Development of microalloyed steel for pipeline applications

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An experimental HSLA steel was produced by the electric arc furnace, vacuum degassing, ladle treatment and continuous casting route. The experimental steel was then rolled in a laboratory using a hot rolling schedule to simulate an industrial controlled hot rolling procedure for the production of plates as closely as possible to investigate the effect of a thermomechanical processing schedule plus the use of water quench, accelerated cooling followed by forced nitrogen gas or air as cooling media, on the mechanical properties of plates. The results showed that the controlled thermomechanical hot rolling schedule of slabs followed by the cooling of plates in either forced nitrogen gas or by accelerated cooling exhibited target properties equivalent to a steel grade API X-80.

Keywords: HSLA steel, Pipeline steel, Thermomechanical processing, Accelerated cooling

Introduction

It has been pointed out that in order to achieve the stringent requirements of pipeline steels, technologies for the steelmaking, plate rolling and pipe making have been improved in order to achieve the feasibility of the production of high grade pipes for critical applications such as sour service, deep water and artic regions.[1] Regarding steelmaking, technologies in Mexico have allowed the production of clean steels by the electric arc furnace, vacuum degassing, ladle treatment and continuous casting route.[2] Production of slabs for pipeline steel grades has involved the control of interstitial and microalloying constituents in parts per million. The reduction in sulphur and phosphorous contents to low levels has reduced the risk of susceptibility of hydrogen inducing cracking and the hardening tendency of segregated regions respectively. The control of inclusion morphology has been achieved by calcium treatment. Soft reduction has also been incorporated during the continuous casting process in order to minimise centreline segregation.[3] With respect to plate rolling technologies, it has been reported that thermomechanically controlled rolling of steel slabs followed by controlled cooling of plates has provide some advantages over conventionally rolled steels, producing plates with a good combination of strength, toughness and weldability.[4] These improvements in properties have also been associated with different strengthening mechanisms, the most important of which is grain refinement, which can be obtained by the control of the rolling condition and by the addition of small quantities of microalloying elements. Here both strength and toughness are improved at the same time.[5] In addition, it can be mentioned that the chemistry of pipeline steels needs to be designed such that it responds to the controlled thermomechanical processing applied to steel slabs by producing an appropriate microstructure through the control of recrystallisation and transformation during rolling, together with a cooling procedure just after the last finish hot rolling pass to control and monitor the transfer time from finishing to cooling, the cooling rates and the cooling temperatures in order to achieve the required yield strength and toughness of modern pipelines demanded by the oil and gas industry.[6,7] The aim of the present work is to present preliminary results on the response of a C–Mn–Ti–Nb–Ni–Cu–Mo slab steel to a controlled hot rolling schedule followed by the application of several cooling media to the hot rolled plate and on the resulting microstructure and mechanical properties.

Experimental

The steelmaking practice adopted to develop either API X-70 5L or API X-80 5L steel grades is initiated by feeding 100% sponge iron to an electric arc furnace. At the end of the melting operation, deslagging was performed and the liquid steel was poured into a ladle furnace at 1680°C and immediately Al was added followed by the additions of electrolytic FeMn, FeNi, MoO_3 and $Ca(OH)_2$. The steel was then sent to the vacuum degassing unit to reduce C to <0·05 wt-% and hydrogen to <2 ppm. During the vacuum degassing process, Al, FeSi and CaF_2 were added and the chemical composition was adjusted by adding FeSi, FeNb, FeTi and CaSi. The resulting chemical composition of the continuously cast steel slab is 0·044C–0·271Si–1·69Mn–0·0091P–0·0016S–0·0103Cr–0·240Ni–0·001–0·2170Cu–0·25Mo–0·031Al–0·0001B–0·0554Nb–0·014Ti–0·007Sn–0·005As–0·0018Pb–0·0037Sb–0·0016Ca–0·0040N_2–0·406Ceq (wt-%).

