NIOBIUM BEARING STEELS IN PIPELINE PROJECTS

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Abstract

Niobium is the primary strengthener and toughening agent in modern linepipe steels. Consumption of FeNb in these products has grown from virtually zero in 1957 to over fourteen million pounds (6000 tonnes) of contained niobium in 2001. During this period there has been a steady increase in strength levels from 42 ksi to 100 ksi and above, as well as requirements for improved toughness at temperatures down to -50°F (-46°C). Pipeline pressures have increased and installation has been accomplished in water depths greater than 9,000 ft. (2,592 m). The required combinations of mechanical properties coupled with ease of field weldability, and resistance to corrosive media such as natural gas containing H_2S and CO_2, are achieved through the use of low carbon contents, alloying with elements such as molybdenum, chromium, copper, nickel and the like and utilizing the beneficial effect of niobium in retarding austenite recrystallization during hot rolling. The latter technologies are collectively described as Thermal Mechanical Controlled Processing (TMCP) practices. A brief history and chronology of the developments are presented and current niobium usage is illustrated with examples for Double Submerged Arc Welded (DSAW), seamless and Electric Resistance Welded (ERW) linepipe. Technical data for recent projects is presented.

Introduction

The first use of niobium in linepipe steels occurred less than fifty years ago (1, 2). Since that time the technology has evolved to the point where almost all high strength linepipe steels rely on small additions of niobium, usually much less than 0.10 percent, to enhance both strength and toughness. "Niobium is a basic building block in the formulation and metallurgy of linepipe steels" so stated Kosasu in 1975 (3). Today these steels consume about one third of all niobium produced or 14 million pounds, sufficient to strengthen 11 million tons of shipped linepipe annually.

History

The effect of niobium in increasing the strength of hot-rolled carbon-manganese steels is reported in the patent literature as early as 1938-1939 (4,5). The exact mechanism was not known but it was surmised that it was predominantly due to beneficial grain refining effects of niobium carbide. The first commercial application in linepipe steel was reported by Barkow (1) and Altenberger (2) in 1961 and 1960 respectively.

The new hot-rolled semi-killed medium carbon steel shown in Table I was substituted for a steel having much higher carbon and manganese contents thereby improving field weldability.

Table I Hot-rolled semi-killed medium carbon steel

Chemical Composition	Weight Percent		
	C	Mn	Nb (Cb)
Min.	0.20	0.89	0.004
Max.	0.27	1.28	0.015
Mean	0.24	1.10	0.008

Other reports at the time (7) indicated that the new steels had poor notch toughness due to the formation of cementite networks on ferrite grain boundaries or the formation of Widmanstatten ferrite during normal air-cooling (8). In time, it was discovered that both problems could be eliminated by increasing manganese content (9) and refining the austenite grain size during hot rolling. The latter being the precursor to the large scale introduction of controlled rolling and other thermomechanical processing methods of austenite (10).

Modern linepipe steels belong to the generic category of materials known as high-strength low-alloy steel (HSLA) or microalloyed steel. This material finds widespread application in heavy plate, bar, sheet, beams, forgings and other steel products, thus technological developments in physical metallurgy and steelmaking have been stimulated by demands from these product sectors as well as by pipeline industry needs and vice versa.

During evolution of linepipe steels over the last 50 years, several essential events, chronicled below, can be credited with changing specifications or stimulating metallurgical developments in both linepipe and plate steel.

Linepipe strengths have increased progressively during the past half century due to the stimuli listed in Table II. The chronology of the evolution is presented in Figure 1, and a very detailed account of prevailing specifications and technical requirements is published elsewhere (11).

Table II Influencing factors on the development of line pipe steels

Date	Event	Industry Reaction
1943	Discovery of ductile-brittle transition in carbon steels.	Introduction of 15 ft-lb CVN energy (20J) requirement into specifications for ship plate.
1954	Above characteristics considered relevant to pipelines.	TÜV introduced 3.5 m-kg/cm^2 energy requirement for pipelines.
1960	Brittle fracture propagation of 13 km in NPS 30 pipeline.	Development of Battelle drop weight tear test (BDWTT).
Dec. 1968 - Jan. 1969	Propagating ductile fracture in non-brittle, supposedly crack resistant, material.	Introduction of minimum Charpy energy requirements based on various fracture models.
1970	Proposed construction of Alaskan/ Canadian gas pipelines (CAGSL)	Steel development frenzy centered on X-80 (551 MPa) and -69°C (-90°F) toughness requirements.
1972	HIC failure in X-65 BP pipeline in Ummshaif (Arabian) Gulf.	Introduction of BP test (NACE TM-02-84 [Solution B]).
1974	Unpredictable fracture arrest in full scale (CAGSL) tests. Attributed to rich gas, separations, high hoop stress and faulty models.	Introduction of crack arrestors, improved fracture arrest modeling and revision of rolling ideas for high strength linepipe.
1978	Stress corrosion cracking failures in newly installed Australian and Canadian pipelines.	Better metallurgical (hardness) controls and improved external coatings. Improved operating practices.
1978	Molybdenum "shortage" and price escalation.	Mo designed out of X-70 steels. Nb-Cr design introduced plus TMCP.
1988/89	Vanadium price increase to $50/kilo	Vanadium eliminated from many steels. Mo and Cr + TMCP substituted.
1990	Development of deepwater oil and gas reserves and design of Oman-India and Black Sea pipeline.	Very heavy wall thickness collapse-resistant DSAW linepipe developed as well as high strength (80 ksi) seamless risers.
1997	Need for very high pressure systems for Arctic development.	Ultra high strength (135 ksi UTS) steels and composite reinforcement of conventional steels considered.

Niobium steels were first introduced in 1959 (1). Prior to that the lowest strength grades were either C-Mn based or strengthened by cold work originating during expansion. The first microalloyed X-52 steels, circa 1953, were vanadium strengthened and usually normalized to develop adequate toughness. However, as the benefits of improved austenite processing (controlled rolling) became known, niobium microalloying emerged as an essential component in hot-rolled linepipe steels often in amounts as low as 0.01%. After forty more years of development, niobium is now found in almost every high strength line pipe steel in concentrations ranging from 0.010 to 0.11%. In the following pages, data of usage in both small and large diameter projects will be presented for seamless (SMLS), electric resistance welded (ERW) and double submerged arc welded (DSAW) product.

