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APPLICATION OF NIOBIUM-MOLYBDENUM STRENGTHENING MECHANISMS IN HIGH STRENGTH LINEPIPE STEELS

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Abstract

The synergistic effects of niobium and molybdenum in lowering austenite-to-ferrite transformation temperatures have been known for approximately 45 years. The benefits have been widely exploited in linepipe steels since 1971 when 485 MPa (X70) linepipe produced by IPSCO [1] was installed in Canada in the TransCanada and Novacorp gas transmission systems. At that time the steels were cast as semi-killed ingots and had inferior transverse Charpy properties due to the presence of MnS and silicate inclusions. Other applications have been found in hot-rolled long products [2] and Nippon Steel's HT80 quenched and tempered plate [3,4]. As linepipe yield strengths have increased to X80, X100 and above, and carbon contents have been reduced to 0.03-0.06 percent, the Nb-Mo combination has become indispensable for producing economical steels when used in combination with chromium, copper and nickel. This paper provides a brief chronology of the adoption of Nb-Mo and Nb- Mo-B alloying since the mid 1960s.

Research and Technological Development

Research by the author [5] was conducted at the U.S. Steel Research Laboratory in Monroeville, PA starting in 1966 and culminating in the casting of 30 ton BOF heats at South Works, Chicago in 1968 and 1969 [6].

The chemical composition of the pilot scale heat is shown in Table I below.

Table I. Chemical Composition and Mechanical Properties of 30 Ton BOF Heat of Nb-Mo-Ni Steel

	Yield Strength, MPa	C	Mn	Ni	Nb	Mo	B (ppm)	Ti	N
As rolled	509-558	0.045	1.25	0.80	0.09	0.37	19	0.023	0.007
Aged 600 °C – 1/2 h	695-758								

The Charpy V-notch transition temperatures of the as-rolled and aged plates were +15 and +30 °C respectively. This was due to the absence of appropriate austenite conditioning knowhow and the strong effect of $NbMo_4C_3$ precipitation in the bainitic microstructure. As time progressed and controlled rolling practices were developed, the steel (without nickel), Table II, was applied by IPSCO in 1971-1972 [7,8,9], and installed in large diameter gas pipelines in Canada which are still operating safely today. In that early application the skelp was rolled on a reversing Steckel Mill in Regina, Saskatchewan and then water cooled.

Table II. Chemical Composition of IPSCO Linepipe, circa 1972 [1]

C	Mn	Nb	Mo	Cu	Ni	Si
0.05	1.75	0.095	0.32	0.25	0.12	0.08

Today almost all steels are fully-killed and continuously cast, and rolling mill and thermal cooling regimes have become very sophisticated, such that steel compositions similar to that presented in Table I are routinely capable of producing linepipe with yield strengths of 690 MPa (X100) and excellent notch toughness [10,11,12].

As part of the Nb-Mo research program, at U.S. Steel continuous cooling transformation (CCT) diagrams were developed for the four steels presented in Table III [13].

Table III. Chemical Compositions of Steels Investigated

Heat No.	Designation	C	Mn	P	S	Si	Al (Total)	N	Nb	Mo
W8583/1	Base Steel	0.018	0.49	0.013	0.017	0.12	<0.005	0.001	-	-
W8620/1	Base + Niobium	0.022	0.52	0.020	0.020	0.12	<0.008	0.001	0.10	-
Y9364/1	Base + Molybdenum	0.018	0.50	0.018	0.019	0.15	<0.002	0.001	-	0.51
Y9360/1	Niobium - Molybdenum (Nb-Mo)	0.014	0.50	0.016	0.017	0.13	0.001	0.001	0.10	0.50

The manganese content was deliberately kept low to facilitate the achievement of very low carbon contents, which thereby maximized solution of niobium carbide with its attendant benefits. The full CCT diagrams for the four steels are presented in Figures 1 to 4, and then are consolidated in Figure 5 where it is simple to compare the effects of the individual and combined (Nb-Mo) elements. The combination of niobium and molybdenum results in a reduction in ferrite/bainite start temperature of >100 °C for cooling rates as low as 0.1 °C/s compared with the individual effects of niobium and molybdenum. This makes it possible to produce uniform, non-polygonal microstructures in both thin and heavy (40 mm) plates.

