Influence of Niobium and Molybdenum on Mechanical Strength and Wear Resistance of Microalloyed Steels

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The HSLA (High-Strength Low Alloy) steels are used in the production of pipes, flanges and connectors to build ducts for ore, oil and gas transport. The conventional processes are the rolling or forging. In the transport of ore and heavy oil, the abrasive particles impair the surfaces and reduce the pipelines lifetime. Therefore, besides the mechanical properties as API 5L, it is important to verify the wear resistance of these steels. In this context, two microalloyed steels were forged in the form of square bars. Thereafter, specimens of these bars were annealed at 930 ºC, quenched at 900 ºC and tempered at 600 ºC. Tensile and wear tests were performed. The results show that molybdenum and niobium present similar effects on phase transformation of steels, promoting a desired acicular ferrite/bainite microstructure and fulfill the mechanical strength of API 5L-X70 standard. The molybdenum has dominating effect in the hardenability when in solid solution, however, after tempering, thermodynamic simulation by FactSage software indicates that niobium probably promotes secondary hardening.

Keywords: *Steels containing niobium and molybdenum, Heat treatments, Mechanical strength of microalloyed steels, Wear tests of microalloyed steels, FactSage software*

1. Introduction

API (American Petroleum Institute) steels are used on a large scale, mainly in the construction of pipelines and accessories to transport oil and natural gas. These pipelines operate at great depths and withstand pressures up to 350 bar in the presence of chlorides, sulfides and other dissolved ions[1]. API steels are also used in the ore transportation; however, the inner walls of the pipes have low wear resistance, when in contact with slurries and abrasive particles[2,3].

The conventional processing of API steels by rolling and forging allow a wide range of thicknesses with control of temperature and plastic deformation during the mechanical forming stages[4]. In forged materials, quenching and tempering heat treatments are necessary to achieve the required mechanical properties.

The grain refining associated to the precipitation hardening by carbides, nitrides and carbonitrides finely dispersed in the matrix are used to increase the mechanical properties. These microalloyed steels usually contain niobium, titanium and vanadium, which ensure good toughness and high tensile strength[5,6]. Additionally, the heat treatment control of microalloyed steels forgings leads to the formation of non-polygonal or acicular ferrite as well as bainite, which further contribute to strengthening[7].

Another chemical element used in these steels is the molybdenum that favors the generation of bainite at relatively low cooling rates and promotes a finer microstructure[8,9]. Molybdenum, together with chromium, plays a unique and important role both by having a marked decreasing effect on the austenite transformation temperature and by forming various carbides with complex constitutions in the steels[10]. Studies have shown that chromium and molybdenum introduce different stoichiometry of carbides according to the chemical composition of the steels[11]. Therefore, in industrial process, adding some molybdenum is a good choice to meet the requirement of strength. The refinement of austenite grains, the microstructure with grain boundary allotriomorphic ferrite, granular bainite and a uniformly dispersion of precipitates in the steel matrix are key aspects in the improvement of mechanical properties, hardness and wear resistance[9,12]. It has been asserted that HSLA steels containing niobium and molybdenum produce a acicular ferritic/bainitic structure with excellent strength-retention characteristics at high temperatures in the range of 600 to

700 ºC, in comparison to conventional HSLA steels containing niobium and vanadium[11,13].

The equipment and tools produced with microalloyed steels forgings are commonly subjected to abrasion by soil, sand, ore powder and so on during service[4]. The wear is mainly controlled by the microscopic stress distribution and microstructure in the contact region[12]. The utilization of proper materials and suitable heat treatment can enhance the wear resistance under the low stress abrasion and improve the service life of the relevant machinery.

Therefore, the present research aims to investigate the hardness, mechanical strength, wear coefficient and corresponding microstructures of microalloyed steels with different levels of niobium and molybdenum after quenching and tempering. In order to understand the effects of carbide precipitation in controlling the grain size, thermodynamic simulations with FactSage software were carried out to analyze the type and solubility temperatures of the precipitates formed in these steels.