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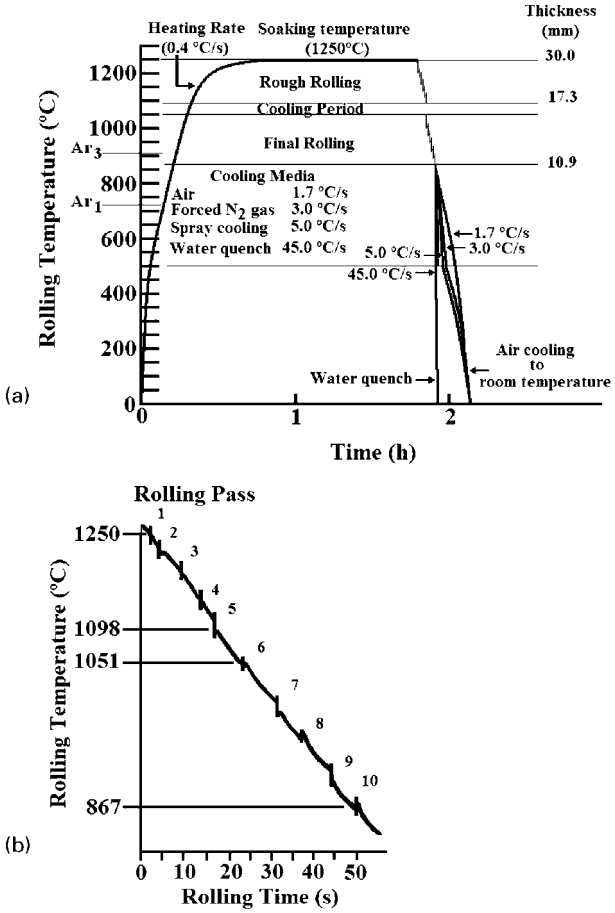
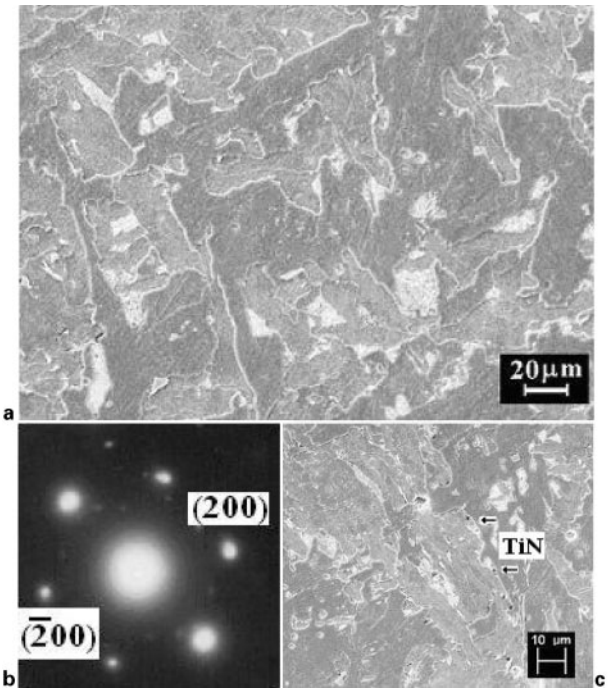


1 ***a*** **heating, soaking and rolling of slabs and cooling of plates in different media and** ***b*** **rolling procedure: steps from 1 to 5 corresponded to rough rolling and steps from 6 to 10 corresponded to final rolling procedure; between steps 5 and 6 there was cooling period until 1050°C**

The controlled hot rolling procedure was performed on a Fenn reversible mill (0·127 m roll, 25 tonnes load and 0·166 m s^{-1} rolling speed). Experimental steel samples of $0{\cdot}03 \times 0{\cdot}01 \times 0{\cdot}3$ m were heated at 1250°C at a heating rate of 0·4°C s^{-1}, soaked for 90 min and immediately hot rolled as shown schematically in Fig. 1. To control the temperature during the rolling and cooling operations, a Pt/Pt–13%Rh thermocouple was welded to one end of each specimen. The rough rolling of the slab was performed from 1250 to 1098°C in five passes, reaching 42·3% of total deformation and an average strain rate of 2·48 s^{-1}. This operation was followed by a cooling period until a temperature of 1051°C was reached. This temperature was taken regarding the solubility of niobium carbonitride in austenite as reported in the literature[8] according to equation (1)

$$\log[\mathrm{Nb}][\mathrm{C}+(12/14)\mathrm{N}] = 3{\cdot}97 - 8800/T \qquad (1)$$