The effect of niobium in reducing A_{r3} temperature is much greater than the effects of other microalloying elements, Figure 6. However, niobium and vanadium can be combined in some cases with good effect, Figure 7.

The Nb-Mo synergistic combination was adopted rapidly by Hoesch [14], Usinor [15], Italsider [16] and other linepipe producers especially for linepipe supplied to the former USSR. However, this came to an abrupt end in 1974 / early 1975 when the price of molybdenum skyrocketed. As a result manufacturers returned to Nb-V alloying, or in the case of Italsider to Nb-0.30 percent Chromium, alloy designs for API Grade X70 linepipe.

As yield strengths have moved upward to 550 MPa (X80), or to 690 MPa on a trial basis, molybdenum has been reintroduced into the linepipe arena, often in combination with higher niobium contents, Figure 8.

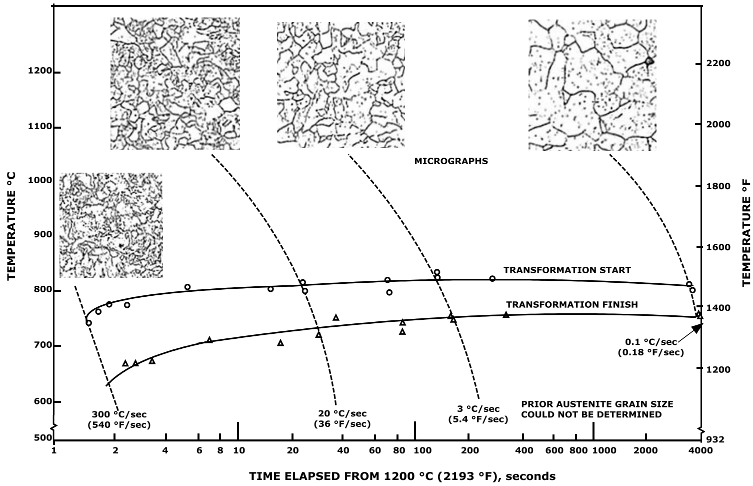

Figure 1. CCT diagram: 0.02%C 0.50%Mn.

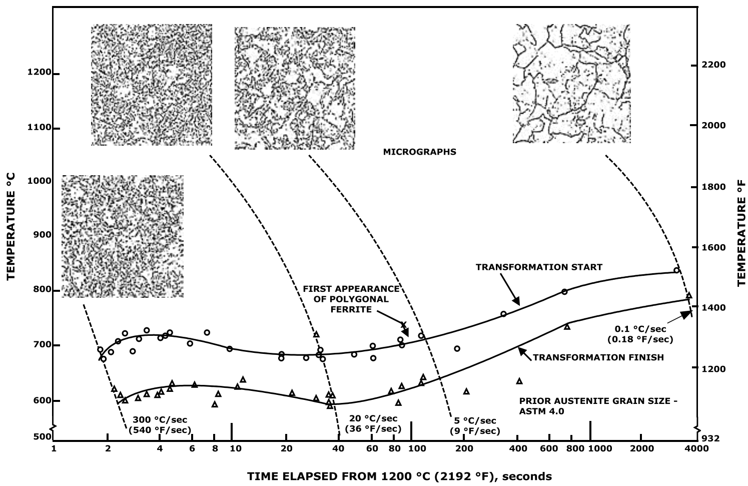

Figure 2. CCT diagram: 0.02%C 0.50%Mn 0.10%Nb.