2. Experimental Procedures

Two steels were manufactured in an induction furnace with a capacity of 200 kg. The liquid metal was poured into an ingot mold of cast iron with approximate size of 85x85x800 mm. The cast ingot was heated at 1050 ºC for two hours and forged in the form of square bars with 38 mm side. Two samples were obtained and analyzed in an optical emission spectrometer to determinate the chemical composition. The forged bars were heated at 930 ºC and cooled inside the furnace to homogenize the microstructure. Cubic specimens with side 15 mm and samples in longitudinal orientation with 15x15x100 mm, were cut and machined according to ASTM E8/E8M to be used in the tensile tests. All specimens were heated at 900 ºC for 30 minutes and cooled in water. Then, they were tempered at 600 ºC for 50 minutes, in order to obtain the maximum contribution by the fine precipitation of carbides in ferrite and to increase the hardenability and the tensile properties[14]. The cooling was done in air.

After quenching and tempering, the cubic samples were prepared according to conventional metallographic methods. For etching, 2% Nital and Lepera were used, with an application time of approximately 30 seconds. The average of five hardness measurements was obtained with a load of 100 kgf using a Rockwell B hardness tester. The microstructures were characterized by Confocal Optical Microscopy (COM) and backscatter electron images (BSE) in a Scanning Electron Microscope (SEM).

The tensile test was carried out according to ASTM E8-00 in an Emic DL1000 universal test machine, load cell of 10000 kgf and 50 mm strain gauge with measurable deformation of 25 mm. Five specimens in each condition were pulled with 1 mm per minute constant strain rate.

The wear coefficients were determined by micro-wear tests using a fixed ball machine and silicon carbide (SiC) as abrasive slurry, with particles size of approximately 5 µm and a concentration of 0,75 g/cm³ (75g SiC in 100 ml distilled water) with rotation of the motor shaft of 150 rpm. The slurry was dripped on the ball surface at a flow-rate of approximately 1 drop per 3 s. The normal load (FN), which was measured by a cell with an accuracy of ± 0.005 N, was 0.24 ± 0.01 N. Consecutive wear craters were obtained, only one sample for each condition, with test times of 5 to 55 min[15]. Five measures of the craters diameters were obtained in each interval of five minutes. For each sliding distance (L), the microabrasive wear coefficient (K) was determined when the permanent wear regime was reached using the following Equation 1[16].

$$K = \frac{V}{L.Fn} \quad (1)$$

Where Fn is the normal load on the surface of the testing ball and V, calculated by the Equation 2, is the worn volume of material.

$$V \cong \frac{\pi.b^4}{32\phi} \quad (2)$$

These values were used to make the graph of wear coefficients. This allows for superior reliability to 95% [17].

Thermodynamic modeling was carried out with the FactSage 7.0 software that is a fully integrated computational system that can access thermodynamic data from different compounds, liquid metallic solutions and others[18]. The simulation calculating of the weight and solubilization temperatures of the nitrides, carbides and sulfides present in the alloys were done with chemical compositions of the steels.

3. Results and Discussion

The chemical compositions of the microalloyed steels are presented in Table 1.

The chemical compositions in Table 1 reveal that the steels are similar, despite the different levels of niobium and molybdenum. The area reduction of about 80% in the forging followed by annealing at 930 ºC was sufficient to homogenize the microstructure and the hardness of the bars.

Table 2 presents the average values of hardness measurements obtained from five different regions of each sample, after annealed (A), quenching (Q) and quenching plus tempering with air cooling (Q+T).

In Table 2 a hardness of 52 HRB is the same in the different sections after annealing. Niobium content influences the grain size, but this mechanism is not able to increase the hardness of the steels after annealed. After quenching,

Table 1. Chemical compositions of microalloyed steels (% in weight).

Steel	C	Si	Mn	P	S	Cr	Ni	Mo	Nb	Ti	V	N (ppm)
0.08 Nb	0.11	0.09	0.33	0.03	0.02	0.37	0.41	0.05	0.08	0.01	0.01	72
0.01 Nb	0.09	0.09	0.42	0.03	0.01	0.29	0.40	0.16	0.01	0.02	0.01	52

Table 2. Rockwell B hardness values after annealed at 930 ºC (A), quenching at 900 ºC (Q) and quenching at 900 ºC plus tempering at 600 ºC (Q+T).