For the steel composition under study a dissolution temperature for the Nb(C,N) of 1067°C was calculated. The final rolling procedure started at 1051°C and ended at 867°C, achieving a total deformation of 37% in five passes with an average strain rate of 2·98 s^{-1}. Immediately after the final rolling pass, the plates were cooled in air, in forced nitrogen gas and accelerated



2 ***a*** **as cast microstructure of steel under study,** ***b*** **electron diffraction pattern of TiN precipitates and** ***c*** **TiN precipitates in α-Fe matrix**

cooling or water quench. The second and third cooling procedures were performed from 867 to 650°C and then the plates were left to cool to room temperature. The microstructure of the resulting plates was observed under a scanning electron microscope (SEM) Stereoscan 440 and a scanning transmission electron microscope (STEM) Jeol 2100. Both microscopes were equipped with EDAX microanalysis. Flat tensile (ASTM E-8) tests were conducted on an Instron 1125 (10 t) test machine at a strain rate of 5×10^{-3} s^{-1}. Charpy V notch tests were performed according to ASTM A370. An optical microscope coupled to an image analyser was used for quantitative determination of grain size and volume fraction of bainite which was carried out by measuring ten fields per sample at ×100. This accounted for a total analysed area of ~6 mm^2 per specimen.

Results and discussion

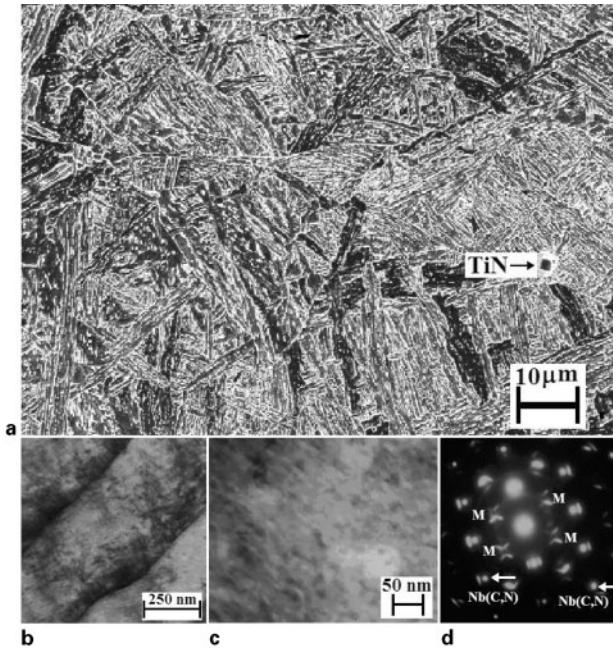
Scanning electron microscopic observations carried out in the slab revealed a microstructure which consisted mainly of ferrite grains with some TiN particles in the α-Fe matrix as shown in Fig. 2. These TiN precipitates were ⩽2 μm in size and identified by EDAX microanalysis. The temperature of precipitation of the TiN was calculated according to equation (2)[2]

$$\log(\mathrm{wt}-\%\mathrm{Ti})(\mathrm{wt}-\%\mathrm{N}) = -15\,200/T + 3{\cdot}9 \qquad (2)$$

For the Ti and N_2 contents of the experimental steel, a TiN precipitation temperature of 1564°C was obtained, which indicated that TiN particles were formed at the liquidus temperature of the steel.

The resulting microstructure after the controlled hot rolling of slabs and cooling of plates showed the following characteristics.