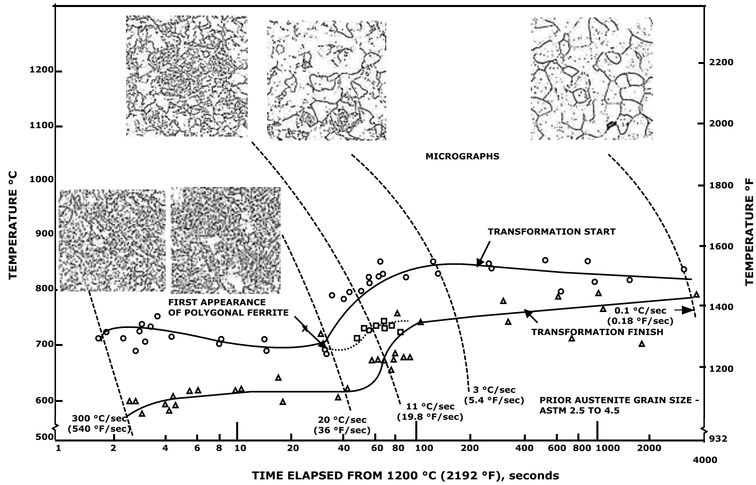

Figure 3. CCT diagram: 0.02%C 0.50%Mn 0.51%Mo.

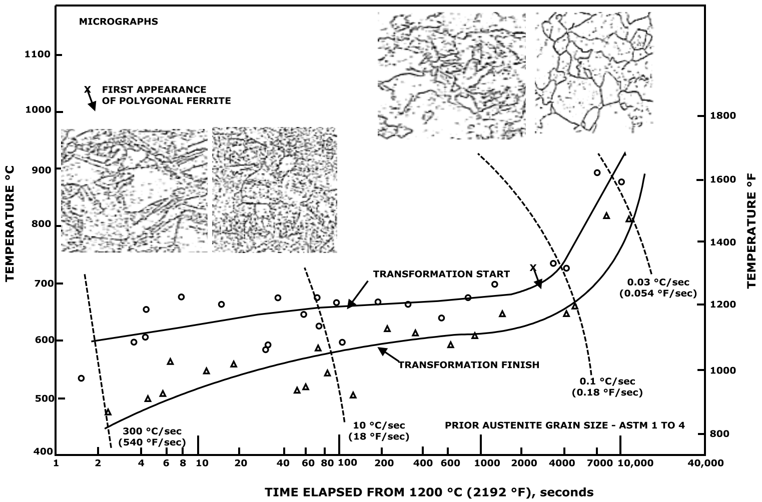

Figure 4. CCT diagram: 0.02%C 0.50%Mn 0.10%Nb 0.50%Mo.

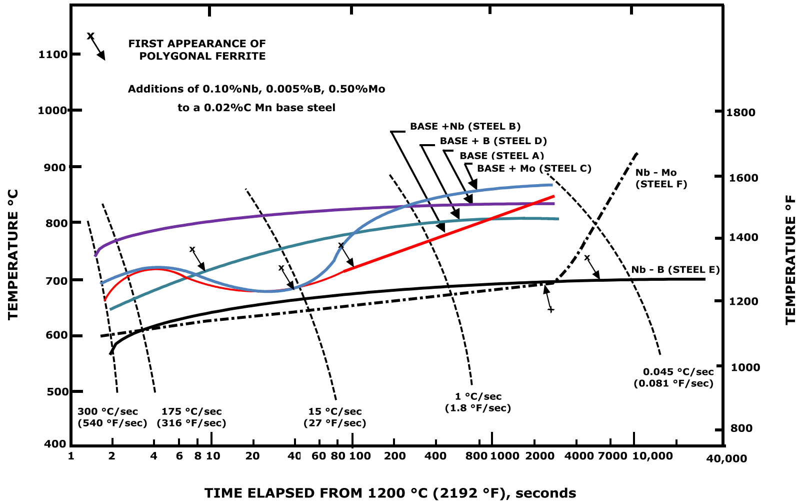

Figure 5. Comparison of transformation-start temperatures for all steels.