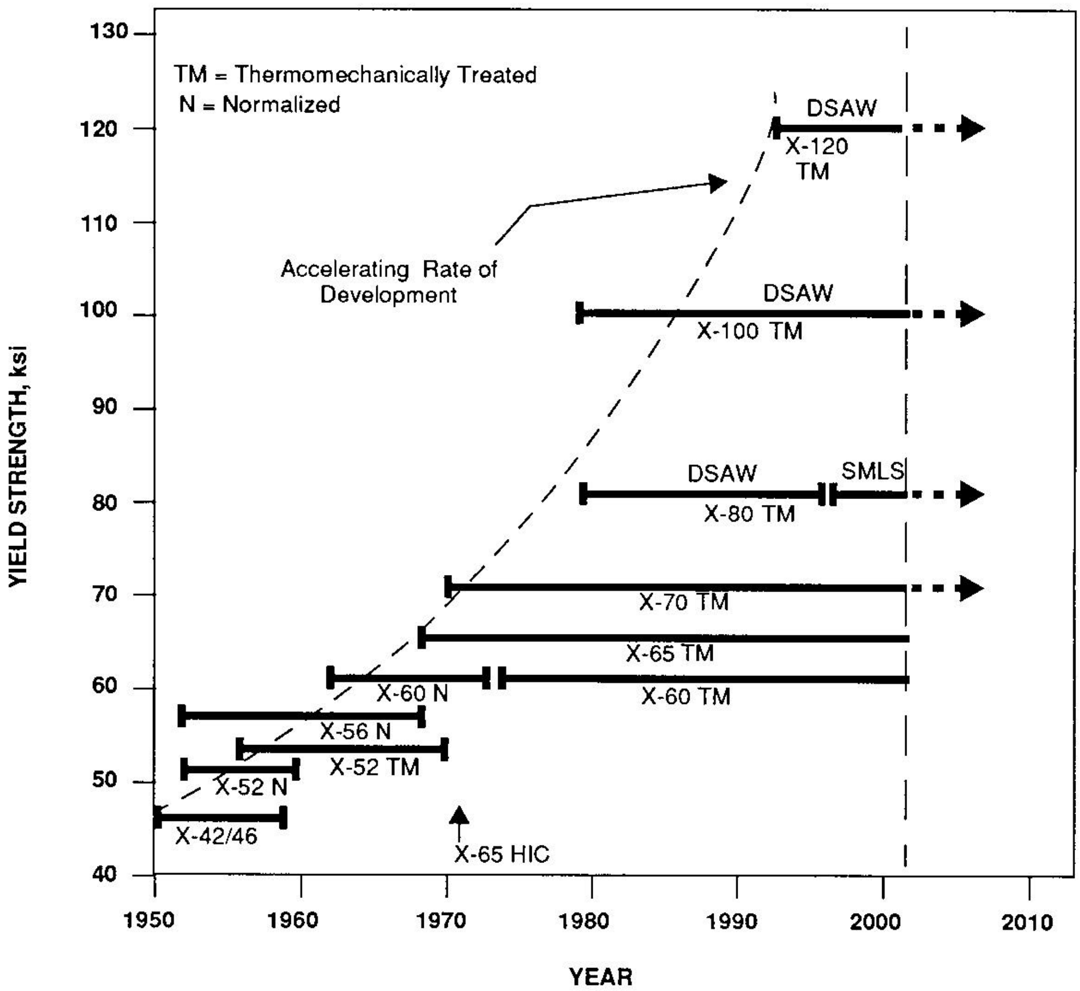

Figure 1: Development periods for high strength linepipe.

The trend toward higher strength levels (up to 120 ksi yield strength and above) has been led by developments in DSAW linepipe where the benefits translate into smaller wall thicknesses for high pressure long distance onshore pipelines. Similar metallurgical approaches are used for high frequency (HF) ERW linepipe, which is made from hot-rolled coiled skelp, but yield strength levels have not yet exceeded 80 ksi. In offshore pipelines the useful yield strength is limited to 65-70 ksi due to the need to guard against plastic collapse. In the most extreme case wall thicknesses in the range 1.125-1.875 inch are being installed as detailed later. In the case of seamless linepipe, quenching and tempering is used to achieve the desired yield strength level, which seems to have plateaued at 80 ksi. Examples of the chemical compositions and niobium contents used for each grade, product type and application will be presented later.

The metallurgical basis for niobium strengthened linepipe is documented from both a fundamental and practical basis in several papers in this volume and in its predecessor (12) and it is not necessary to repeat the details here. However, it is useful to highlight the development track, which has been followed, and this is summarized in Figure 2.

