NIOBIUM ROLE IN QUENCHED AND TEMPERED LOW ALLOY STEELS: A REVIEW*

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Abstract

In recent decades countless works have been published on the influence of niobium in the thermomechanical rolling of structural low carbon steels. On the other hand, its role in quenched and tempered steels has been much less investigated and discussed, perhaps due to the limited effect of niobium on austenite hardenability due to the high temperatures required for its full dissolution, which prevents its wide adoption for this application. The evolution of electron microscopy techniques, particularly MET and EBSD, has shed more light about the effect of niobium on the microstructural morphology of quenched and tempered martensite. This work aims to review the role of niobium in quenching and tempering metallurgy of low alloy steels, in order to promote its use in more efficient alloy designs from an environmental and cost point of view. As an example, the addition of 0.060% Nb to a steel used for the manufacture of OCTG quenched and tempered pipes increased yield strength from 719 MPa to 796 MPa due to the additional hardening contributions of martensite refining, dislocation density and precipitation.

Keywords: Niobium; Quenching and Tempering; Martensite; Precipitation.

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1 INTRODUCTION

The search for steels with higher sustainability and lower costs is leading to optimization in their alloy designs, i.e., the use of elements that have a lower carbon footprint and cost. A recent example is the partial replacement of manganese by niobium in structural steels [1]. It is very opportune to extend this approach to other steel classes. Therefore, the objective of this work was to clarify the role of niobium in low alloy steels subjected to quenching and tempering, including those with higher carbon contents.

Niobium is well known for its role in the thermomechanical rolling of low carbon structural steels, with or without a final accelerated cooling, but it is also used, to a lesser extent, in quenched and tempered steels. The effects of niobium in austenite transformation during quenching are twofold. As solid solution, it increases hardenability and, consequently, mechanical strength after quench; under suitable tempering conditions, it can also increase mechanical strength through precipitation hardening. In precipitate form, niobium refines austenite grain size, which eventually can lead to a loss of hardenability, but also refines the resulting martensitic microstructure, increasing its strength and toughness. The role of this hardening mechanism became clearer with the advancement of electron microscopy techniques, particularly EBSD analysis [2].

The use of niobium to increase austenite hardenability poses a practical problem, as the dissolution of its precipitates requires very high temperatures, generally higher than 1050°C, depending on niobium, carbon and nitrogen contents of steel. Generally, this is not a problem in the thermomechanically controlled processing with direct quenching of low carbon flat steel products, as slab reheating temperature generally is very high, even above the necessary for full niobium dissolution, as the slab:plate thickness reduction rate is very high, requiring relatively long rolling times associated with high loss of rolling stock temperature. For its turn, conventional heat treating of medium carbon engineering steels generally uses lower austenitization temperatures, in the range of 800 to 900°C, in order to reduce energy consumption and carbon footprint. Besides that, the higher carbon content of such steels increases dissolution temperature of niobium far beyond 1050°C, further complicating the situation.

Most studies about the effect of niobium on hardenability are focused on the austenite transformation in the Coarse Grain Heat Affected Zone (CGHAZ) of welded joints. The CGHAZ, near of the fusion zone of the joint, reaches extremely high temperatures during the welding process, which surpass the dissolution temperature of niobium in austenite and, therefore, enable its hardenability increase effect [3].

2 THE EFFECT OF NIOBIUM IN QUENCHING AND TEMPERING

2.1 Austenite Grain Size and Precipitation

Wang [2] studied the effect of niobium on the microstructure of steels used in the manufacture of quenched and tempered oil country tubular goods (OCTG). Their basic chemical composition was 0.25% C, 0.25% Si, 0.50% Mn, 1.00% Cr, 0.75% Mo and 0.080% V+Ti. Four alloys were tested with different contents of niobium: 0.003%, 0.015%, 0.030% and 0.060%. Samples of these steels were austenitized at 900°C for 30 minutes, water quenched and tempered at 700°C. The effect of niobium on the prior austenite grain size (PAGS) can be seen in Figure 1(a) [2]. One can see that