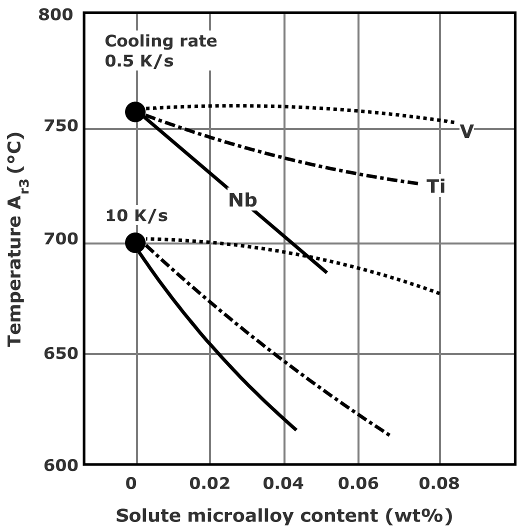

Figure 6. Effect of solute microalloying elements on the A_{r3} temperature.

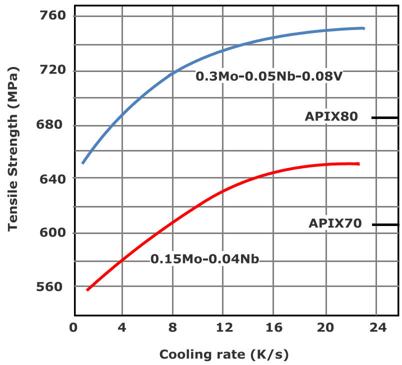

Figure 7. Tensile strength vs cooling rate in IAC processed 19 mm (0.75 in) plates.

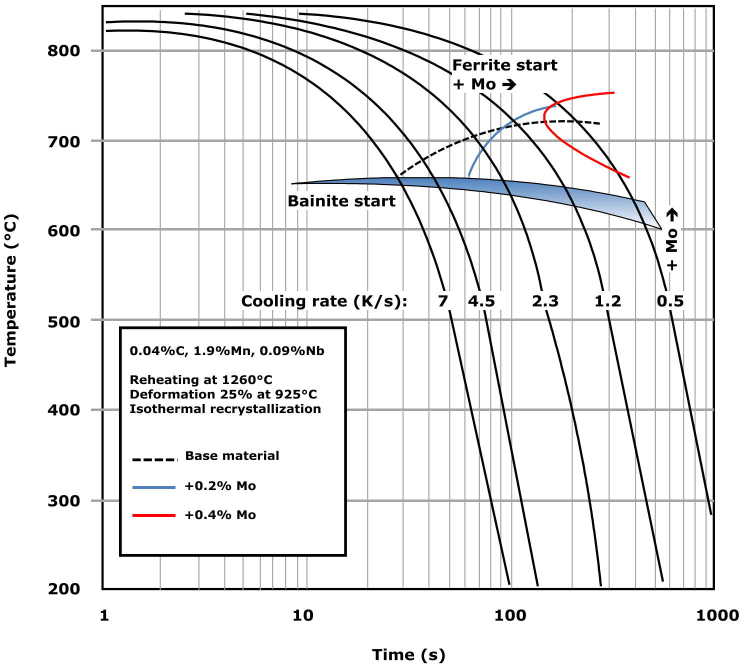

Figure 8. Influence of Mo content on transformation behavior of low-carbon 0.09%Nb steels (base: 0.04%C-MnCuNi).

The higher niobium (0.10%), molybdenum combination is particularly useful for production of spiral seam linepipe since strip mill rolling reductions tend to be limited compared with plate mill processing.

Recent examples have been presented by Salzgitter [17] for 14, 18.8 and 25 mm skelp. Data for 18.8 mm skelp are shown in Table IV.

Table IV. Chemical Composition for 18.8 mm Skelp wt%

C	Mn	Si	Nb	Ti	Mo	Cr	Al	N
0.05	1.78	0.31	0.092	0.018	0.12	0.18	0.04	0.004

Slabs 253 x 1550 mm cast using soft reduction were free of edge cracks and required no flame scarfing thereby permitting hot charging. A transfer bar size of 52 mm was utilized and the finish rolling temperature was 820-835 °C. Mechanical properties for the above and related trials are presented in Figure 9.