Steels	A	Q	Q+T
0.08 Nb	52 ± 2	84 ± 2	82 ± 1
0.01 Nb	52 ± 1	105 ± 2	97 ± 2

there was an increase in hardness, due to the presence of displacive constituents in steels, mainly acicular ferrite, bainite and the martensite/austenite microconstituent (MA). In this case, the hardness values of steel containing 0.16 molybdenum is greater than the 0.05 one. This suggests that the hardenability effect of molybdenum is dominating, because it has a beneficial effect when the cooling rate is high and promotes the constituents formation, with high density of dislocations[9,10]. The reduction of hardness after tempering at 600 ºC may be justified by a probable formation of ferrite and cementite from MA.

Regarding the mechanical properties, Table 3 presents the average values and the standard deviations from five tests after each heat treatment.

According to the tensile tests in Table 3, after tempering at 600 ºC, the values of the forged steels are consistent with the standard API 5L-X70[19]. In both steels, the elongation results are in accordance with the standard, different from quenching at 900 ºC, where the values are reduced by the presence of MA. Because the higher content of molybdenum in steel containing 0.01 Nb, the delay of the ferrite formation promotes a more regular acicular ferrite with lower bainitic microstructure that increases the tensile strength[8,9]. Therefore, it is important to control the heat treatment for achieving the suitable microstructure and mechanical properties of the microalloyed steels for use in the petrochemical industry.

With relation to the wear coefficients in Figure 1a, the values as calculated by the Equation 1, decrease with time and approach the steady state after 50 minutes. In this case Nb 0.01 steel presents a wear coefficient slightly higher than steel containing 0.08 Nb, after quenching. However, after quenching plus tempering, is slightly lower. These

(a)

(b)
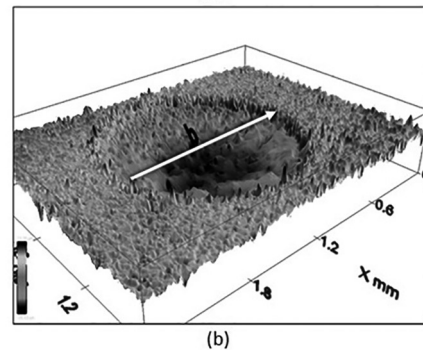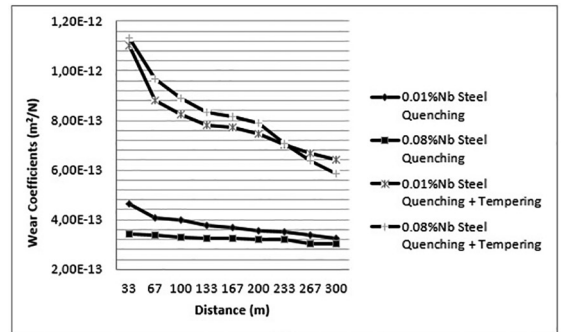
Figure 1. Wear coefficients of steels after quenching at 900 ºC and quenching at 900 ºC plus tempering at 600 ºC (a) and wear crater in the specimen surface of the steel (b). The arrow indicates the crater size after the test (COM).

results reinforce the hypothesis of a large amount of $Cr_{23}C_6$ and $Mo_{23}C_6$ carbides in 0.01 Nb steel, after tempering, as shown in the thermodynamic simulation. In Figure 1b it can be noted the scar after touching the steel ball on the specimen surface.

Figures 2a and 2b present the microstructures of microalloyed steels after annealing at 930 ºC with cooling in the furnace, in which a matrix of polygonal ferrite and islands of perlite compose the structures. In this paper the microstructural classification was made according to the definition by Araki and colleagues[20] and Krauss and Thompson[21].

Table 3. Yield strength (σ_e), tensile strength (σ_{max}) and elongation of steels after quenching at 900 ºC (Q) and quenching at 900 ºC plus tempering at 600 ºC (Q+T).