PAGS decreased significantly from 18.1 to 8.2 μm as niobium content increased from 0.003 to 0.030%. Then PAGS decreased slightly to 6.4 μm for the maximum niobium content of 0.060%, indicating some saturation in the refining effect. Figure 1(b) [2] shows that the increase of niobium content increased the volume fraction of precipitates in the as-quenched martensite (i.e., the austenite immediately before water quenching) but decreased its equivalent diameter. This fact is also described in another study about the austenitization of NbTiV microalloyed steels, where it was found that higher niobium contents could decrease the overall particle size by preventing the precipitation of large size Ti-rich carbonitrides during solidification [4]. This precipitate evolution explains the PAGS refining effect of niobium. Similar findings were also made by other authors [5,6].
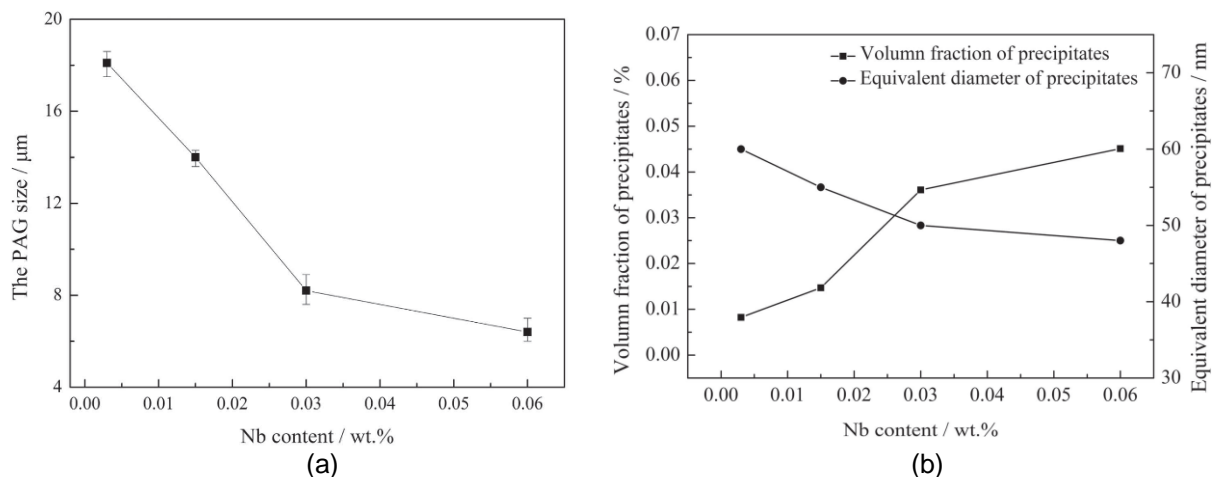

Figure 1: Effect of niobium in the (a) prior mean austenite grain size, (b) volume fraction and equivalent diameter of precipitates in as-quenched martensite [2].

On the other hand, it is interesting to note that, in boron steels, niobium and molybdenum can preserve the hardenability increase promoted by that element, as the segregation of carbon to the austenite grain boundaries is hindered by the precipitation of Nb–C or Mo–C clusters of carbides inside the grains, avoiding the massive formation of $Fe_{23}(C,B)_6$ in these grain boundaries which impairs the boron hardenability effect, as seen in Figure 2 [7].

2.2 Austenite Transformation

Niobium has a large misfit with austenite lattice, which results in its low solubility in this phase. Therefore, it segregates to the grain boundaries and has one of the strongest interactions with them. This results in a decrease in the local driving force for ferrite formation, increasing the energy required for its nucleation and hindering carbon diffusion. Niobium also exerts a solute drag effect on the austenite-ferrite interface. So, even a small amount of solute niobium can strongly retard austenite transformation, decreasing Ar_3 temperature [8]. Apparently dissolved niobium has a stronger effect on diffusional austenite transformation, that is, the formation of ferrite and pearlite. Therefore, after continuous cooling, niobium containing steels may have more displacive transformation products, like bainite, in final microstructure than niobium free steels. On the other hand, higher niobium contents tend to precipitate in austenite and then increase Ar_3, reversing its effect on hardenability. So, solute niobium amount must be limited to 0.025-0.050% in order to increase austenite hardenability, as shown in Figures 3(a) and (b) [9,10].