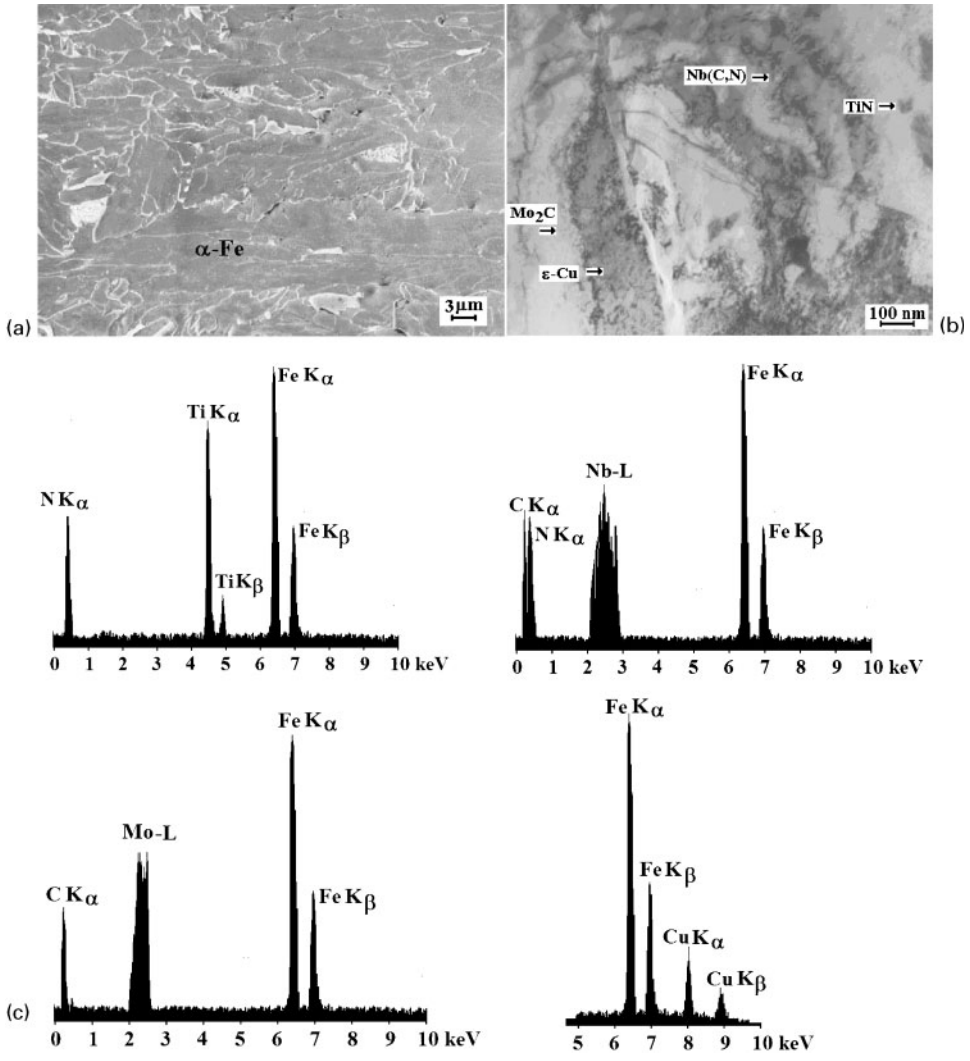
The hot rolled plates which were water quenched showed predominantly a martensite structure as shown



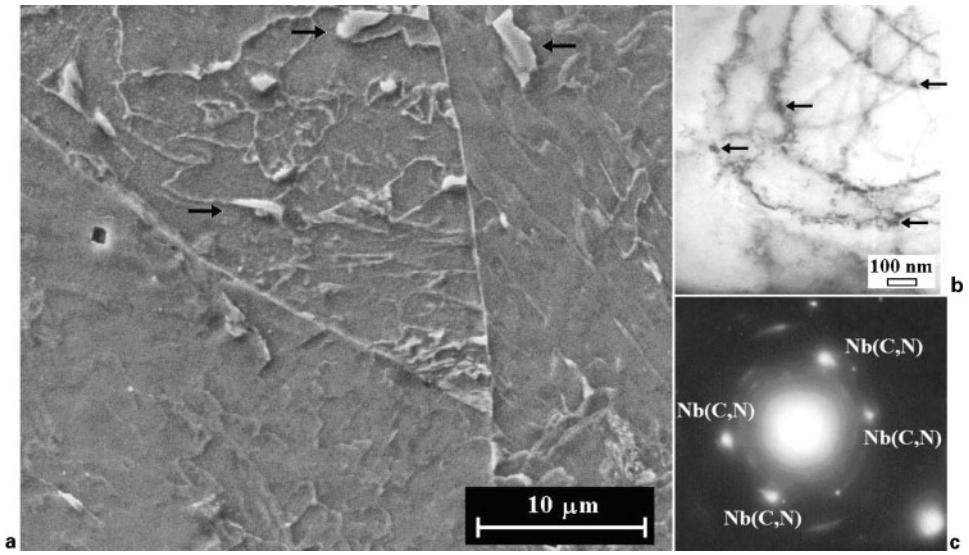
3 ***a*** **microstructure observed in plates which were hot rolled plus water quenched to room temperature,** ***b*** **martensite laths,** ***c*** **precipitates in martensite laths and** ***d*** **electron diffraction pattern in which presence of Nb(C,N) in martensite lathes is identified**

