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On the processing of Fe–C–Mn–Nb steels to produce plates for pipelines with sour gas resistance

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Abstract

Several steel plates in the as-hot rolled plus cooled condition were studied, in order to evaluate the impact of the steelmaking route and the controlled thermomechanical processing plus the cooling media, on the resulting microstructure and mechanical properties of steel plates, which will be processed to produce large diameter steel pipes with sour gas resistance. The steelmaking route to produce the slabs involved the use of 100% sponge iron which was feed into an electric arc furnace, vacuum degassed, ladle treated and continuously casted. After soaking, a controlled thermomechanical processing schedule was applied to steel slabs followed by air or accelerated cooling of plates. Most of the resulting steel plates cooled in air showed a banded structure, which sometimes presented a central segregation region. The worst plates with a central segregation region showed intermetallics compounds in it. After modifications of the steelmaking route and to the controlled thermomechanical/cooling schedule, a steel plate with a ferritic microstructure plus 0.5 vol% of bainite was obtained. This microstructure together with the resulting mechanical properties, fulfilled the API grade 5L X-70 properties, required in modern steel pipes demanded by the oil industry.

Keywords: Thermomechanical processing; Steels; Pipeline; Microstructure; Mechanical properties

1. Introduction

Nowadays, the demand of high strength steels for pipeline with sour gas resistance has increased. It has been pointed out that manufacturing this kind of steel pipe requires a strict steelmaking practice and a controlled thermomechanical schedule with an additional accelerated cooling procedure [1]. With regards to the steelmaking practice, it has been mentioned that worldwide developments have allowed the production of steels with microalloying constituents which are controlled in mass parts per million [2], allowing better response to further processing. For instance, reducing carbon contents (<0.05 wt.%) improves weldability and reduce heat affected zone hardness. Low sulfur contents improve hydrogen induced cracking and low phosphorous contents reduces the hardening tendency of segregated regions. Sulfide shape control is also advised, in order to improve notch toughness and resistance to sour gas degradation of pipelines [3].

Regarding steel chemistry, this needs to be designed in order to respond to the controlled thermomechanical processing together with the accelerated cooling procedures to achieve the required yield strength and toughness of modern steel pipes demanded by the oil industry. For instance, one of the most relevant applications of controlled rolled steels is plate skelp for diameter pipes up to 36 inches, where the API grade 5L X-70 steel has become the major applied steel grade. The steel chemistry that fulfil the mechanical properties equivalent to API grade 5L X-70 steel with sour gas resistance has been of the Fe–C–Mn–Nb type, and for that reason, several studies have been carried out in order to correlate niobium contents with controlled rolling schedules [4,5] plus the effect of accelerated cooling [6] in order to achieve two goals: sour gas resistance and X-

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70 and/or X-80 properties [5,7]. This work reports results on experimental trials to produce and to process a steel of the Fe–C–Mn–Nb type capable to respond to the controlled thermomechanical processing/cooling schedule of steel plates which can fulfill the API grade 5L X-70 properties.

2. Experimental procedure

In order to study the impact of steel chemistry and thermomechanical processing of resulting steel plates, several API grade 5L X-70 steel plates were analyzed with a nominal composition shown in Table 1. The steelmaking route to produce the slabs involved the use of 100% sponge iron which was fed into an electric arc furnace, vacuum degassed, ladle treated and continuously casted.

The controlled thermomechanical processing involved the rough rolling of slabs in the range of temperatures between 1200 and 1020 °C, where deformation, recovery and recrystallization of γ-grains take place. This controlled rolling procedure took advantage of niobium additions, which precipitates out as fine niobium carbonitrides at lower temperatures in the austenite range, stabilizing the deformation substructure of the elongated γ-grains and preventing or at least retarding recrystallization.

The final rolling procedure started at $\sim$1020 °C and finished at about 790 °C or at $\sim$890 °C. The resulting plates, where the final rolling pass ended at $\sim$790 °C, were air cooled to room temperature. The resulting plates where the final rolling pass ended at $\sim$890 °C, were immediately accelerated cooled until a temperature of $\sim$670 °C was reached ($\sim$6 °C s^{-1}) and then they were air cooled to room temperature.