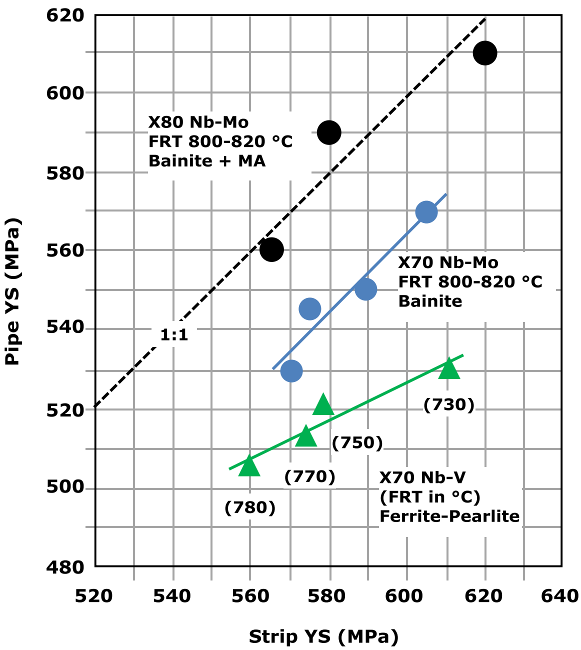

Figure 9. Influence of alloying concept and microstructure on the yield strength in as-rolled material and flattened pipe sample.

The low carbon Nb-Mo concept is appealing to the strip mill operator since the higher rolling temperatures for the HTP concept lead to less wear on rolls and bearings, reduced risk of mill overload, reduced load on the crop shear and generally faster processing time. The economic benefits claimed by the authors [17] are presented below:

Economic Comparison for Low Carbon 0.10 Percent Niobium versus Conventional Nb-V Concept

- Moderately higher alloying cost.
- Lower CE_{IIW} (-2 points) and P_{cm} (-5 points).
- Can be cast with a slab width bigger than the required final strip width:
  ⇒ Increased continuous casting capacity.
- Bending properties in the hot strand are improved:
  ⇒ Flame scarfing can be eliminated.
  ⇒ Hot charging becomes possible.
- Enhanced solubility of microalloying elements due to low C:
  ⇒ Reduced slab residence time in reheating furnace.
- High delivery temperatures after discharging from the furnace:
  ⇒ Slab width reduction of up to 300 mm in the sizing press.
- Increased processing temperatures due to higher T_{NR}:
  ⇒ Entire sequence of hot rolling is accelerated.
  ⇒ Larger processing window along the entire process chain from slab to pipe.
- Lower plastic deformation resistance at increased finishing temperature:
  ⇒ Higher rolling temperatures and shortened production times can be achieved.
  ⇒ Reduced wear on bearings, drives and rolls as well as crop shear.
- Wide bainitic (AF) range in the CCT:
  ⇒ Increases processing window on the run-out table / down coiler.
  ⇒ Enables synergies between microstructural and precipitation strengthening.
  ⇒ Reduces production complexity.

The discussion thus far concerning the benefits of the Nb-Mo synergy has concentrated on their combined effect in lowering the A_{r3} temperature. However, there is also a strong yet subtle effect related to the formation of $NbMo_4C_3$ carbides after transformation. A small amount of molybdenum (0.08–0.12%) dramatically increases the volume fraction of NbC type precipitation. This phenomenon was extensively studied by Kanazawa et al in the early 1960s [3,4]. The Nb-Mo-C ternary referenced in their publication(s) is presented below [17]. Examples of recent utilization of the concept will be presented later.