(a) B steel   (b) Nb and B steel   (C) Mo and B steel
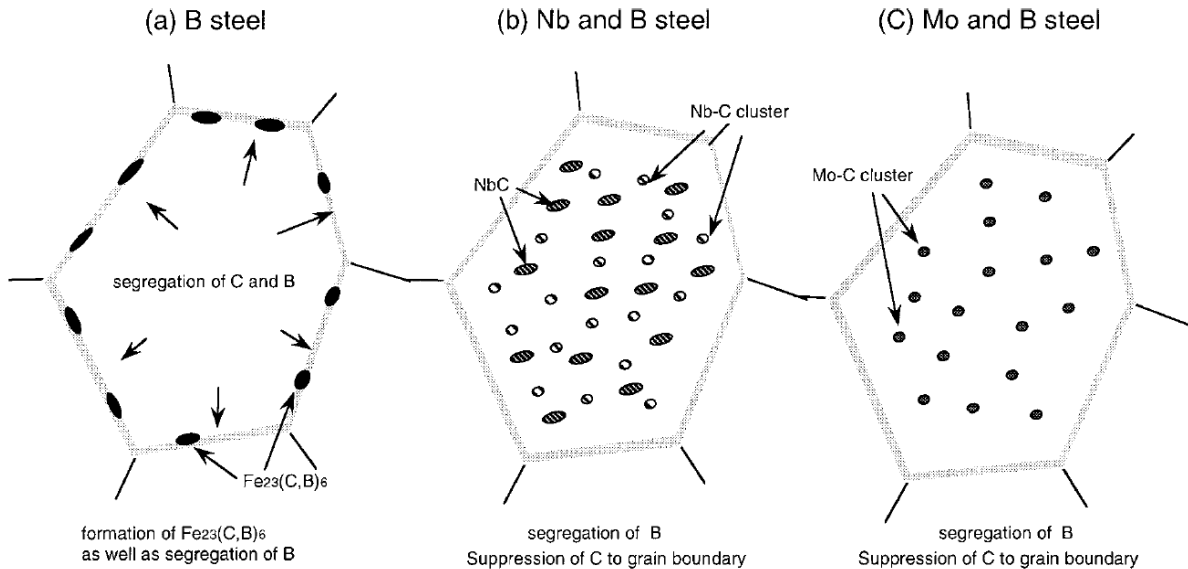
Figure 2: Mechanism for suppression of formation of $Fe_{23}(C,B)_6$ in austenite grain boundaries due to combined addition of Nb and B or Mo and B [7].
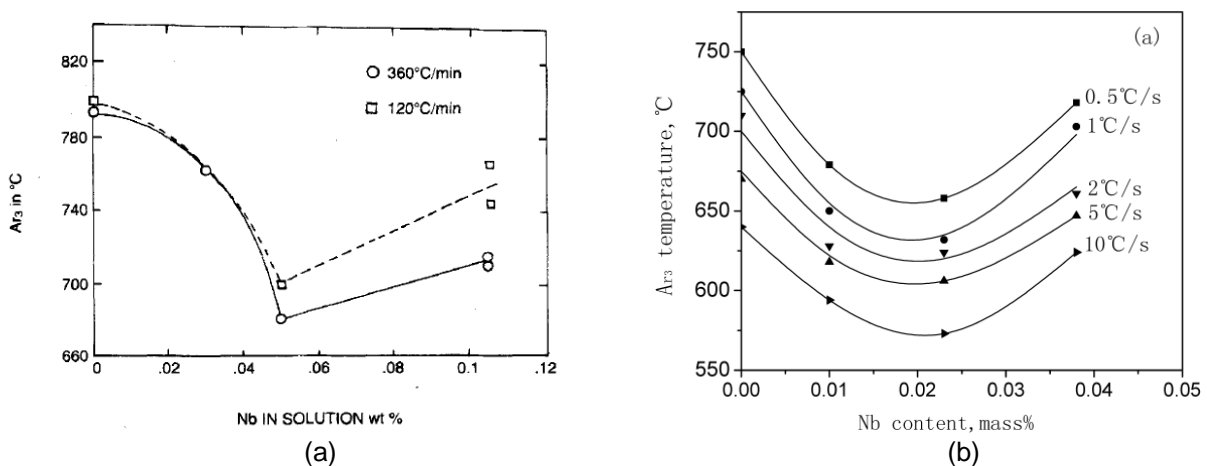

Figure 3: Effect of niobium in solution in Ar_3 temperature: (a) 0.07% C, 1.5% Mn steel [9], (b) 0.11% C, 1.15% Mn, 0.20% Si steel [10].

Fazeli [11] studied the effect of niobium in austenite transformation of a steel for X80 pipes with the following chemical composition: 0.06% C, 1.65% Mn, 0.24% Mo, 0.034% Nb, 0.012% Ti and 0.0050% N. CCT diagrams were determined for this alloy under two conditions: one assuming niobium almost totally precipitated in austenite (0.009% Nb_{Sol}), and the other assuming niobium fully dissolved in austenite (0.034% Nb_{Sol}). The initial austenitization of both conditions was carried out by heating the samples at 1,300°C for 35 seconds. In the first case, this austenitization was followed by cooling to 900°C, holding at this temperature for 20 minutes and finally following continuous cooling. In the other case no holding at 900°C was performed, continuous cooling was immediately applied after the initial austenitization. The CCT diagrams for these two conditions, considering previous austenite grain sizes of 5 μm and 80 μm, can be seen in Figure 4(a) and (b). As expected, niobium must be in solid solution to increase austenite hardenability, which additionally increased for coarser PAGS. Similar results were got by other researchers [8,12-14].