Microstructure characterization of the steel plates was carried out using a Stereoscan 440 scanning electron microscope. Electron probe microanalysis (Philips 1200) and thermogravimetric analysis (Cole Palmer) were used to characterize central segregation regions of steel plates. Tensile tests on the steel plates were carried out in an Instron 1125 testing machine, using flat specimens. During the experiments a crosshead speed of 5.0 mm min^{-1} was employed. V-notch charpy tests were also carried out. Both tests were performed according to the standard ASTM A-370.

3. Results and discussion

In order to identify the effects of the adopted steelmaking practice to produce the slabs and the thermomechanical processing/cooling schedule to produce the plates, several steel plates were analyzed. For instance, Fig. 1 shows a set of different microstructures observed in the analyzed steel plates. As can be seen, the microstructure consisted of: (i) ferrite grains with a low content of bainite (Fig. 1a); (ii) a ferrite microstructure with some patches of pearlite (Fig. 1b); (iii) a microstructure consisting of ferrite and pearlite bands (Fig. 1c); (iv) a banded microstructure with the presence of a slightly central segregation region (Fig. 1d); (v) a banded microstructure with a central segregation region (Fig. 1e); and (vi) a banded microstructure with a heavy central segregation region plus intermetallic in it (Fig. 1f). The microstructures observed in Fig. 1c–f were obtained after applying a controlled rough rolling schedule, in the range of temperatures between 1200 and 1020 °C, followed by a controlled final rolling schedule in the range of temperatures between 1020 and 790 °C and then, the plates were let to cool in air, until room temperature was reached. The microstructures observed in Fig. 1a,b were obtained after modifying the steelmaking practice, applying the same rough rolling schedule (as above) to slabs, followed by a controlled final rolling process in the range of temperatures between 1020 and 890 °C, accelerated cooled from 890 to 660 °C (6 °C s^{-1}) and air cooled to room temperature.

Additional data of the structure observed in Fig. 1 is shown in Table 2, for instance, the ferrite grain size was almost constant but the per cent of pearlite increased up to 10.8%. This amount of pearlite could depend on both; the chemical composition of the steel and its cooling rate during solidification (microsegregation). For instance, in areas of high concentration of elements (i.e. C and Mn), pearlite will be formed after reaching the Ar_1 temperature, giving rise to ferrite–pearlite bands after rolling. Macrosegregation was observed as a centerline segregation, and in some samples, a heavy central segregation region was detected.

Regarding results of the analysis of the central segregation region, Fig. 2d shows the distribution of concentrations of manganese and chromium as they occur in centerline segregation of plates. As can be seen, the manganese content has a nominal composition of approximately 1.5 wt.% in ferrite at both ends of central

Table 1
Nominal composition of API 5L X-70 heats under study (in wt.%)

C	Mn	Si	S	P	Al	Nb	Cu	Cr	Ni	Ti	Ca	N_2
0.037	1.50	0.14	< 0.003	< 0.015	0.03	0.09	0.27	0.26	0.16	0.010	0.0025	0.0040

