

## **SOLUBILITY AND PRECIPITATION OF CARBIDES CONTAINING NIOBIUM AND MOLYBDENUM IN LOW ALLOY STEELS**

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### **Abstract**

Niobium and molybdenum have been critically important alloying additions in steels for several decades. Niobium typically contributes through careful control of niobium carbide precipitation in austenite and ferrite, which enables grain refinement and precipitation strengthening, although solute effects on recrystallization and transformation kinetics can also be important. Molybdenum is a powerful hardenability agent and is extensively used to influence austenite decomposition kinetics and microstructure development in many steels. Molybdenum and niobium have been employed together in steels, and more recent investigations suggest that interactions associated with combined niobium plus molybdenum additions may provide synergistic enhancements beyond the separate effects of the individual elements. Molybdenum can enhance the benefits of NbC precipitates by reducing the carbide coarsening kinetics. This behavior has been suggested to be important in fire-resistant constructional steels, and high strength, formable automotive hot-rolled sheet steels. More recently, similar effects have been obtained in austenite, where enhanced grain refinement during high temperature carburizing simulations has been confirmed in Nb+Mo modified alloys. The objective of the present paper is to provide some perspective on the physical metallurgy fundamentals influencing a variety of such applications, including solubility of niobium and molybdenum carbides in ferrite and austenite, and the precipitation and coarsening behavior of mixed (Nb,Mo) carbides.

### **Introduction**

Niobium and molybdenum are common alloying elements in many steels and as small additions contribute important enhancements to microstructure and properties. These two elements may be added individually or in combination, along with other important alloying additions in steels. Their individual effects are due to solute effects on grain boundaries or transformation interfaces, and through precipitation-related phenomena. More recently, “synergistic” effects of combined additions of niobium and molybdenum have been reported to provide additional benefits in some applications.

Niobium “microalloying” is employed in a variety of steels, such as thermomechanically processed high-strength, low-alloy (HSLA) steels where substantial grain refinement and precipitation strengthening are achieved. Niobium is dissolved before hot deformation, and subsequent rolling temperatures are designed so that niobium precipitates as niobium carbide (or

carbonitride) on the deformation substructure of the austenite, suppressing subgrain migration and thus delaying recrystallization. During transformation upon subsequent cooling, ferrite nucleation from the deformed or “pancaked” austenite is accelerated, leading to grain refinement. Niobium remaining in solution prior to transformation may enhance hardenability (ie. suppress diffusional transformation) due to solute drag, and then subsequently precipitate as a carbonitride at lower temperature in ferrite, where its solubility is lower, and provide dispersion strengthening. Niobium carbonitrides can also provide important boundary pinning effects during conventional heat treatments, leading to ferrite grain refinement upon annealing of cold-worked steels, or microstructure refinement of a variety of steels following austenitization, including such processes as quenching and tempering, normalizing, carburizing, etc. Formation of stable carbonitrides may also be employed to reduce solute interstitial concentrations in applications such as “interstitial-free” steels or stainless steels.

Molybdenum is also employed in a broad range of steels, often because of its potent effects (as a solute) on hardenability, suppressing the formation of diffusional transformation products such as ferrite or pearlite, in favor of bainite or martensite. Molybdenum also participates in various carbide precipitation reactions, and contributes temper resistance or secondary hardening in a number of steels. Finally, molybdenum is an important addition in pitting-resistant stainless steels, contributing to performance through chemical rather than microstructural effects.

### **Solubility Considerations**

The solubility of alloy carbides or carbonitrides is an important consideration in understanding driving forces for precipitation or dissolution behavior and has a critical influence on whether the alloying elements are in solution or precipitated. The solubility is strongly influenced by temperature and a variety of compositional variables. Consequently, solubility considerations are critical in tailoring the various interactions between key processing temperatures and alloy chemistry to enable precipitation and avoid dissolution/coarsening, etc. for a particular application and processing configuration. Solubility thus represents the basis for design of some important aspects of steel alloying and processing.

The solubility of important carbide and nitride forming species is typically greater in austenite than in ferrite. Solubilities are frequently represented in the form of “solubility products” for MX compounds such as niobium carbide or niobium nitride, and solubility products of mixed precipitates such as carbonitrides have also been addressed.

