubular Products of America. Therefore, the supply and demand situation in the future, e.g. 1985, is open to question. However, it is reasonable to assume that optimization of capacity and/or minimization of cost will remain an important consideration then, as it is today. N-80 is a product that can be made by normalizing or quenching and tempering. For the more demanding applications, the superior properties associated with the finer Q & T structure are necessary. However, L-80 grade exists to fill these requirements by means of its restricted property limits. Therefore, the normalizing approach with optimized toughness through alloy design is desireable to maximize heat treating capacity. It should be realized that there can be situations where no increased capacity is available with normalizing vs. quenching and tempering but they are exceptions rather than the rule. Adjustment of chemistry to give the desired hardenability plus niobium for structural refinement is the key to the alloy design - a Cr-Mn steel modified with niobium is suggested in Table IV. Addition of molybdenum vs. Cr-Mn and/or adjustment in carbon content are obvious alternatives depending on the details of facilities, etc.

Summary

This review indicates that there are benefits to be realized by the addition of niobium to achieve structural refinement in heat treated OCTG particularly those intended for application in sour gas and corrosive environments. Specifically, the niobium increases the resistance of quenched and tempered steels to sulfide stress cracking (SSC) at a given strength level. Table V was prepared by extracting appropriate data from the API survey for 1980. An estimate of C-90 and higher strength products intended for sour gas and related applications can be made from this table. Although the producing countries are not grouped ideally, e.g. Canada and Japan are in the same category, it is reasonable to project that over 30,000 tons/yr. of steel with niobium may well have been made in 1980 given the apparent utilization of this addition by the Japanese producers to enhance properties. As more producers of SSC resistant grades enter the marketplace and as higher strength products (at least up to 100 KSI) are developed, the benefits achievable with niobium-addition should be utilized around the world.

Table IV. Suggested Chemistry for Optimized N-80 Production by Normalizing.

% C	% Mn	% si	% Cr	% Nb
.33/.38	1.20/1.50	.15/.35	.80/1.10	.02/.04

Table V. Tonnage in 1980 of Restricted Yield Strength Grades beyond C-75 and L-80 - Presumed to be Primarily C-90 (issued by API).

	Casing (metric tons)	Tubing (metric tons)
US	4,339	
Europe	841	2,746
Japan, Canada South America, and Elsewhere	41,454	12,696

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