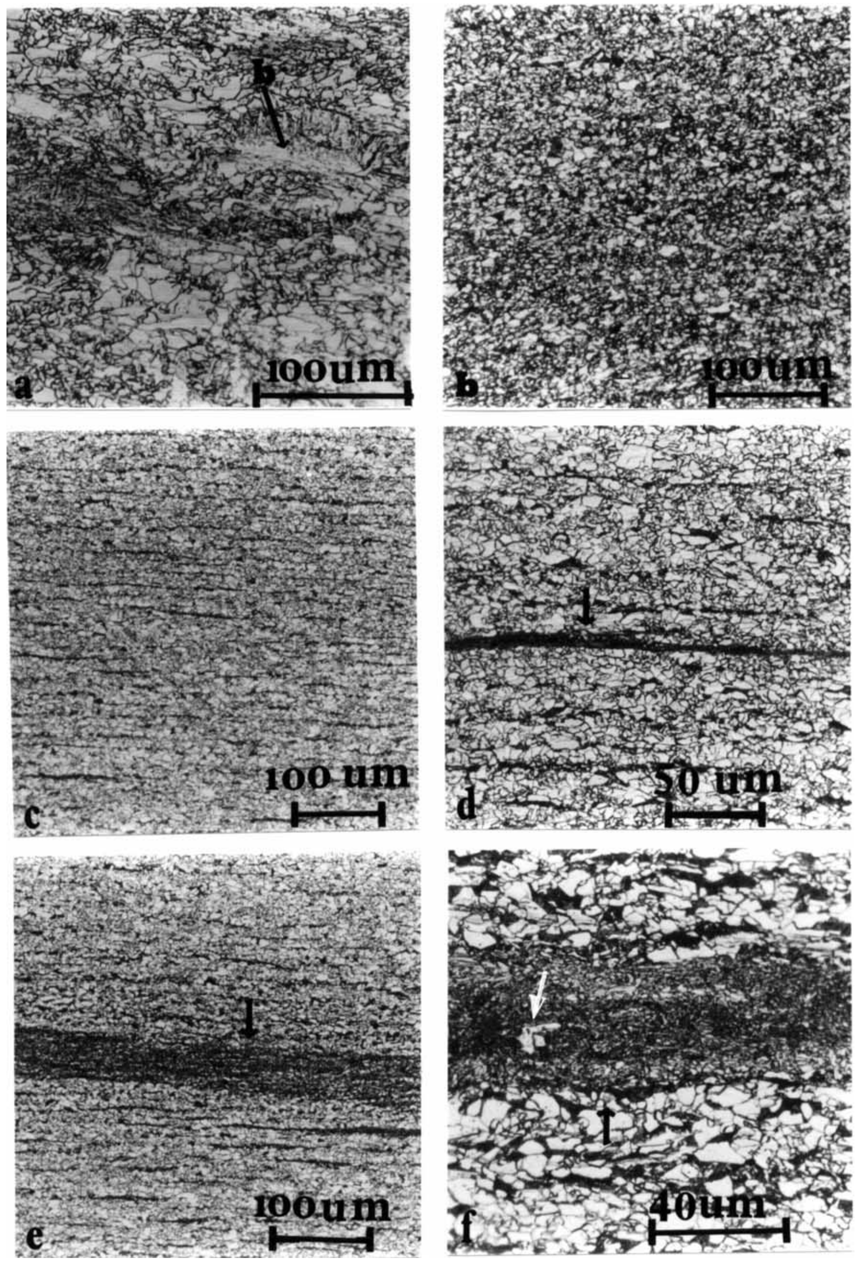

Fig. 1. A set of different microstructures observed in the steel plates under study. (a) Ferrite grains with some bainite grains (marked with b), (b) ferrite grains with patches of pearlite, (c) ferrite and pearlite bands, (d) a banded microstructure with the presence of a slightly central segregation region (shown by an arrow), (e) a banded microstructure with a central segregation region and (f) a banded microstructure with a heavy central segregation region plus intermetallic in it (shown by a white arrow).

segregation, increasing up to 2.35 wt.% in areas across the band itself where the main microstructure is pearlite. Chromium content increased too, from 0.25 to 0.35 wt.%. No other elements were detected to be segregated in central areas. In addition, cubic-like intermetallics were observed in central segregation regions. These intermetallics were identified by means of WDX microanalysis and thermogravimetric analysis as the intermetallic Fe_2Nb (Fig. 3). Non-metallic inclusions were randomly distributed in the steel plate and rarely observed in central segregation regions. These non-metallic inclusions with a spherical morphology were identified as $CaO \cdot Al_2O_3$ by means of EDAX microanalysis.

As was expected, the worst mechanical properties were obtained in samples with a heavy central segregation region plus the presence of intermetallic compounds in it (see Table 3). Therefore, the next action was to

Table 2
Analysis of microstructure showed in Fig. 1

Structure	Ferrite G.S. (μm)	Pearlite (%)	Bainite (%)	Thickness of central segregation (μm)	Intermetallics
Ferrite + bainite (1a)[a]	11.45	None	< 0.5%	None	None
Ferrite + patches of pearlite (1b)[a]	12.74	4.2	None	None	None
Banded structure (1c)[b]	13.37	8.4	None	None	None
Banded structure + slightly central segregation (1d)[b]	11.45	8.9	None	3.4	None
Banded structure + central segregation (1e)[b]	12.86	9.3	None	8.9	None
Banded structure + heavy central segregation (1f)[b]	12.14	10.8	None	10.5	Fe_2Nb

[a] Rough rolling (1200–1020 °C); final rolling (1020–790 °C) and accelerated water cooling to 660 °C and the cool in air until to room is reached.
[b] Rough rolling (1200–1020 °C); final rolling (1020–890 °C) and cool in air until room temperature is reached.