in Fig. 3, and with an average grain size measured in the rolling direction of 40 μm. Also the presence of rectangular/cuboids TiN (2 μm) particles was observed. De Ardo and co-workers[9] have observed this kind of larger size particles (size range up to 3 μm) and identified them as almost pure TiN. In martensite lathes the presence of precipitates which were identified by electron diffraction patterns as Nb(C,N) was observed. These precipitates showed an average particle size of 10 nm. Because niobium carbonitrides were the only observed precipitates under this cooling condition (apart from TiN), it was assumed that the alloying additions of Cu and Mo giving precipitation hardening were retained in solid solution after quenching. Ghosha *et al.*[10] and Akhlaghi and Ivey[11] studied the structure and properties of high strength steels, and under similar cooling conditions they reported only the presence of NbC and/or NbN, in agreement with the present results.

The microstructure observed in hot rolled plates which were air cooled to room temperature showed mainly a ferrite microstructure with some flattened ferrite grains closely parallel to the sheet plane (Fig. 4*a*), with grain size dimension measured in the rolling direction of 35 μm. During transmission electron microscopic (TEM) observations (Fig. 4*b*) the presence of several precipitates with particle sizes between 5 and 50 nm was detected, corresponding to the large TiN



4 ***a*** **microstructure observed in plates which were hot rolled plus air cooled to room temperature,** ***b*** **TEM photograph where precipitates were identified and** ***c*** **EDAX spectra of precipitates**



5 ***a*** **microstructure observed in plates which were hot rolled plus cooled in forced nitrogen gas, in which arrows show some patches of bainite,** ***b*** **TEM photograph where some precipitates were observed and showed by arrows and** ***c*** **electron diffraction pattern taken in areas of precipitates which identified them mainly as Nb(C,N)**

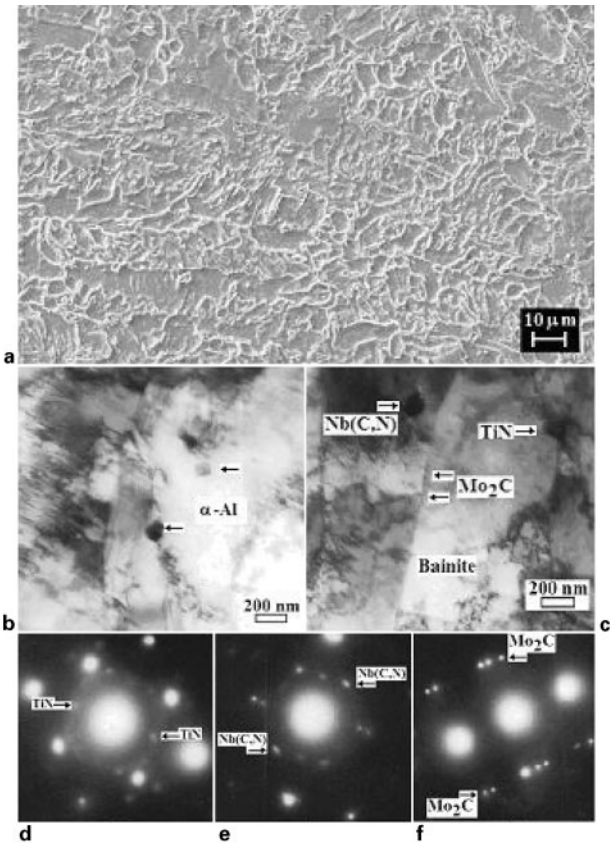
particles which were formed at the liquidus temperature of the steel. Identification of smaller precipitates was performed by means of STEM microanalysis as shown in Fig. 4*c*, which allowed to detect the presence of precipitates of the Nb(C,N), Mo_2C and the ε-Cu type. Nb(C,N) precipitates showed a size between 10 and 20 nm and the other precipitates showed sizes between 5 and 10 nm. The precipitation of these particles was reached because the relatively low cooling rate ($1{\cdot}7^{\circ}C\ s^{-1}$) was reached during the cooling of the plate in calm air.