2.3 Martensite Morphology

However, even precipitated in austenite, niobium has a beneficial effect on the final mechanical properties of quenched steel. Niobium promotes refining of the PAGS due to the pinning effect of its precipitates on grain growth during austenitization before quenching. This more refined austenite will promote the refinement of martensite substructure formed after quenching [15]. It is an effect analogous to what is observed in microalloyed steels subjected to thermomechanical rolling, where the transformation of refined and strain hardened austenite leads to the formation of ferrite with an intensely refined grain size.
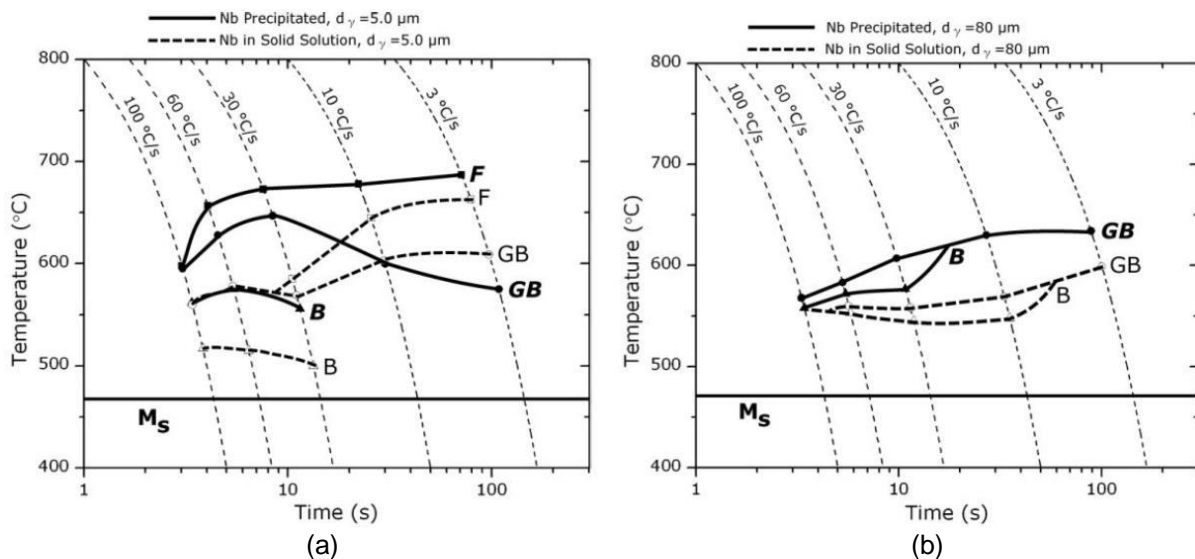
Figure 4: CCT diagrams showing the combined effect of cooling rate and niobium state on austenite transformation for (a) 5 µm grain size and (b) 80 µm grain size [11].

Lath martensite is formed after the quenching of low carbon austenite. It forms through a coherent transformation and has a near Kurdjimov-Sachs (KS) relationship with the parent austenite. As shown in Figure 5(a) and (b) [16], lath martensite has a typical hierarchical microstructure which can be characterized at multiscale: packet, block and lath at the descending size. A prior austenite grain is composed of several martensite packets having the same habit plane; each packet is then divided into martensite blocks, which contain several laths having the same crystallographic orientation. The lath boundaries have low-angle disorientation, while the packet and block boundaries have high-angle disorientation.

Figure 6 [2] shows the effect of niobium over packet and block sizes, where it can be seen that all of them showed a significant degree of refining as the niobium content increased and PAGS decreased, as shown in Figure 1(a) [2].

A similar effect was noted in another research [17], where the addition of 0.050% Nb to a hot stamped medium carbon steel, with chemical composition 0.36% C, 0.24% Si, 1.39% Mn, 0.19% Cr and 0.005% B, promoted the formation of very fine carbonitrides, with maximum size of 50 nm, during the austenitization at 950°C for 5 minutes before quench in a water-cooled stamping mold. This promoted a reduction of PAGS from 17 to 11 µm and a decrease of martensite lath size from 316 to 124 nm, resulting in a significant increase in mechanical properties: yield strength, from 1316 MPa to 1476 MPa; tensile strength, from 2011 to 2179 MPa; and elongation was even improved, from 5.9 to 6.6%.

2.4 Tempering

It is known that during the tempering of steels containing carbide-forming elements, like niobium, vanadium, titanium, molybdenum and chromium, at a relatively high temperature, above 500°C, a fine precipitation of carbides occurs after the dissolution of cementite, leading to secondary hardening. These elements have an extremely small solubility in ferrite, leading to a fine precipitation of alloy carbides with high driving force [18]. The contribution to mechanical strength due to niobium precipitation will depend on its solute content in martensite, as well adequate tempering conditions in terms of temperature and duration.