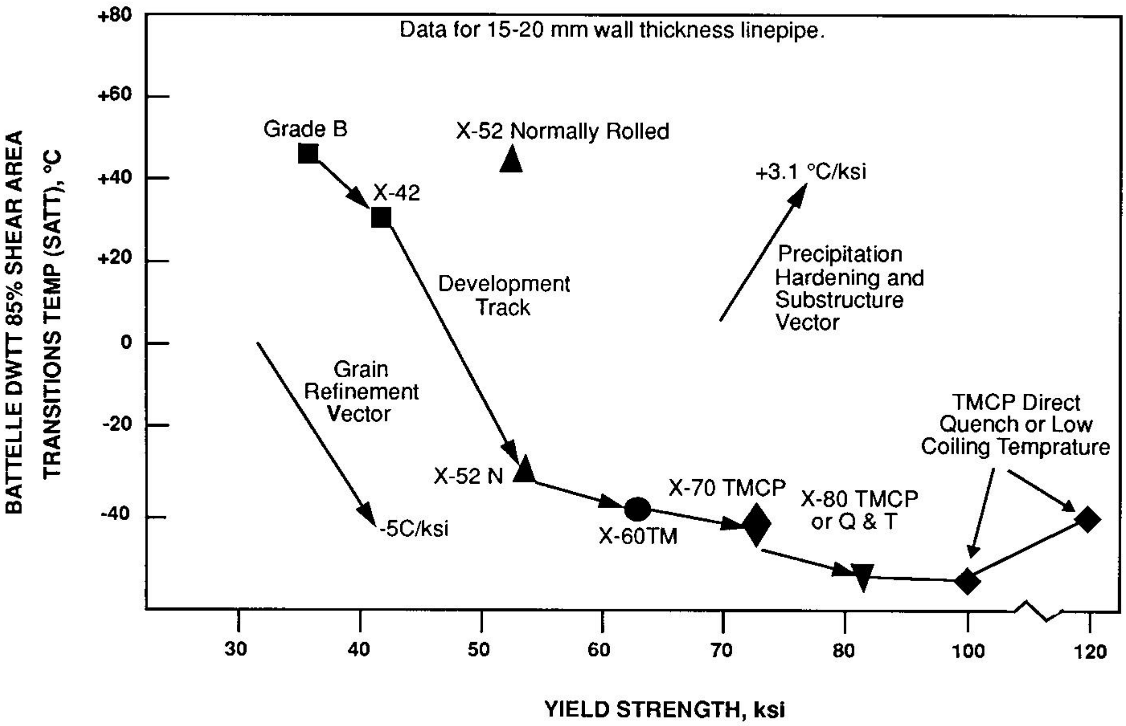

Figure 2: Progress of development showing simultaneous increase in toughness with strength (also with time).

The Grade B and X-42 steels referenced in Figure 2 had very poor toughness from both a fracture energy absorption and impact transition temperature viewpoint. The low absorbed energies in the Charpy test were related to high carbon and sulphur contents and poor steel cleanness especially in the case of semi-killed steels, whilst the high Charpy and Battelle Drop Weight Tear Test transition temperatures were caused by the coarse ferrite grain sizes and high carbon contents. In such steels the useful niobium content was less than 0.03% and even at that level care was required to avoid the appearance of poor microstructures in hot rolled product (8). As a consequence, the early high strength steels often relied on normalizing to achieve adequate grain refinement. In the mid to late 1960's the benefits of low finish rolling temperatures were discovered and thermomechanical processing was quickly introduced on a broad scale. Simultaneously, lower carbon contents were introduced (Figure 3), which were simulated both from an alloy design perspective to aid niobium carbide solubility and from an end user (specification) initiative to improve field weldability. This led to dramatically improved toughness in the X-60 and X-70 steels shown in Figure 2. Steels of this type were successfully used in the construction of the Alyeska oil pipeline in 1973 as referenced in Figure 3. A typical chemical composition for such steels, which were produced in Japan, is shown in Table III below:

Table III Early controlled line pipe microalloyed steel produced in Japan

C	Mn	Si	S	P	Al	V	Nb	N
0.12	1.50	0.25	0.006	0.020	0.025	0.08	0.03	0.007

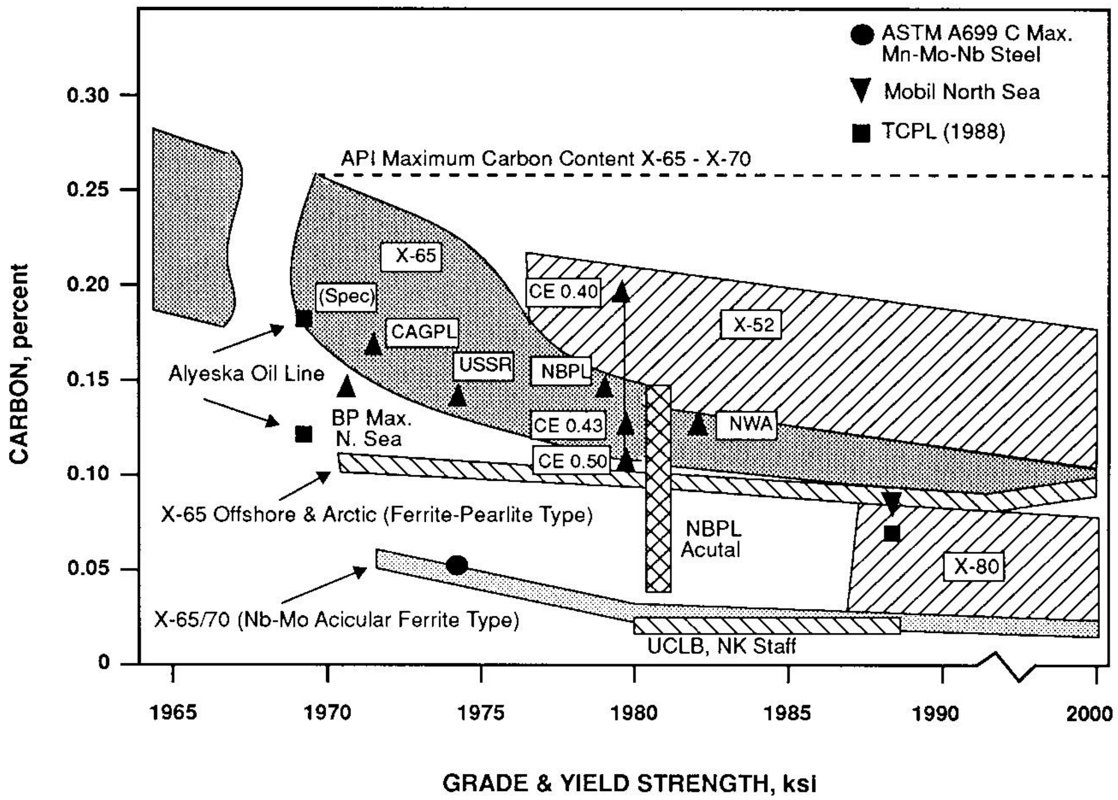

Figure 3: Evolution of low carbon contents for high strength pipeline steels.

During the 1970-1980 decade, major improvements in steelmaking and refining took place, many of which affected alloy design and niobium microalloying technology. Continuous casting replaced ingot casting, and ladle refining processes were introduced which facilitated desulphurisation, carbon removal, calcium treatment and the production of very high toughness clean steels.

The improvements in toughness attributable to sulphur removal are shown in Figure 4. Further demands for sour service linepipe pushed sulphur levels down to 0.002% and below by 1980. In the latter steels, manganese was usually reduced to minimize segregation and niobium was used in amounts around 0.04% to maintain strength and notch toughness.