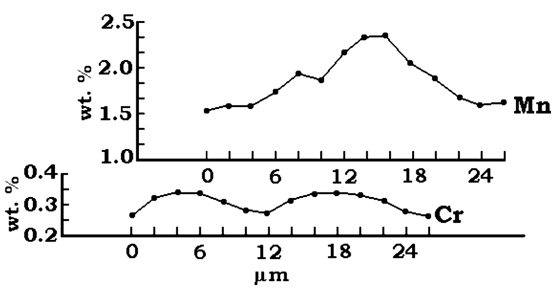

Fig. 2. Distribution of concentrations of manganese and chromium as they occur in centerline segregation of plates for Fig. 1e. It was

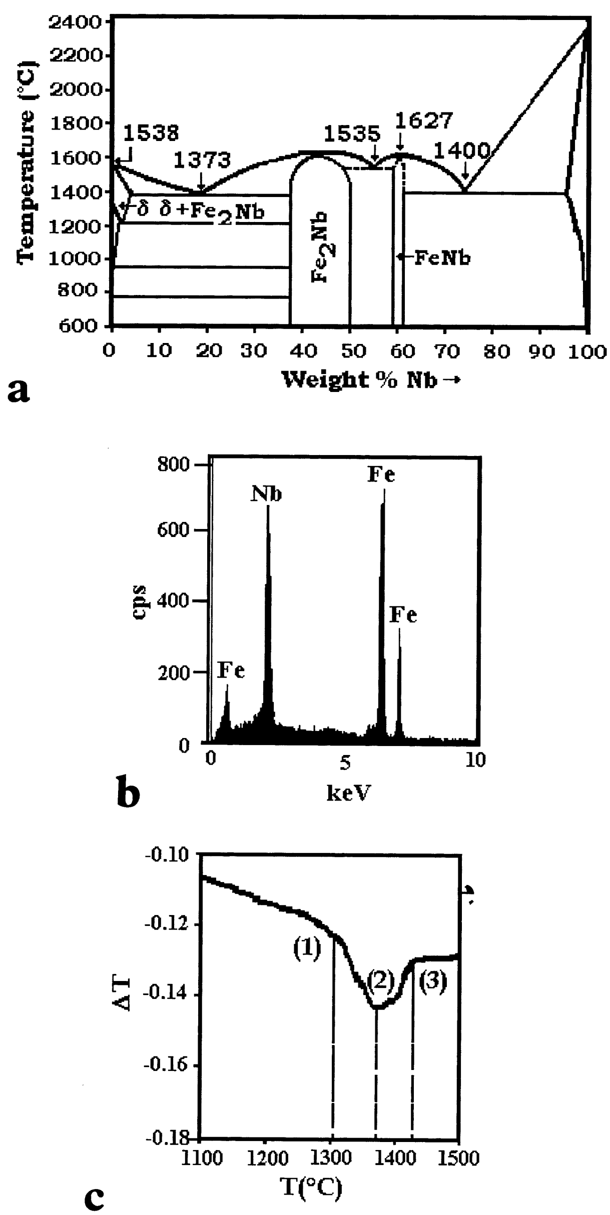

Fig. 3. (a) Fe–Nb phase diagram, (b) plot of counts vs. keV for the intermetallics observed in centerline segregation, (c) plot of temperature difference versus temperature obtained in TGA experiments (1 = 1310 °C, 2 = 1377 °C, 3 = 1425 °C). The temperatures indicated the beginning and end of Fe_2Nb precipitation.

modify the steelmaking practice because the steel chemistry was designed to obtain low levels of sulfur, oxygen and nitrogen, relying on maximization of niobium solute concentration during austenite processing to obtain high strength levels, also the low phosphorus content and the calcium-treatment in the steel together with the finishing rolling temperatures/cooling procedures where chosen to produce an uniform microstructure.