(a)

(b)
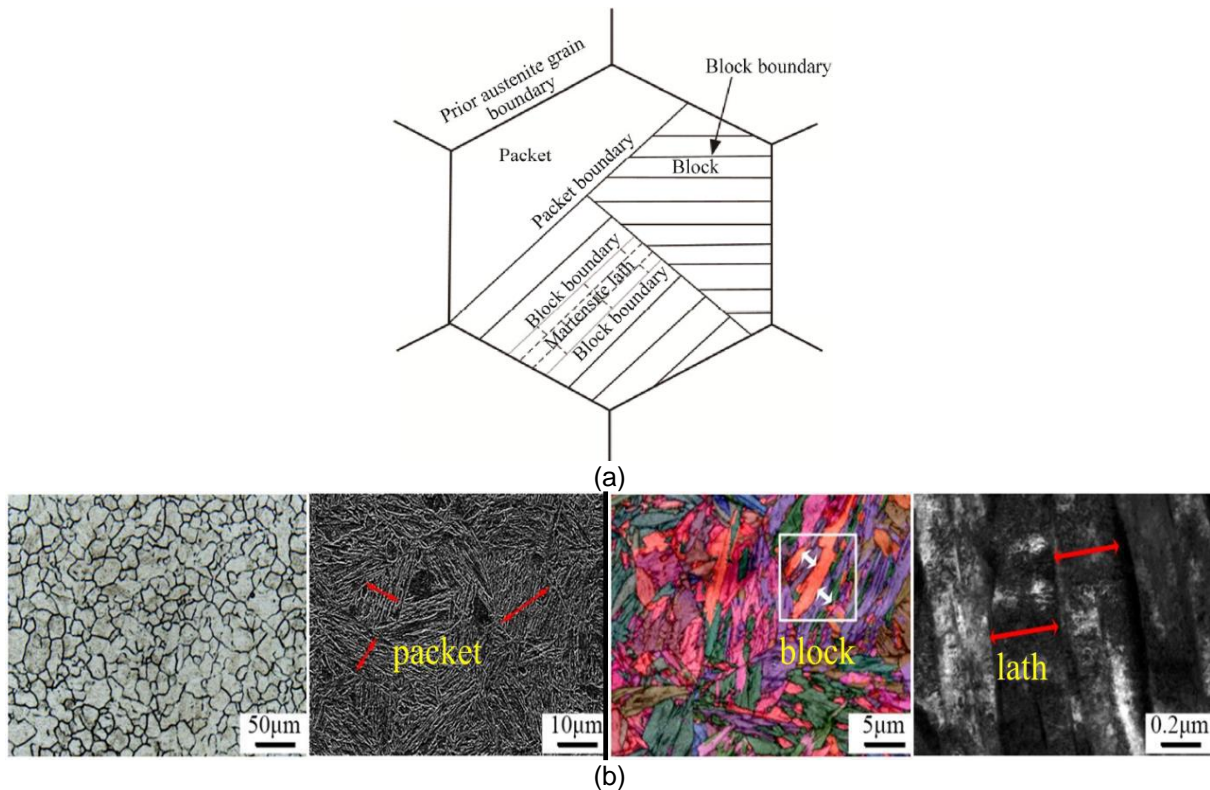
Figure 5: (a) A simplified diagram of the constituents of lath martensite [17]; (b) Their appearance in the OM, MEV, EBSD and MET, respectively [16].
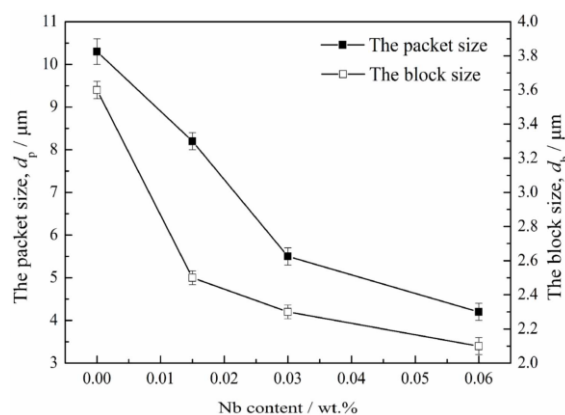
Figure 6: Effect of niobium in the packet and block sizes [2].