A representative X-60 steel composition, circa 1980, is presented in Table IV below. Such steels were used for construction of several major pipelines in Saudi Arabia and the North Sea.

Table IV X-60 grade produced in the early 80’s

Size	Chemical Composition, wt. percent								
	C	Mn	Si	S	P	Al	Nb	Ti	N
30" OD x 0.600" wt.	0.07	0.95	0.20	0.003	0.015	0.03	0.04	0.012	0.005

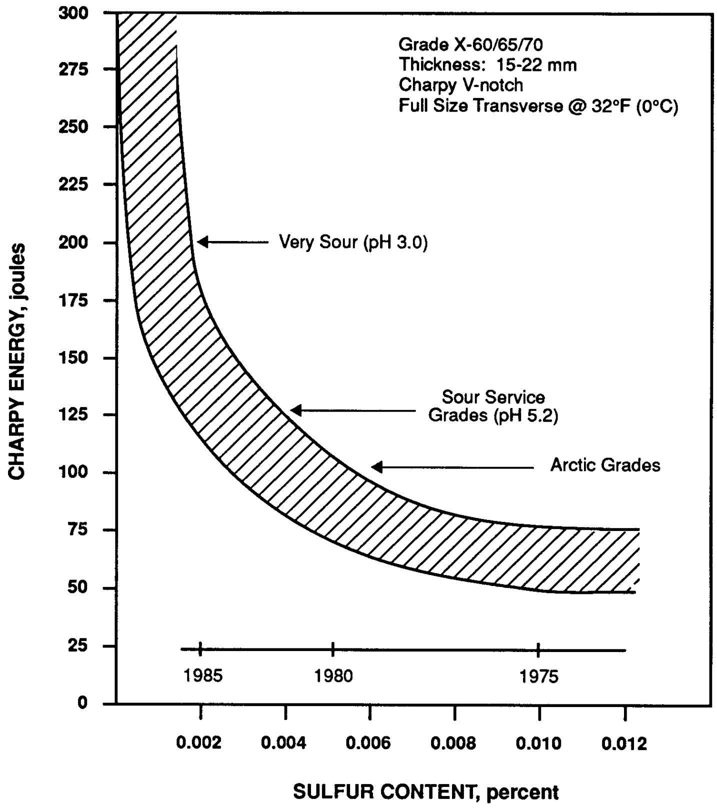

Figure 4: Effect of sulphur content on toughness of linepipe.

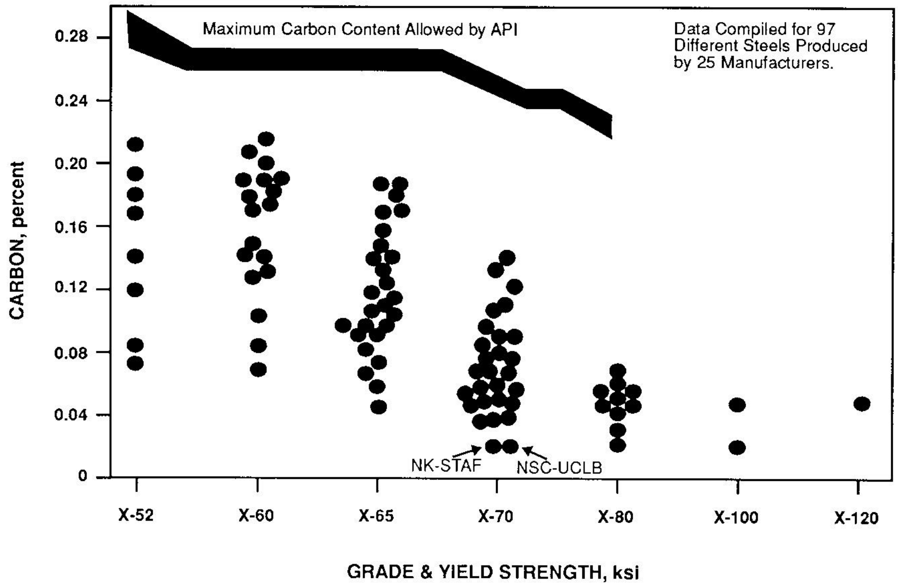

Figure 5: Relationship between carbon content and yield strength for typical pipeline steels.

It should be noted that as carbon contents were reduced, slightly higher niobium contents became metallurgically effective, which resulted in increasing reliance on niobium, culminating today in the combination of 0.10 percent niobium and 0.03 percent carbon in certain X-70 steel formulations (13, 14).

The tertiary portion of Figure 2 details the evolution of Grade X-80 linepipe on a commercial basis and additional data from widespread research on a ultra-high strength steel with yield strength approaching 120 ksi. All such steels depend on complex thermo-mechanical processing of low carbon, heavily niobium modified, C-Mn steels, Figure 5, containing between 0.045% and 0.095% niobium(15-19). Representative steel compositions are presented in Table V.

The rolling practices for such steels must be capable of delivering adequate grain refinement and maximizing the other strengthening components depicted in Figure 6.