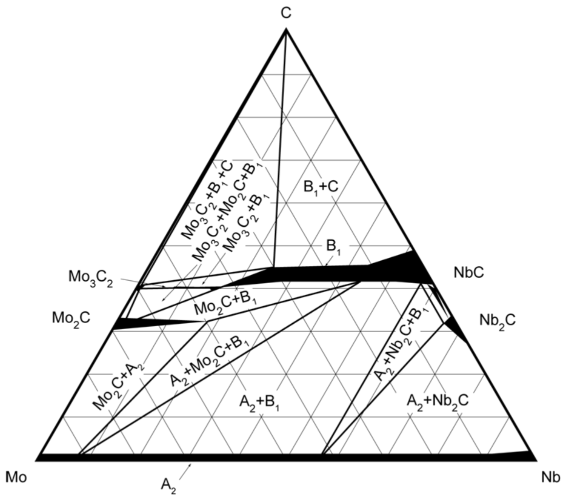

Figure 10. Phase diagram of Nb-Mo-C alloy at 1900 °F (1038 °C) (by Rudy [18]).

The use of niobium contents of 0.10 percent is not a recent phenomenon, although the trend towards 550 MPa (X80) designs has stimulated recent applications. A few milestones are presented in Table V below.

Table V. Commercialization of HTP Linepipe

Year	**Manufacturer**	**Maximum Niobium Content**	**Project**
1972	IPSCO	0.07 – 0.11	TCPL-Nova
1974	Algoma Steel-Canadian Phoenix	0.14	TCPL
1975	Hoesch	0.15	MA-75
1980	Hoesch	0.10	Czech Republic
1998	ArcelorMittal – PMT	0.095	Pemex (Cantarell)
2004	OSM – Napa Pipe	0.095	El Paso (Cheyenne Plains)
2005	Angang – Julong (JCO)	0.10	CNPC (X-70) First West East Project
2008	Multiple (7-8) Mills	0.11	CNPC (X-80) Second West East Project

The rapid growth of high quality linepipe manufacture is presented in Figure 11.

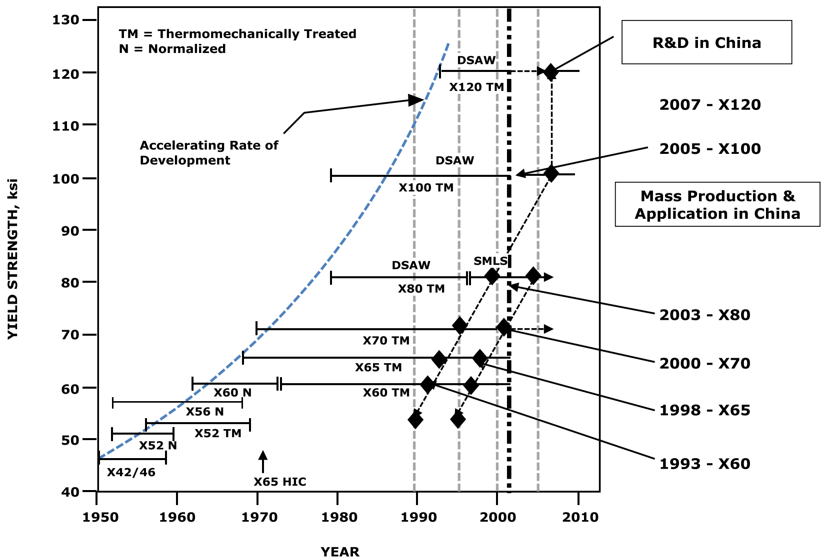

Figure 11. Development of high strength linepipe capability in China.

The most recent examples of Nb and Nb-Mo alloying as practiced in China have been presented in numerous papers at recent conferences [19,20] and several are summarized in Table VI.