Two steels were compared in a study about the effect of niobium on the tempering kinetics of low carbon steels [5]: a CMn steel with 0.15% C, 1.39% Mn, 0.39% Si and

0.0040% N, and a similar alloy, but with an addition of 0.031% Nb. Both were austenitized at 1075°C and 1100°C, respectively, for 30 minutes, aiming to get the same PAGS value, and then quenched in a mixture of water and ice. Subsequently they were tempered at 300, 400, 500 and 600°C during 300, 900, 1800 and 3600 s. According to this work, only 0.014% Nb would be dissolved in austenite immediately before quenching. Figure 7 shows the decrease in hardness along time observed at the several tempering temperatures for the (a) CMn steel and (b) CMn+Nb steel. One can see that that the niobium steel showed lower hardness decrease, especially at higher tempering temperatures, and even a secondary hardening could be observed after 900 s at 600°C.
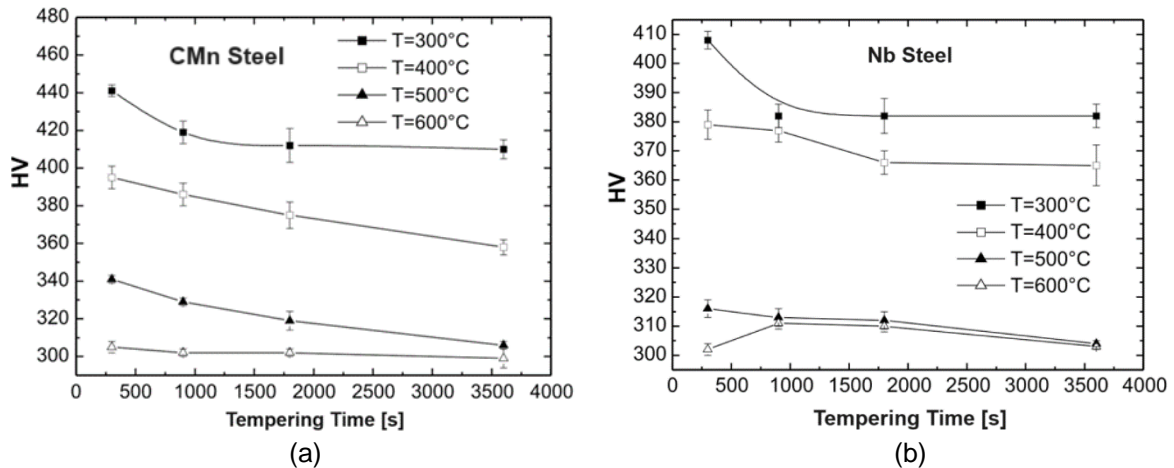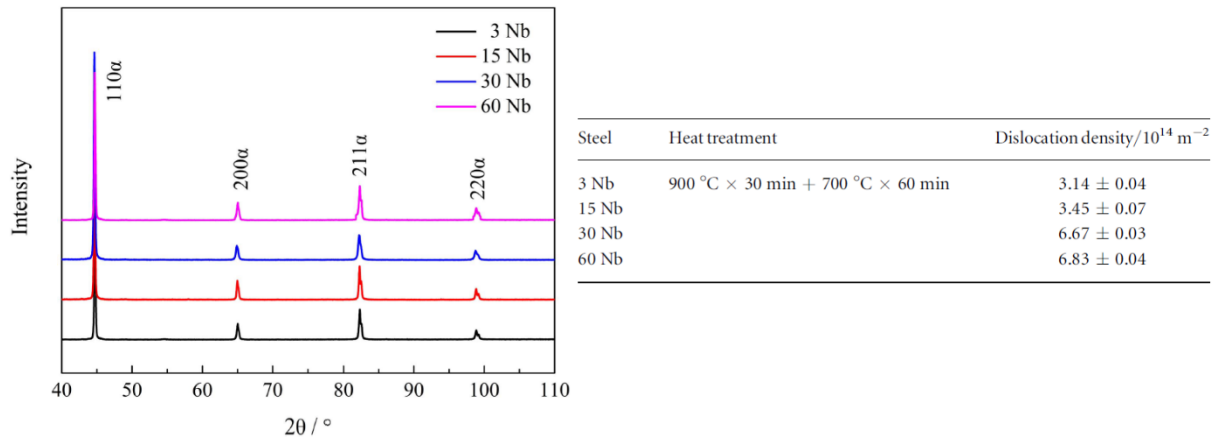

Figure 7: Effect of tempering temperature and time over hardness of quenched (a) CMn steel and (b) CMn+Nb steel [5]

The values of tempering activation energy Q for both steels were calculated in this same work [5], being equal to 130 kJ/mol for the CMn Steel and 180 kJ/mol for the CMn+Nb steel. It was concluded that the tempering kinetics for the CMn steel was limited by the activation energy for the diffusion of carbon in ferrite (85 kJ/mol), while for the CMn+Nb steel the limitation was due to the activation energy for the diffusion of niobium in ferrite (257 kJ/mol) [5]. Similar results were also got during the tempering of the medium carbon steel 42CrMo4, with or without 0.050% Nb [6].