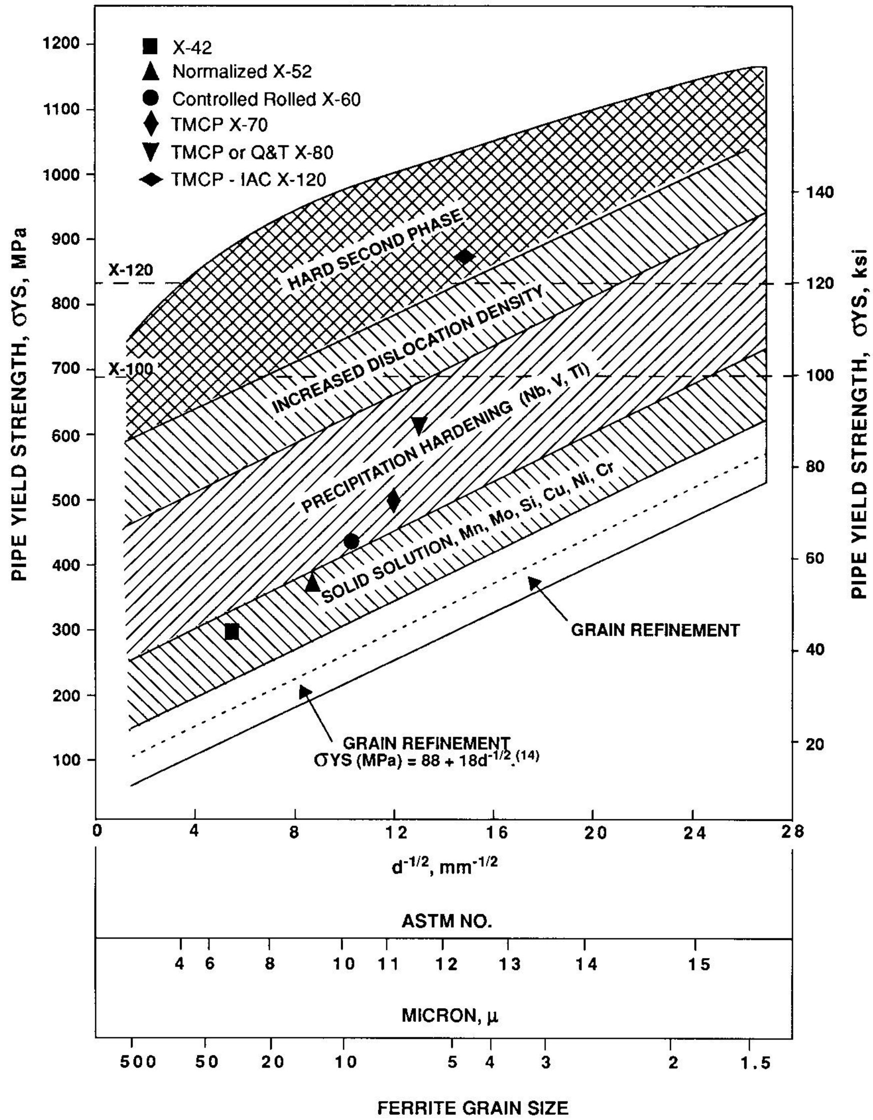

Figure 6: Required combination of strengthening components for hot rolled plate and skelp.

Table V Representative steel compositions for high grade line pipe steels

Year	C	Si	Mn	P	S	Nb	V	N	Ti	Mo	Cu	Ni	Cr	B	Ceq	Pcm	Grade	Wall Th. (in)	Dia.	Water Cooling	Ref.
1988	0.02	0.13	1.88	0.021	0.003	0.042	--		0.014		0.29	0.47		0.0009	0.39	0.146	X-100	0.750 (19.1 mm)	36"	DQ	16
1988	0.05	0.26	1.74	0.014	0.001	0.038	0.047		0.011	0.20	0.27	0.45		--	0.41	0.173	X-100	0.750 (19.1 mm)	36"	DQ	16
1988	0.06	0.25	1.80	0.005	0.002	0.04	0.04		0.02	0.19	Yes	Yes		No	0.44	0.20	X-100	0.750 (19.1 mm)	30" (763 mm)	IAC FCT 300°C	17
1990	0.06	0.16	1.85	0.020	0.001	0.044	--		0.014	0.20	--	0.20		--	0.43	0.175	X-100	0.750 (19.1 mm)	36"	AC DQ	16
1995	0.06/ 0.08	0.25	1.85/ 2.0	0.015 max.	0.002	0.045	--	0.005	0.015/ 0.02	0.25/ 0.30	0.20/ 0.25	0.20/ 0.25					X-100	0.800 (20.3 mm)	28"	IAC	
1997	0.03	0.18	1.60	0.010	0.002	0.07			0.011	0.20	--	0.30	0.50	0.0008			X-120	1.00 (25 mm)	28”	IAC	
1998	0.04	0.30	1.95			0.045	--	0.004	0.012	0.30	0.32	0.30					X-100	0.80 (20.3 mm)	36”	IAC	
1998	0.05	0.24	2.00			0.04	--	0.003	0.019	0.10	0.04	0.03					X-100	0.60 (15.2 mm)	36”	IAC	
2000	0.06	0.35	1.90	--	--	0.05	--	0.004	0.018	0.28	--	0.25	--	--	0.46	0.19	X-100	0.629 (16 mm)	36"	IAC	18
2000	0.07	0.09	1.80	0.004	0.002	0.048	--	0.004	0.011	0.21	0.29	0.51	0.16	--	0.50	0.21	X-100	0.750 (19.1 mm)	30"	AC	19
2000	0.05	0.23	1.94	0.008	<0.003	0.040	--	0.002	0.008	0.10	0.17	0.42	--	--	0.44	0.18	X-100	0.750 (19.1 mm)	30"	AC	19
2000	0.08	0.26	1.86	0.010	<0.002	0.047	--	0.003	0.015	0.27	0.24	0.21	0.03	--	0.48	0.22	X-100	0.750 (19.1 mm)	30"	AC	19
2000	0.07	0.29	1.73	0.003	<0.002	0.037	0.040	0.004	0.014	0.22	0.22	0.20	0.04	--	0.45	0.20	X-100	0.750 (19.1 mm)	30"	AC	19

The steels used for production of DSAW linepipe are processed on conventional plate mills (18), Steckel mill facilities (19), or heavy strip mills (for <24 inch diameter linepipe), whereas skelp for HFERW linepipe is produced either on conventional hot strip mills or increasingly by direct conversion of thin (50-125 mm) slabs.

Typical steel compositions of Grade X-80 linepipe produced on a conventional hot strip mill are presented in Table VI. Chemical compositions of Grades X-52 to X-70 skelp produced from thin slabs are shown in Table VII.