Figure 5*a* shows the microstructure observed in specimens hot rolled and cooled in forced nitrogen gas, which consisted mainly of ferrite grains (with an average grain size of 10 μm, measured in the rolling direction) with some patches of bainite growing from ferrite grain and subgrain boundaries. During SEM observations the presence of TiN precipitates with a particle size <2 μm was detected. The TEM observations performed in this specimen showed the presence of small precipitates with a size of ~ 20 nm (Fig. 5*b*), which were identified mainly as Nb(C,N) by means of electron diffraction patterns (Fig. 5*c*).

The microstructure observed in specimens hot rolled plus accelerated cooled, consisted of ferrite plus bainite grains with an average grain size of 12 μm, measured in the rolling direction. Bainite developed in ferrite grain or subgrain boundaries. TEM observation performed in this specimen showed the presence of particles which were identified by means of electron diffraction patterns as TiN, Nb(C,N) and Mo_2C, as shown in Fig. 6.

Table 1 shows the mechanical properties reached after cooling the plates in different media and with reference to the target properties. The controlled hot rolling procedure accompanied by the cooling of plates by means of an accelerated cooling procedure reached target properties equivalent to an API X-80 steel grade.

As has been mentioned[12] that state of the art HSLA steels have a minimum yield strength of 550 MPa and are usually microalloyed with Ti and Nb, where Ti levels are high enough to form TiN to remove the N from solid solution and the excess of Ti is available to enhance precipitation strengthening of fine carbides formed by the microalloying elements. Nb additions play a critical role in delaying recrystallisation during the last stage of the hot rolling procedure. In the present work, both Ti



6 ***a*** **microstructure observed in plates which were hot rolled plus accelerated cooled,** ***b*** **TEM photograph of α-Fe grains with TiN and Nb(C,N) precipitates,** ***c*** **TEM photograph of bainite with TiN, Nb(C,N) and Mo_2C precipitates and** ***d***, ***e*** **and** ***f*** **electron diffraction pattern taken in areas of precipitates which were identified as TiN, Nb(C,N) and Mo_2C**

and Nb were observed as TiN and Nb(C,N) precipitates with a cubic and a more or less spherical morphology respectively. Other precipitates such as Mo_2C and ε-Cu were also identified. The optimum ratio of Ti/N for best grain refinement has been suggested to be close to the stoichiometry value of 3·42 : 1,[13] and in this work a Ti/N ratio of 3·5 : 1 was achieved.

Regarding the addition of Nb, it has profound effects on the improvement of properties through grain refinement and precipitation hardening.[14] In order to obtain these desirable effects, it is necessary to dissolve the Nb(C,N) during reheating of the slab and then to control its precipitation properly in the subsequent rolling and cooling process.[15,16] Here precipitation of Nb(C,N) was controlled during the thermomechanical processing of the slab by initiating the final rolling procedure at $\sim$1051°C, taking into account the Nb, C and N contents of the steel.

On the other hand, it has been mentioned[17] that the strengthening mechanisms for microalloyed steels (as in the present study) involve grain size, solid solution hardening, dislocation hardening, precipitation strengthening and transformation hardening. The relationship between yield strength and microstructure is not direct for this kind of steel. An estimate of the base yield strength in terms of chemical composition and grain size has been carried out using a relationship as shown in equation (3),[18] which is developed for plain carbon steels and used by researchers[19,20] to determine the yield strength in terms of C, Mn, Si and P additions, and grain size for microalloyed steels.

$$\sigma_{base} = \sigma_o + [15{\cdot}4 - 30C + 6{\cdot}094/(0{\cdot}8 + Mn)]d^{-1/2} \quad (3)$$

where $\sigma_o = 63 + 23Mn + 53Si + 700P$, giving a variation of yield stress ($\sigma_{base} = 123 + 6{\cdot}5d^{-1/2}$), which is close to $\sigma_{base} = 108 + 13{\cdot}6d^{-1/2}$ and $\sigma_{base} = 109 + 16{\cdot}2d^{-1/2}$ and is used during the structure/property analysis of similar microalloyed steel grades[12,21] respectively.