Niobium carbide equilibrium solubility products have been published by a variety of investigators, and examples are shown in Figure 1 using the following solubility product expressions for NbC in ferrite ( $\alpha$ ) and austenite ( $\gamma$ ) [1,2].

$$\log_{10}[Nb_{\alpha}][C_{\alpha}] = 3.90 - (9930/T_K) \quad (1)$$

$$\log_{10}[Nb_{\gamma}][C_{\gamma}] = 2.26 - (6770/T_K) \quad (2)$$

In these expressions,  $[Nb]$  and  $[C]$  represent the solute niobium and carbon concentrations (wt.%) in austenite or ferrite, respectively, in equilibrium with NbC at a given temperature ( $T_K$  in Kelvin). The curves in Figure 1 are “solubility isotherms” that represent the loci of niobium and carbon solubilities for different temperatures. The change in scale between Figures 1(a) and 1(b) should be noted, and illustrates the much lower levels of niobium and carbon concentrations that are soluble in ferrite as compared to austenite. The strong temperature dependence of solubility is clear in both austenite and ferrite (solubilities of the order of hundredths of a weight percent are common in austenite, while thousandths of a weight percent are typical in ferrite), as well as the strong influence of carbon concentration on the niobium solubility. These composition and temperature dependencies provide the means (and constraints) for alloy and process design. Niobium may precipitate or dissolve in austenite depending on composition and processing, but precipitates should usually be expected at temperatures in the ferritic regime for typical alloys.

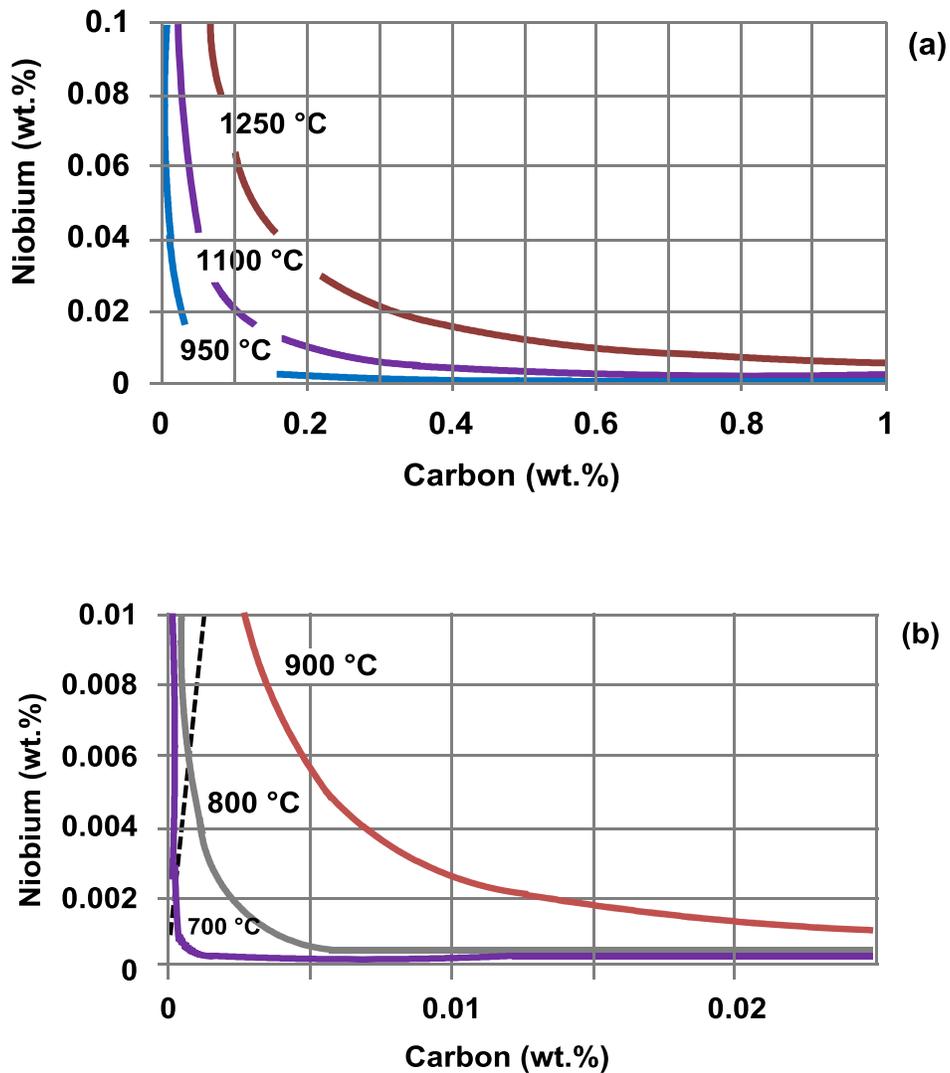


Figure 1. NbC equilibrium solubility isotherms at selected temperatures in austenite (a) and ferrite (b). The dashed stoichiometric line is shown in (b).