Table VI Hot strip mill processed X-80 grade

Company	C	Mn	Si	P	S	Ni	Nb	Mo	Al	Ca	N	Ti
NSC [21]	0.06	1.29	0.20	0.010	0.002	0.31	0.019	0.26	0.024		0.005	0.017
BHP [22]	0.075	1.59	0.31	0.018	0.001	--	0.057	0.22	0.026	0.0011	0.006	0.013

Table VII Chemical compositions of grades X-52 to X-70 skelp produced from thin slabs

Vendor	**1**	**2**	**3**
Pipe Grade	0.375" X-65	0.250" X-65	0.400" X-65
C	0.06	0.03	0.035
Mn	0.826	1.29	1.41
P	0.009	0.007	0.012
S	0.003	0.007	0.005
Cb	0.04	0.06	0.035
Si	0.03	0.378	0.26
Ti	0.003	0.015	--
Cu	0.07	0.116	0.1
Ni	0.03	0.049	--
Mo	0.01	0.016	0.23
Cr	0.05	0.056	--
V	0.001	0.039	--
Al	0.04	0.023	0.031
B	0	0.001	--
Ca	0.002	0	0.0025
N	0.007	0.007	--

The mechanical properties achieved with the thin slab feedstock are presented in Table VIII.

Table VIII Mechanical properties achieved with thin slab feedstock

Vendor	Yield Strength (ksi)		Tensile Strength (ksi)		
	Ring Expansion	API-Strap	Pipe Body	Weld	
1	76.5	77.5	88.5	80.0	Pipe Results
2	80.0	75.5	85.5	87.0	Pipe Results
3	--	81.1	91.0	--	Skelp Results

Seamless product for use in linepipe and oil and gas riser systems is available up to the 80 ksi yield strength level and is increasingly produced by quenching and tempering. In recent years carbon contents have been reduced to below 0.10% to improve field weldability, to improve weld heat affected zone (HAZ) toughness and fatigue resistance, and to reduce HAZ hardness so as to improve resistance to stress corrosion cracking (SSC).

Examples of the chemical compositions of seamless line pipe are presented Table IX below.

Table IX Chemical compositions os seamless line pipe

Grade	C	Mn	Si	Ni	Nb	V	Cu	Mo	Cr	B	Dia.	wt.	Ref.
X-80	0.04	1.50	0.15	1.00	0.06	--	0.90	0.25	0.50	--	8"	19.1 mm	23
X-80	0.06	1.29	0.20	--	0.019	--	--	0.26		0.0008	14"	25.4 mm	24
X-70 (sour)	0.07	1.35	0.15	--	0.03	0.05	--	0.16	--	--	10"	34.0 mm	25

The aforementioned examples of linepipe steel compositions mainly relate to product required for low temperature or sweet (i.e. treated non-corrosive) gas service. However, many developments have occurred in regions producing gas containing H_2S, CO_2 and chlorides. Depending on the concentrations of each of the above, the water content and ease and feasibility of inhibition, the end user may elect to use either carbon steels or more highly alloyed corrosion resistant grades. The general framework concerning material selection is shown in Figure 7. Examples of the high alloy and clad technologies are presented in the literature (26) and elsewhere in this volume (13). Examples of modern sour service carbon steels used for production of DSAW linepipe for the Black Sea Pipeline are presented in Table X below.

Table X Chemical composition of 30" O.D. X-65 31.8 mm linepipe (Blue Stream Project)

Source	**Mill A**	**Mill B**	**Mill C**	**Mill D**
C	0.05	0.04	0.05	0.06
Mn	1.45	1.27	1.31	1.44
Si	0.17	0.24	0.31	0.14
S	0.0006	0.0002	0.0006	0.0004
P	0.012	0.005	0.009	0.011
Cu	0.26	--	0.15	0.27
Ni	0.27	0.23	0.07	0.26
Cr	0.04	0.27	0.03	0.12
Mo	0.12	0.2	0.13	0.01
V	0.04	--	0.057	0.042
Nb	0.05	0.04	0.043	0.036
Ti	0.009	0.01	0.015	0.017
Al	0.029	--	0.029	0.035
N	0.004	0.003	0.0029	0.0044
Ca	0.0017	0.0014 to 0.0037	0.0024	0.0023
CE	0.36	0.37	0.33	0.37
Pcm	0.16	0.14	0.14	0.17

In another recent development a very low manganese steel has been developed (27) which is less sensitive to casting conditions, desulphurisation capability and inclusion shape modification technology than conventional sour service steel compositions. The loss of "hardenability" in the low manganese steel is compensated for by the use of higher solute niobium contents, by alloying with copper, nickel and molybdenum (either singly or in combination) but most beneficially with chromium. The latter element reduces centerline segregation tendency and preserves the beneficial effect of copper in reducing hydrogen permeation into the steel at moderate pH levels, Figure 8 (28).

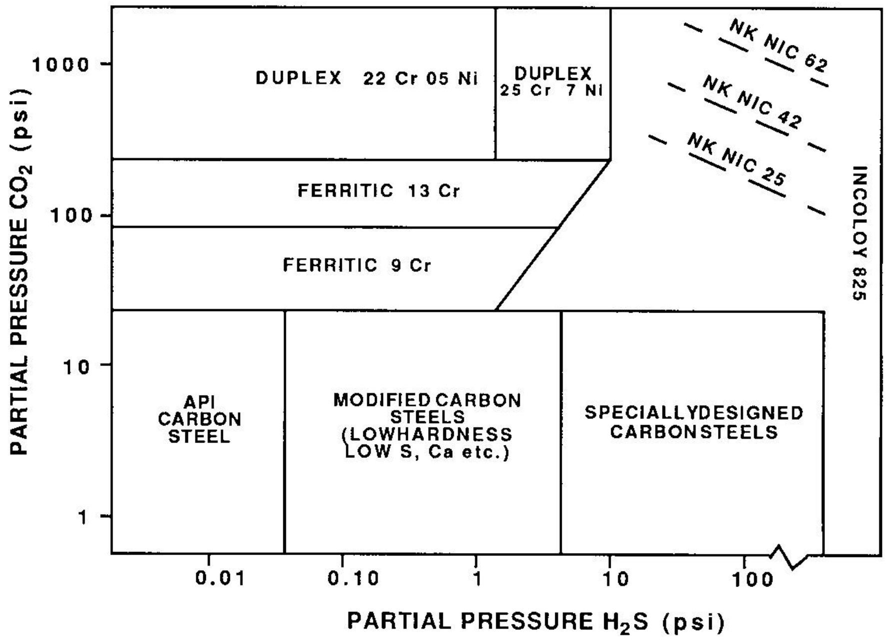

Figure 7: Material selection guidelines, 150°F (65°C).