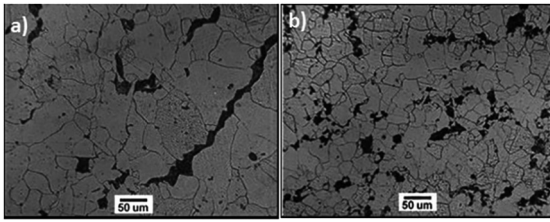| Steels	Heat Treatment	σ_e (MPa)	σ_{max} (MPa)	Elongation (%)
0.08 Nb	Q	630 ± 11	885 ± 10	9.0 ± 1.5
0.08 Nb	Q+T	472 ± 13	535 ± 15	18.0 ± 1.0
0.01 Nb	Q	670 ± 08	935 ± 10	9.3 ± 0.6
0.01 Nb	Q+T	526 ± 05	598 ± 06	16.0 ± 0.7

Figure 2. The figures show the microstructures of the annealed steels containing 0.01 (a) and 0.08 Nb (b). In the second, the grains are smaller because the higher niobium content (Nital 2% - COM).

Figures 3a and 3b present the microstructures of quenched and quenched plus tempering with cooling in air of microalloyed steel containing 0.08% niobium. In the first, acicular ferrite (AF), bainite (B) and martensite/austenite (MA) white islands appear inner the grain from the rapid water cooling. In the second, it can be noted grain boundary allotriomorphic ferrite (GBA) plus bainite, represented by the sheaves of ferrite parallel with discontinuous carbides[22]. The acicular constituents increase the yield and tensile strength of the material. The disposition of the ferrite plates in different orientations is responsible for the difficulty of crack propagation in the material[23].
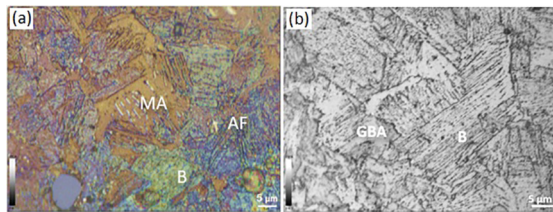

Figure 3. 0.08 Nb steel: the first shows the microstructure after quenched at 900 ºC (Lepera - COM). The second shows the microstructure after quenched at 900 ºC and tempered at 600 ºC (Nital 2% - COM).

Figures 4a and 4b present the microstructures of quenched and quenched plus tempering with cooling in air of microalloyed steel containing 0.01% niobium. In the first, after quenching, the microstructure is mostly composed of grain boundary alotriomorphic ferrite (GBA), Widmanstatten ferrite (WF), acicular ferrite (AF) and bainite (B)[12,22]. After tempering in Figure 4b, it is possible to observe the acicular ferrite and bainite and in this case, the needles of ferrite grow in different directions.
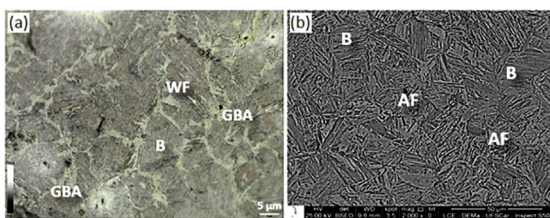

Figure 4. 0.01 Nb steel: the first shows the microstructure after quenched at 900 ºC (Nital 2% - COM). The second shows the microstructure after quenched at 900 ºC and tempered at 600 ºC (Nital 2% - MEV).

Despite Figure 4a does not show the MA phase, this constituent was also observed in lower amount in this steel. With relation to the tempering at 600 ºC in Figures 3b and 4b, MA phase disappears in both steels. Thus, there is an increasing elongation with yield strength and tensile strength reduction. In this condition, it is possible to form ferrite and cementite from retained austenite and martensite by a reconstructive mechanism, which may justify the decrease in hardness after this treatment as shown in Table 2. Moreover, accelerated cooling in the steels containing niobium and molybdenum, favor the formation of non-polygonal or acicular ferrite as well as bainite, which further contribute to strengthening[9,22].

In both steels the microstructures indicate the presence of grain boundary allotriomorphic ferrite. The presence of thin layers of this constituent reduces the austenite grain surfaces, as potential nucleation sites for bainite, and favors the microstructural transformation from bainite to acicular ferrite[24].