Two modifications in the steelmaking practice were adopted: (i) it was determined the melting point of the employed FeNb–ferroalloy in order to be added at temperatures above its melting point. For instance, before this analysis, the ferroniobiun (Fe–60 wt.% Nb) was added to the liquid steel at a temperature of ~ 1580 °C, however, the determined melting point of this ferroalloy was ~1627 °C, therefore, during ladle additions of the ferroalloy, this was partially melted and due to its density (~8.3 g cm^{-3}), the ferroalloy was drawn to the bottom of the ladle and intermetallics of the Fe_2Nb-type were formed and located in the center of the slab. Therefore, the Nb content in the FeNb–ferroalloy was increased from 60 to 70 wt.%, in order to decrease its melting point from 1627 to 1590 °C (see Fig. 3). During the steelmaking practice, the ferroalloy was added to a temperature of ~1600 °C. It was not longer detected the presence of this intermetallic, because of the complete dissolution of the FeNb–ferroalloy, ii) the

Table 3
Mechanical properties achieved in plates with central segregation

Required tensile properties for API grade 5L X-70 steel						
Yield Strength[a]		Ultimate tensile strength[b]		Elongation[c]		TCVN[d]
Trans. ksi (MPa))	Long., ksi (MPa	Trans. ksi (MPa	Long., ksi (MPa))	Trans. (%)	Long., (%)	lb-ft (J)
54.2 (373.4)	45.4 (312.8)	57.8 (398.2)	49.4 (340.3)	28	20	9 (12.2)
51.2 (352.7)	55.4 (381.7)	60.3 (415.4)	58.5 (403.0)	29	26	24 (32.6)

[a] Yield strength: transversal 67.7 ksi (460 MPa), longitudinal 63.8 ksi (440 MPa).
[b] Ultimate tensile strength: transversal 76.9 ksi (530 MPa), longitudinal 73.2 ksi (505 MPa).
[c] Elongation: transversal 32%, longitudinal 32%.
[d] Transverse charpy V-notch: 111 ft-lb (81.87 J) a −58 F (−50°C) at the centerline.

Table 4
Length of columnar and equiaxed region as a function of superheat for slabs of 25 cm in thickness (data is for half slab)

Superheat (°C) →, length of region (cm) ↓	20	30	40
Columnar	7.5	10.0	12.5
Equiaxed	5.0	2.5	–

liquid steel was casted with a maximum superheat of ~ 20 °C, decreasing the length of the columnar zone, allowing at the same time the formation of an equiaxed zone in the central region of the slab, giving rise to better distribution of the elements and the elimination of the heavy central segregation region (see Table 4).

With respect to the controlled hot rolling procedure, it can be mentioned that niobium was added (up to 0.09 wt.%) in order to maximize grain refinement and improve both strength and toughness, taking advantage that the final controlled rolling schedule was carried out in a temperature range where austenite will no longer recrystallize during multipass deformation [8,9].

Sellars [10] pointed out that to obtain an austenite microstructure that will produce a finest and uniform ferrite grain size on transformation, one possibility will be to produce deformed and elongated austenite grains by inhibiting recrystallization between passes using the effect of strain induced precipitates. The other possibility is to produce a fine fully recrystallized grain structure by finishing the rolling above the temperature for strain induced precipitation. The first option was applied to the steel under study. A maximum delay of 220 s was allowed between the end of the rough rolling schedule and the beginning of the finish rolling schedule, to reach a temperature of 1020 °C which permits strain induced precipitation of niobium carbonitrides [11], in order to reduce or suppress recrystallization before the beginning of the initial finish rolling schedule. Accelerated cooling of plates immediately after the last finish rolling pass will lead to ferrite grain refinement and finer precipitation of Nb(C, N). In the investigated steel composition, the final rolling schedule started at a temperature of ~1020 °C, to facilitate a proper conditioning of the austenite phase at relatively high rolling temperatures, enabling high solute niobium content at the finish rolling temperature. The best result is shown in Fig. 1a in terms of microstructure which corresponded to a finer grained ferrite with bainite as reported in Refs. [12,13]. During the controlled rolling schedule, plate steel properties equivalent to the API

Table 5
Mechanical properties achieved in plates in the as-controlled hot rolled plus accelerated cooled condition