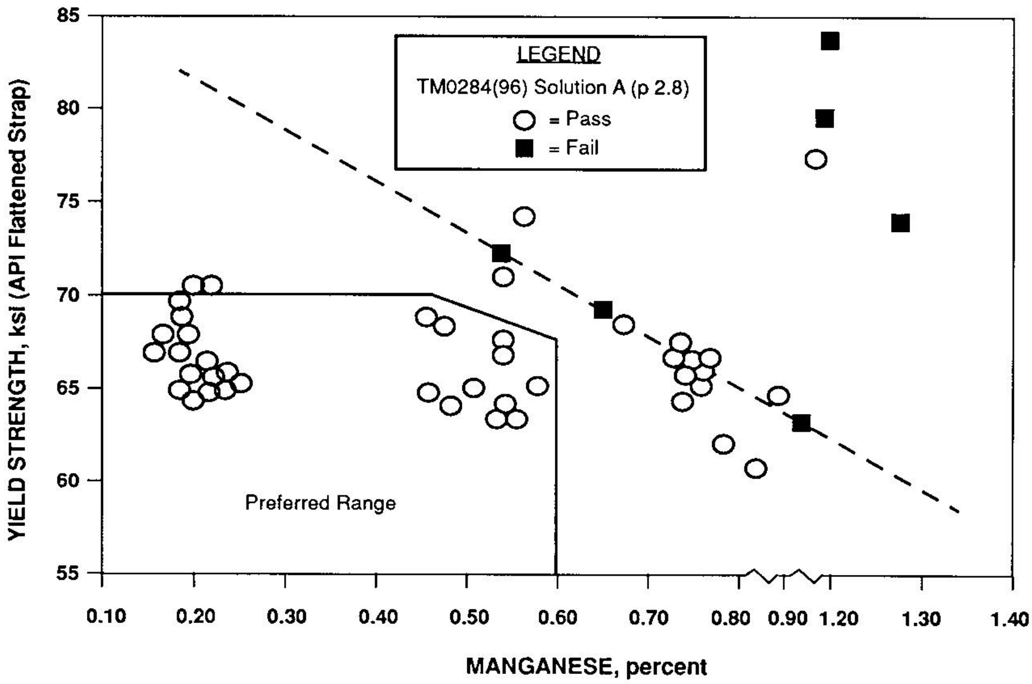

Figure 8: Stepwise cracking resistance as a function of manganese and yield strength (27).

The steel can be produced most conveniently in strip mills and Steckel mills but interrupted accelerated cooling, TMCP processing is also indicated. Results from trial production are presented in Figure 9.

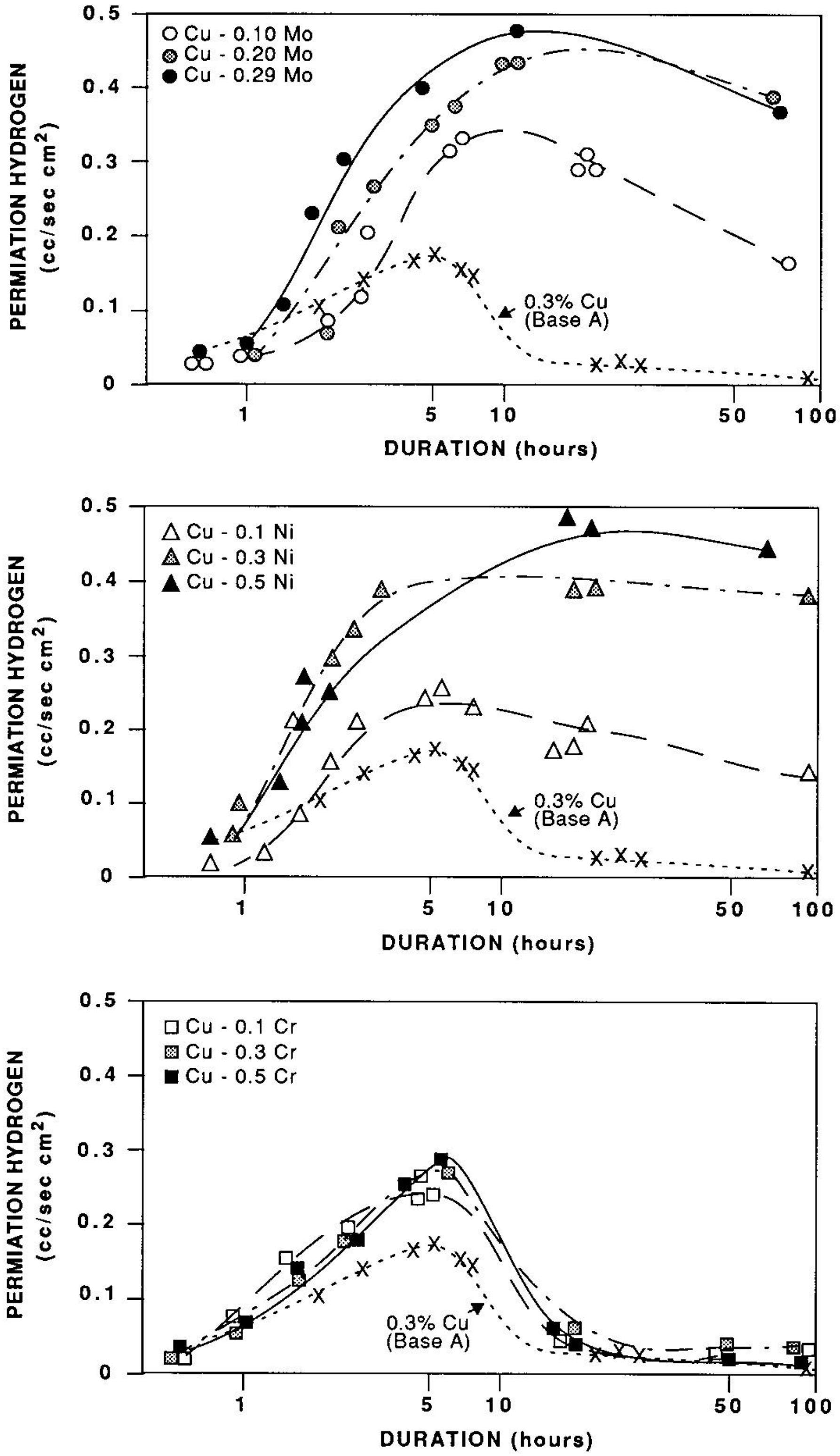

Figure 9: Effects of Mo, Ni and Cr on Cu-bearing steels.