Table VI. Chemical Compositions of Chinese Hot Rolled Coils API Grade X80 (550 MPa) [18]

Mill Name	C	Mn	Cr	Mo	Nb	V	Ti	N	Thickness
N. China Petroleum	0.06	1.88	-	0.33	0.056	-	0.023	0.005	14.6 mm
	0.07	1.89	-	0.24	0.055	0.05	0.011	0.004	14.6 mm
Jining	0.04	1.80	-	0.28	0.070	-	0.011	N.R.	18.4 mm
From TGRC Paper*	0.046	1.81	0.18	0.31	0.062	0.005	0.009	N.R.	18.4 mm
Angang	0.04	1.88	0.27	0.10	0.10	-	0.012	0.005	18.4 mm
Shougang	0.04	1.80	0.30	0.15	0.095	-	0.015	N.R.	18. 4 mm
Nanjing	0.045	1.82	0.27	0.12	0.092	-	0.012	N.R.	18.4 mm

*Tubular Goods Research Center of the China National Petroleum Corporation
N.R. – Not Reported

The route map(s) for the First and Second West-East Pipeline Projects are presented in Figure 12. The overall length of the Second Pipeline is 9226 km of which the mainline used 4770 km of 48" OD x 18.4 mm API Grade 550 MPa (X80) with the balance 42" OD API Grade 485 MPa (X70). Approximately 72 percent of the linepipe was manufactured using the spiral seam route, truly an impressive performance after only 10 years of serious Chinese pipelining. The future is likely to be even more impressive as plans emerge for the third, fourth and even sixth and seventh massive projects.

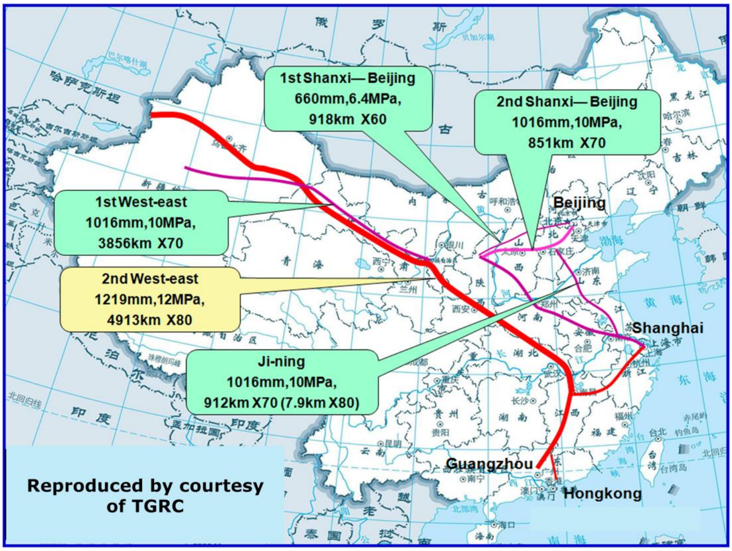

Figure 12. Recently installed pipeline systems in China.

Conclusions

There is a well documented strong synergistic effect of niobium and molybdenum on the austenite to ferrite transformation temperature which produces bainitic microstructures at relatively slow cooling rates. The effect is enhanced by reduction in carbon contents to 0.06 percent and below and by increasing niobium contents to close to the stoichiometric ratio with carbon and nitrogen.

The concept was first introduced commercially in 1971/2 by Canadian produced X70 linepipe installed in the TransCanada and Novacorp pipeline systems. The strengths levels have since moved up incrementally to X80, X100 and X120, but the latter two API 5L/ISO 3183 Grades have yet to find significant commercial usage. It is likely that the ultra-low carbon niobium-molybdenum alloying approach will continue to find favor amongst both producers and end users based on the achievable strength, toughness, weldability and fracture arrest characteristics, all combined with relative ease of manufacture compared with the traditional Nb-V alloying approach.

References

1. E.C. Hamre and A.M. Gilroy-Scott, "Properties of Acicular Ferrite Steels for Large Diameter Linepipe," *Proceedings of Microalloying 75, International Symposium on High-strength, Low-alloy Steels,* Washington, DC, (1-3 October 1975), 375-381.

2. P. Maitrepierre et al., "Transformation Characteristics and Properties of Low-carbon Niobium-boron Steels," *Memoires Scientifiques de la Revue de Metallurgie,* (5 June 1978), 355-369.