Then the base yield strength was calculated only for the steel sample which reached target properties (in the controlled hot rolling plus accelerated cooling condition) taking into account a final grain size of 12 μm (0·012 mm, measured in the rolling direction) and the corresponding C, Mn, Si and P additions (in wt-%). The grain size strengthening plus solid solution hardening mechanisms accounting for the base yield strength gave a value of 196 MPa.

Regarding the dislocation hardening contribution, it can be estimated using equation (4)[21]

$$\sigma_{disl} = \alpha M G b \rho^{1/2} \quad (4)$$

where α is a constant (0·3), M is the average Taylor factor for polycrystals (=3 for bcc crystals), b is the magnitude of the Burger's vector (0·248 nm), G is the shear modulus (81·6 GPa for Fe[9,22]) and ρ is the dislocation density. With an average value of $\rho = 8{\cdot}3 \times 10^{13}$ m^{-2} estimated by determining the number of dislocations in thin regions of the TEM foils of the accelerated cooled sample, a dislocation hardening contribution of 172 MPa was obtained.

Additional information has been reported in order to estimate the precipitation hardening contribution according to equation (5)[23–25]

$$\sigma_{pp} = (0{\cdot}538Gbf^{1/2}/X)(\ln X/2b)(\text{Ref}\cdot\ 10) \quad (5)$$

where f is the volume fraction of precipitates and equal to $0{\cdot}5 \times 10^{-3}$ for the accelerated cooled specimen with a corresponding average diameter of precipitates (X= 10 nm), giving a precipitation hardening contribution of 73 MPa.

The estimation of contribution to bainite transformation hardening can be derived according to equation (6)[21]

$$\sigma_{vs} = \sigma_{base} + \sigma_{dis} + \sigma_{ppt} + \sigma_{tranf} \quad (6)$$

Feeding the values for the grain size strengthening plus solid solution hardening, dislocation hardening and precipitation hardening mechanisms into equation (5), a value of 111 MPa for the bainite transformation hardening contribution was obtained.

As has been reported,[21] the estimation of contribution of all the strengthening mechanisms for microalloyed steels is not simple. However, the relationship between the microstructure and the yield strength of microalloyed steels can be expressed by equation (6). From the results of this analysis, it was quantified that grain size plus solid solution and dislocation hardening mechanisms contributed to 65% of the yield strength and 35% corresponded to precipitation and phase transformation hardening.

Regarding the steel grade under development, it can be mentioned that target properties of the resulting high strength ferrite–bainite steel were achieved through the application of a thermomechanically controlled hot rolling schedule followed by an accelerated cooling procedure ensuring values of 552 MPa of 0·2%YS, 638 MPa of UTS, 28·3% of elongation and 107 J of absorbed energy due to a contribution of grain size,

Table 1 Mechanical properties of plates cooled in different media

		0·2%YS		UTS			Charpy (−7°C)		
Cooling media	Cooling rate, °C s^{-1}	MPa	ksi	MPa	ksi	Elongation, %	Ft-lb	J	Grain size[¶], μm
W*	45	498	72·2	711	103·2	16·7	30	41	40
AC[†]	5	552	80·1	638	92·6	28·3	79	107	12
F[‡]	3	600	87·0	738	107·1	21·5	85	115	10
A[§]	1·7	498	72·2	592	85·9	27·0	31	107	35
Target		552–655	80–95	621–690	90–100	20_{min}	78	105	

*Water quench.
[†]Accelerated cooling.
[‡]Forced nitrogen gas.
[§]Air cooling.
[¶]Determined in the rolling direction.

solid solution hardening, dislocation hardening, precipitation strengthening and transformation hardening.

Conclusions

1. The chemical composition of the steel under study responded positively to the controlled thermomechanical processing and the applied cooling media allowing the target properties equivalent to a steel API X-80 5L grade to be reached.

2. After the hot rolling of slabs and depending on the cooling media used, the plates showed a microstructure which consisted of martensite (water quench), ferrite plus patches of bainite (forced nitrogen gas), ferrite plus bainite grains (accelerated cooling) and ferrite grains aligned parallel to the rolling direction (air).

3. Target properties achieved in plates showed a microstructure which consisted of ferrite plus bainite grains with an average grain size of 12 μm.

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