Required tensile properties for API grade 5L X-70 steel						
Yield Strength[a]		Ultimate tensile strength[b]		Elongation[c]		TCVN[d]
Trans. ksi (MPa)	Long., ksi (MPa)	Trans. ksi (MPa)	Long., ksi (MPa)	Trans. (%)	Long., (%)	lb-ft (J)
74.5 (514.0)	67.5 (465.7)	82.5 (569.2)	79.0 (545.1)	54	32	299.0 (405.3)
75.0 (517.5)	68.0 (469.2)	82.0 (565.8)	78.5 (541.6)	48	33	216.6 (293.7)
72.0 (496.8)	67.5 (465.7)	80.5 (555.4)	78.0 (538.2)	57	31	217.0 (294.1)
75.0 (517.5)	70.0 (483.0)	83.0 (572.7)	80.5 (555.4)	60	34	299.0 (405.3)
73.5 (507.1)	73.0 (503.7)	81.0 (558.9)	82.5 (569.5)	60	27	299.0 (405.3)
71.0 (489.9)	73.5 (507.1)	82.0 (565.8)	83.5 (576.1)	60	27	287.6 (389.9)

[a] Yield strength: transversal 66.7 ksi (460 MPa), longitudinal 63.8 ksi (440 MPa).
[b] Ultimate tensile strength: transversal 76.9 ksi (530 MPa), longitudinal 73.2 ksi (505 MPa).
[c] Elongation: transversal 32%, longitudinal 32%.
[d] Transverse charpy V-notch: 111 ft-lb (81.87 J) a −58 F (−50°C) at the centerline.

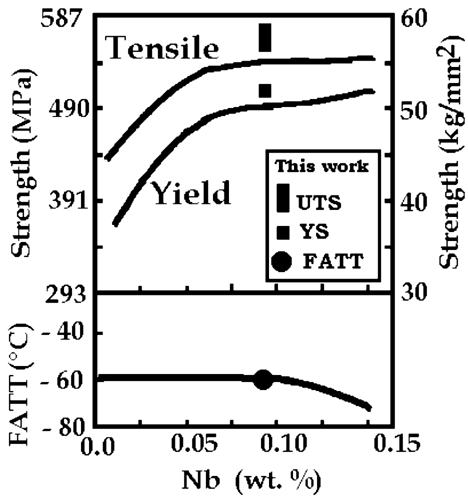

Fig. 4. Plot of mechanical properties vs. niobium content.

grade 5L X-65 were obtained after finishing at rolling temperatures below 800 °C followed by air cooling of the plates and with a microstructure similar to that shown in Fig. 1c. They did not reach the aimed API grade 5L X-70 steel properties. Then, after modifying the steelmaking practice and finishing at rolling temperatures of ~890 °C followed by an accelerated cooling (~6 °C s^{-1}), with an end cooling temperature of ~660 °C and then the steel plate was air cooled to room temperature, the achieved mechanical properties corresponded to the aimed API grade 5L X-70 steel, as shown in Table 5 and with a microstructure shown in Fig. 1a.

As was noticed, the resulting properties obtained during these trials were the result of the interrelationship between chemical composition and processing conditions. For instance Fig. 4 shows the effect of niobium content on the mechanical properties of 0.03 wt.% C, as reported in Ref. [14], together with the results obtained in this research. In spite that processing conditions were slightly different, both yield and tensile strength (for 0.09 wt.% Nb) corresponded to the API grade 5L X70 without deterioration of toughness.

4. Conclusions

1. The steelmaking practice to produce the API grade 5L X-70 steel was modified, to meet stringent requirements of sour service pipelines. This modification was carried out during ladle treatment of the steel and involved the proper addition of ferroalloys taking into account its melting point.
2. Heavy centerline segregation with the presence of intermetallics was avoided by adding the FeNb–ferroalloy at a temperature ≥1600 °C and casting the steel with a maximum superheat ~20 °C.
3. Mechanical properties of the steel under study fulfilled the required properties of the API grade 5L X-70, after applying a controlled thermomechanical rolling schedule plus an accelerated cooling procedure.
4. It was observed that niobium contents up to 0.09 wt.% in low interstitial steels generated outstanding properties even with rather high finishing rolling temperatures.

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