3. S. Kanazawa et al., "Combined Effect of Nb and Mo on the Mechanical Properties of Nb-Mo Heat-treated High Strength Steel with 80 kg/mm^2 Strength Level," *Transactions of the Japan Institute of Metals,* 8 (2) (1967), 105-112.

4. S. Kanazawa et al., "On the Behavior of Precipitates in the Nb-Mo Heat-treated High Strength Steel having 80 kg/mm^2 Tensile Strength," *Journal of the Japan Institute of Metals,* 31 (171) (1962), 113-120.

5. J.M. Gray, "Mechanical Properties and Microstructure of Low-carbon Hot Rolled High Strength Low Alloy Steels" (Report 89-018-015 (1), U.S. Steel, 28 November 1969).

6. P.E. Repas, "Evaluation of Plate and Sheet Products from 30 Ton BOF Heats of an Experimental Mn-Ni-Cb-Mo-B Steel" (Report 89-018-011 (6), U.S. Steel Research Center, 28 May, 1971).

7. A.P. Coldren et al., "Microstructure and Properties of Low Carbon Mn-Mo-Cb Steels," *Proceedings of Processing and Properties of Low Carbon Steels, The Metallurgical Society of AIME,* New York, (1973).

8. G. Tither, A.P. Coldren, and J.L. Mihelich, "Influence of Processing on Properties of Molybdenum Steels for Pipeline" (Paper presented at the CIM Annual Conference of Metallurgists, Toronto, Canada, 25-28 August 1974).

9. R.L. Cryderman et al., "The Development of High Strength Hot-Rolled Mn-Mo-Cb Steel" (Paper presented at the 14th Mechanical Working and Steel Processing Conference, Iron and Steel Div. AIME, Chicago, Illinois, 19 January 1972), volume X, 114.

10. X. Dianxiu, S. Chengjia, and S. Weihue, "Microstructure and Mechanical Properties of X100 Grade High Strength Linepipe," *Proceedings of the Third International Seminar on High Strength Linepipe,* Xi'an, China, (28-29 June 2010), 81-85.

11. L. Yang, Z. Weiwei, and G. Shaotao, “Tensile Properties and Strain Ageing of X100 Pipeline Steel” ibid, 86-95.

12. L. Shaopo et al., “Development of X100 Pipeline Plates using TMCP and Tempering Technology” ibid, 235-238.

13. J.M. Gray, W.W. Wilkening, and L.G. Russell, “Transformation Characteristics of Very-low Carbon Steel” (Report 89-002-015 (3), US Steel, 15 May, 1969).

14. K. Taeffner et al., “Technology of Hot Strip and Plate Production for Large Diameter Line Pipe,” *Proceedings of Microalloying 75,* Washington, DC, (1-3 October 1975), 425-434.

15. M. LaFrance et al., “Use of Microalloyed Steels in the Manufacture of Controlled-rolled Plates for Pipe,” *Proceedings of Microalloying 75,* Washington, DC, (1-3 October 1975), 367-373.

16. M. Civallero, C. Parrini, and N. Pizzimenti, “Production of Large-diameter High-strength Low-alloy Pipe in Italy,” *Proceedings of Microalloying 75,* Washington, DC, (1-3 October 1975), 451-468.

17. S. Bremer, V. Flaxa, and F. Knoop, “A Novel Alloying Concept for Thermo-mechanical Hot-rolled Strip for Large Diameter HTS (Helical Two Step) Line Pipe,” *Proceedings of ASME 7th International Pipeline Conference 2008,* Calgary, Alberta, Canada, (29 September–3 October 2008), 489-495.

18. E. Rudy, Monatshefte für Chemie 92, volume 4, 846.

19. *Proceedings of CNPC Tubular Goods Research Institute 2nd International Seminar on X80 and Higher Grade Line Pipe Steel 2008,* Xi'an, China, (23-24 June 2008).

20. *Proceedings of 3rd (CNPC) International Seminar on High Strength Linepipe 2010,* Xi'an, China, (28-29 June 2010).