The amounts of the precipitates shown in Figures 5a and 5b were predicted by the FactSage software and the results are used just as indicators to the patterns in these steels. According to deviations from the equilibrium conditions, the FactSage can't be employed for precipitates forming during the continuous cooling. These simulations are made considering the most thermodynamically probable products and the values need to be confirmed by another technique, such as transmission electronic microscopy (TEM).
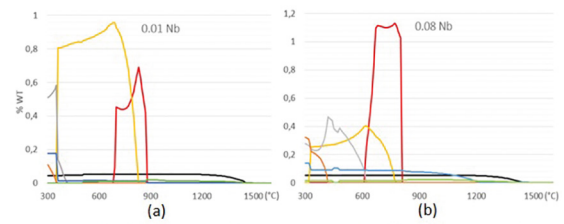

Figure 5. Thermodynamic simulation performed on 0.01 (a) and 0.08 (b) niobium steels.

It can be noted the presence of cementite, MC, M_7C_3 and $M_{23}C_6$ carbides, mainly of chrome and molybdenum, and at higher temperatures, niobium and titanium carbides and nitrides and manganese sulfide.

In microalloyed steels, niobium, vanadium and titanium, even with levels lower than 0.15%, promote the formation of carbides finely dispersed in the matrix, during the austenite/ferrite transformation[25]. As in the literature, simulation results indicate the presence of carbides and nitrides of niobium and titanium. The formation of these precipitates in forging can be responsible for the slightly smaller grain size in the 0.08 Nb steel (Figure 2.b). The simulation also indicates the formation of M_7C_3 and $M_{23}C_6$ chromium carbides and MC and $M_{23}C_6$ molybdenum carbides in the range of 300 to

800 ºC. Moreover, literature results indicate that molybdenum contents lower than 0.5 % is ineffective in the secondary hardening phenomena, it is possible that the relative higher amount of precipitation in 0.01 Nb steel, mainly $Cr_{23}C_6$ and $Mo_{23}C_6$, can justify the value shown in Figure 1a[26].

The thermodynamic simulations also indicate the probable precipitation of NbC for the 0.08 Nb steel at the tempering temperature. Figures 6a and 6b show the MX type precipitation in both steels. It is known that MX type precipitates promotes a finely dispersed precipitation in the matrix and contributes to wear resistance[27].
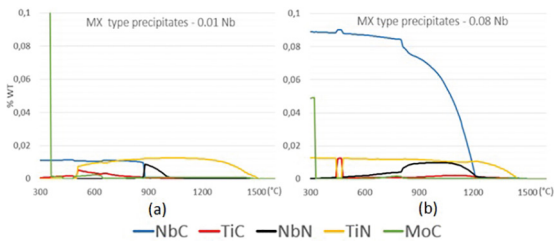

Figure 6. MX type simulation on 0.01 (a) and 0.08 (b) niobium steels.

Regarding the wear resistance after quenching, steels with similar type of microstructure show a linear decrease in weight loss with decreasing grain size[28]. So, it is possible that higher amount of niobium is responsible for grain refining and the better wear performance in 0.08 Nb steel after quenching.

With relation to yield and tensile strength, the microstructural analysis of other samples after quenching and quenching plus tempering conditions, reveals a higher amount of acicular ferrite and bainite in 0.01 Nb steel. According to the literature, this combination is the most indicated in the mechanical strength of microalloyed steels. It is possible that the higher molybdenum content is responsible for this result[9,13].

4. Conclusions

The results of this research show that:
- The steels microstructures with acicular ferrite and bainite after quenching and tempering are suitable to meet the values of standard API 5L-X70;
- According to the wear coefficients and simulation, the higher amount of niobium in 0.08 Nb steel promotes grain refining which appears to lead to a better wear performance after quenching;
- Regarding the microstructure, molybdenum can be replaced by niobium, because identical microstructure can be obtained using adequate heat treatments;
- Molybdenum is responsible for a greater amount of acicular and bainite ferrite in 0.01 Nb steel;
- Acicular ferrite associated with bainite is indicated to a better performance in mechanical strength of microalloyed steels;

- It is possible control the heat treatment for achieving the suitable microstructure and mechanical properties of the microalloyed steels for use in petrochemical industry.

5. Acknowledgement

6. References

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