Another effect of niobium is the increase of dislocation density in martensite, as shown by [2]. Figure 8 shows the X-Ray diffraction patterns and the corresponding values of dislocation density in as-tempered martensite with different niobium contents. The dislocation densities increased from 3.14×10^{14} to 6.83×10^{14} m^{-2} with niobium content increasing from 0.003 to 0.060 wt.%. As subgrain boundaries could act as obstacles for dislocation movement, it can be inferred that the progressive refinement of the martensite microstructure by increasing niobium content may contribute to the rise in dislocation density, which may enhance yield strength. It must be observed that dislocation density certainly was higher in the as-quenched austenite, but unfortunately this information was not available in this paper.

The precipitation during tempering was characterized in the niobium steels studied by [2]. During tempering at 700°C, niobium-rich (Nb,Ti,V)(C,N) precipitated due to the decreased solubility in ferrite. The precipitated mass fraction increased with higher niobium contents. These precipitates nucleated preferentially on sub-boundaries and dislocations in ferrite, so the increase of sub-boundaries and dislocation density, as seen in Figure 8, may also contribute to the increased mass of niobium-rich (Nb,Mo,V)(C,N). Above all, the average equivalent diameter of the precipitates in the

as-tempered steels decreased while their volume fraction increased with higher Nb contents, as one can see comparing Figures 1(b) and 9 [2].

Steel	Heat treatment	Dislocation density/10^{14} m^{-2}
3 Nb	900 °C × 30 min + 700 °C × 60 min	3.14 ± 0.04
15 Nb		3.45 ± 0.07
30 Nb		6.67 ± 0.03
60 Nb		6.83 ± 0.04

Figure 8: Patterns of X-ray diffraction of as-tempered samples with various niobium contents and values of the dislocation density calculated from such patterns [2].
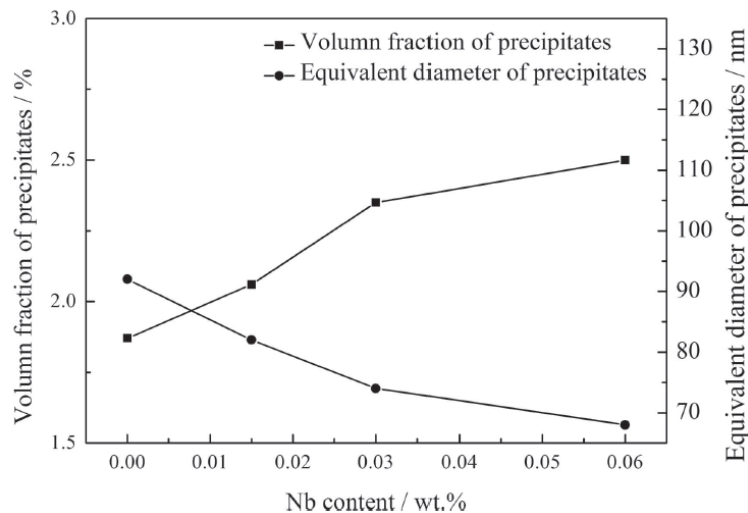
Figure 9: Effect of niobium in the volume fraction and equivalent diameter of precipitates in as-tempered martensite [2].

2.5 Hardening Mechanisms

As is widely known, the hardening mechanisms that contribute to final mechanical strength of steel are ferrite basic strength, solid solution, grain refinement, dislocation density and precipitation [2]. The first two contributions were assumed to be constant for the several niobium steels studied in that work.

Regarding the grain refinement mechanism, the block width d_b can be regarded as the minimum structural parameter controlling the yield strength σ_y of lath martensite, following the classical Hall-Petch relationship, as seen in equation (1) [2]. The value adopted for the Hall-Petch coefficient k_y was proposed by [19], being equal to 440 MPa µm$^{0.5}$.

$$\sigma_y = \sigma_0 + \frac{k_y}{d_b^{-0.5}} \tag{1}$$

For its turn, the dislocation density hardening contribution can be estimated according to the equation (2) [2]:

$$\sigma_{disc} = \alpha \, M \, g \, b \, \rho^{0.5} \tag{2}$$

where **α** is a fitting constant (0.15), **M** is the average Taylor factor (2.5 for ferritic steel), **b** is the vector of Burger (0.25 nm), **G** is the shear modulus (80 MPa) and **ρ** is the dislocation density, whose values can be got in the table seen in Figure 8.

Precipitation strengthening in microalloyed steels is mainly controlled by the Orowan mechanism, as carbonitrides are too difficult to be cut by dislocations [2]. Generally, the strength increase from the Orowan mechanism can be calculated by the equation (3):

$$\sigma_{ppt} = \frac{0.538 \, G \, b \, f^{0.5}}{2 \, r} \, ln\left(\frac{2 \, r}{2 \, b}\right) \tag{3}$$

where **G** is the shear modulus (80 MPa), **b** is the vector of Burger (0.25 nm), **f** is the volume fraction and **r** the average diameter of the precipitates. The values of the last two parameters can be got in Figure 9.