End User Issues

Specifications for modern linepipe reflect developments in steelmaking and rolling technology and end user expectations concerning the performance of the completed pipeline.

As improvements in manufacturing capability have occurred, greater restrictions have been placed on impurity contents, residuals and particularly on "carbon equivalents" and more recently on carbon itself. Weldability is best defined in terms of a carbon-weighted formula such as Pcm (29), when carbon is less than 0.12 percent and this is reflected in the latest edition of the API 5L Linepipe Specification (30).

The HAZ hardness and thus toughness of field girth welds correlates very closely with heat input and Pcm as shown in Figure 10 (31).

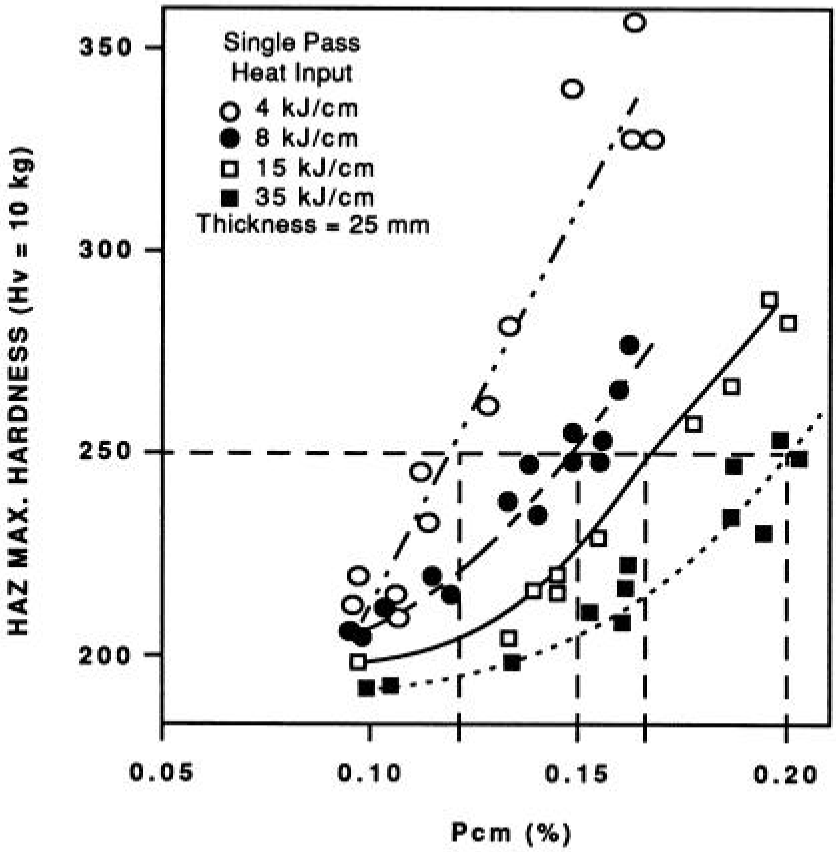

Figure 10: Effect of carbon equivalent (Pcm) and heat input on HAZ hardness of X-70 linepipe (10).

The experience gained over the years has spawned the promulgation of proprietary steel specifications by each major end user in an effort to prescribe, for the benefit of the producer, acceptable steel compositions for each strength level. Examples of chemical compositional limits for API X-70 product are presented in Table XI where they are seen to be much more restrictive than limits in the basic API 5L document (30).

A minimum niobium content of 0.020 % often appears in specifications when fabrication of bends by induction heating is contemplated. Niobium prevents austenite grain coarsening at high peak bending temperatures (32) and thereby improves notch toughness of the completed bend. A detailed discussion of hot bending applied to 0.09% niobium high strength and sour service linepipe grades is presented elsewhere (33).

Table XI Typical chemical composition restrictions for high quality grade X-70 (483 MPa) linepipe

Element	Chemical Composition (%)				
	Maximum				Minimum
	API 5L 42nd Ed.[30]	Submerged Arc Welded	HFERW	Seamless (Q&T)	All Products
C	0.23	0.06*	0.08	0.12	
Mn	2.00**	1.65	1.60	1.65	
Si	--	0.50	0.50	0.50	
Al	--	0.060	0.060	0.060	0.015
S	0.05	0.005*	0.003*	0.006*	
P	0.04	0.020	0.020	0.020*	
Cu	--	0.40	0.40	0.40	
Ni	--	0.25	0.15	0.20	
Cr	--	0.30	0.10	0.10	
Mo	--	0.25	0.10	0.10	
Nb***	0.005 min.	0.08	0.070	0.050	0.020
V***	0.005 min.	0.10	0.080	0.10	
Ti***	0.005 min.	0.025	0.025	0.025	
N	--	0.009	0.009	0.009	
Ca	--	0.0050	0.0050	0.0050	0.0008
CE	--	0.39	0.39	0.41	
CEN	--	0.31	0.31	0.31	
Pcm	--	0.19	0.18	0.19	

* For sour service C - 0.05% max., S<0.0015% max., P - 0.010% max.
** Depending on carbon content.
*** Either singly or in combination.

Summary and Conclusions

The paper presents a chronology of the events leading to the extensive and basically essential use of niobium in high strength linepipe steels. Niobium microalloyed linepipe steels are produced by all pipe making methods which includes DSAW, HFERW and the seamless processes.

Pipe with yield strengths up to 120 ksi is available coupled with excellent toughness and field weldability. Superior resistance to sour hydrocarbons is found in steels up to and including the API Grade X-70 strength levels.

The paper presents chemical compositions of a wide range of steels from many different projects manufactured throughout the world by the three predominant manufacturing processes. It is concluded that niobium microalloying is very versatile and that niobium an indispensable element in modern high strength, high performance linepipe.

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