The measured value of yield strength and the sum of the calculated contributions of the hardening mechanisms can be seen in Table 1. The refining of martensite microstructure was the most effective hardening mechanism, followed by dislocation density and precipitation. As seen before, higher niobium contents resulted in a decrease in block size, higher fraction of finer precipitates, and higher dislocation densities, which resulted in increased contributions of all these hardening mechanisms. Summarizing, the addition of 0.060% Nb to this steel increased yield strength from 719 MPa to 796 MPa due to the hardening contributions of martensite refining (77 MPa or 57%), dislocation density (10 MPa or 13%) and precipitation (23 MPa or 30%) [2].

Table 1: Total value of real yield strength (σ_y) and respective calculated contributions from several hardening mechanisms: grain size (σ_{gr}), dislocation density (σ_{dis}) and precipitation (σ_{ppt}). The $\Delta\sigma$ values refer to the contribution of niobium for each hardening mechanism [2].

Steel	σ_y [MPa]	σ_{gr} [MPa]	σ_{disc} [MPa]	σ_{ppt} [MPa]	$\Delta\sigma_{gr}$ [MPa]	$\Delta\sigma_{disc}$ [MPa]	$\Delta\sigma_{ppt}$ [MPa]
3 Nb	719	259	110	47	0	0	0
15 Nb	745	285	115	54	26	5	7
30 Nb	783	323	118	63	64	8	16
60 Nb	796	336	120	70	77	10	23

However, is necessary to note that total precipitation hardening in this case was not exclusively due to niobium, but also to vanadium and, probably, titanium, which are also present in the chemical composition of these steels.

Figure 10 shows the effect of niobium content in steel on yield strength, tensile strength and elongation. One can observe that, between 0.030 and 0.060% Nb, there was some saturation in the niobium effect on yield strength, while tensile strength keeps showing a significant effect and the elongation value has stabilized.
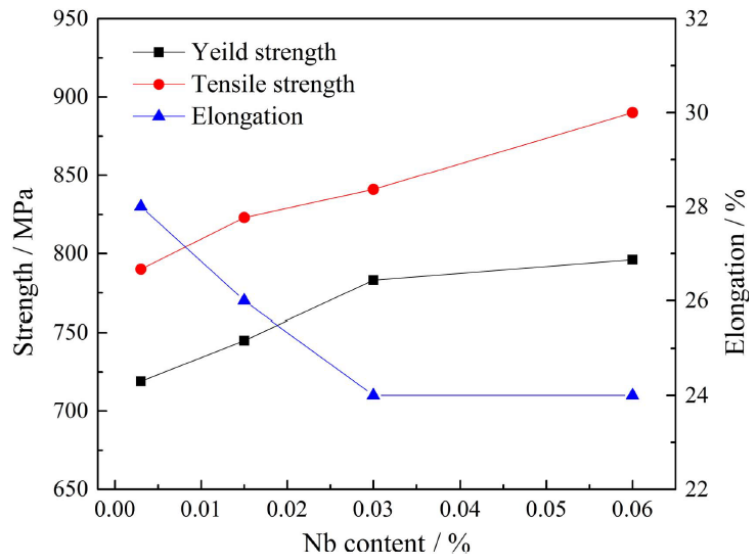
Figure 10: Effect of niobium addition on yield strength, tensile strength and elongation of a steel used for the manufacture of OCTG pipes [2].

3 CONCLUSION

The highlights of this review about the niobium influence in quenched and tempered low alloy steels can be summarized as follows:

- Niobium in solid solution promotes a significant hardenability increase up to a maximum content of 0.050%. However, as its dissolution temperature in austenite is much higher than that of other alloy elements, generally niobium is not used aiming to a significant increase of hardenability.
- On the other hand, the already well-known effect of niobium precipitates in restricting the grain growth of austenite and on the ferritic microstructure obtained after its transformation also occurs in martensite obtained after quenching, promoting an increase in mechanical strength and, most probably, toughness of the final product.
- Furthermore, it was verified that niobium promotes an increase in the dislocation density in martensite, which promotes an additional increase in mechanical strength.
- Niobium present as solid solution in martensite may precipitate during tempering. If this treatment is carried out at high temperatures, about 550°C, and for adequate periods of time, this precipitation can further contribute to the increase of mechanical strength.
- In one specific case of steel used for the manufacture of quenched and tempered OCTG pipes, the addition of 0.060% Nb increased yield strength from 719 MPa to 796 MPa due to martensite refining, increase of its dislocation density and precipitation.

Acknowledgments

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