In comparison to niobium carbide, molybdenum carbide solubilities have been less well documented. Molybdenum forms an  $M_2C$ -type carbide in tempered martensitic steels containing substantial molybdenum additions, but also participates in the precipitation of carbides of  $MC$ -type stoichiometry that commonly form in microalloyed HSLA steels. Equilibrium solubility products in ferrite and austenite for these carbides have recently been calculated by Pavlina *et al.* [3], and are given by the following relationships:

For  $Mo_2C$

$$\log_{10}[Mo_{\alpha}][C_{\alpha}]^{1/2} = 4.00 - (5088/T_K) \quad (3)$$

$$\log_{10}[Mo_{\gamma}][C_{\gamma}]^{1/2} = 3.04 - (2814/T_K) \quad (4)$$

For  $MoC$

$$\log_{10}[Mo_{\alpha}][C_{\alpha}] = 3.19 - (4649/T_K) \quad (5)$$

$$\log_{10}[Mo_{\gamma}][C_{\gamma}] = 1.29 - (523/T_K) \quad (6)$$

Definition of terms similar to equations (1 and 2)

The solubilities of these Mo-carbides are higher than typical microalloy carbides such as NbC, TiC and VC [3], and Mo-carbides are also much more likely to precipitate in ferrite than in austenite (due to their high solubility in austenite). While  $Mo_2C$  is somewhat more stable than MoC, the solubility of MoC in ferrite is of greater interest in microalloyed steels; Figure 2 shows solubility isotherms for MoC in ferrite for temperatures of 500, 600 and 700 °C. Even in ferrite, it is clear that molybdenum solubility is quite high, of the order of tenths of a weight percent in low carbon steels. Molybdenum solubility is reduced when molybdenum precipitates with other species such as niobium in a mixed carbide or carbonitride. The solubility of such a mixed carbide,  $(Nb_xMo_{1-x})C$ , has recently been addressed by Enloe *et al.*, and will be discussed further below, with respect to precipitation behavior recently reported in Nb-Mo steels [4-6].

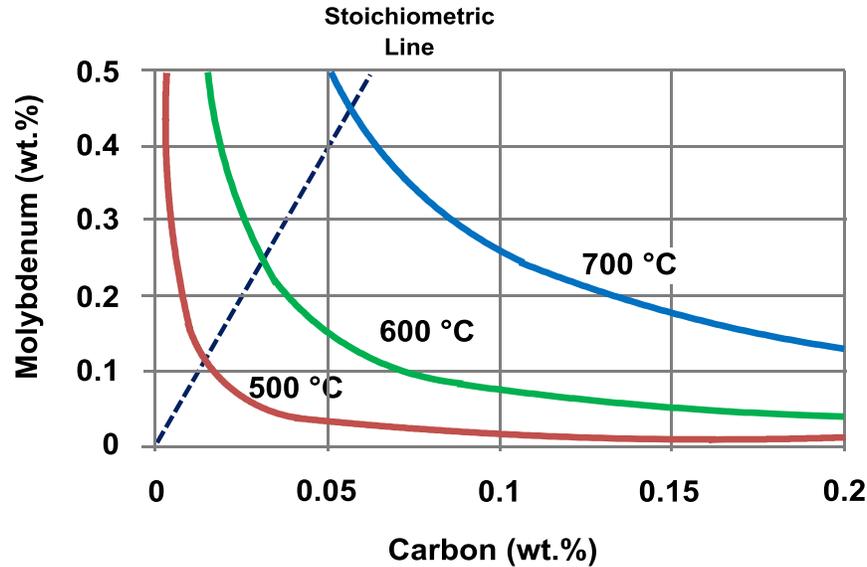


Figure 2. MoC solubility isotherms in ferrite at 500, 600 and 700 °C, calculated based on the recent solubility product analysis of Pavlina *et al.* [3]. The dashed line indicates stoichiometric (1:1 atomic basis) ratios of Mo to C.

### Applications of Combined Nb+Mo Alloying Additions

Niobium and molybdenum are added individually or in combination to many families of steels to exploit the various benefits of these important elements. The synergistic effects of combined additions are of special interest here, wherein molybdenum influences the behavior of niobium carbide. Early work [7] reported a greater fraction of (Nb,Mo)(C,N) precipitates and precipitate refinement during tempering of steels containing both niobium and molybdenum. Molybdenum is now believed to reduce the coarsening kinetics of NbC, and it is this effect that has led to some recent applications in steel development. These applications have included fire-resistant constructional steels, where resistance to precipitate coarsening improves high temperature strength [8]. Molybdenum additions to Nb- or Ti-microalloyed steels are also being employed in high-strength hot-rolled sheet products having high hole expansion performance and enhanced precipitation strengthening [9-11], and more recently have been investigated for high temperature carburizing of gears, used herein to illustrate physical metallurgy principles in Nb+Mo steels.

Vacuum carburizing is growing in importance, and Nb-microalloying has been employed to develop a fine array of NbC precipitates to suppress austenite grain growth at the elevated temperatures associated with vacuum processing, since the fatigue properties of carburized (martensitic) gears are well known to benefit from a refined PAGS (prior-austenite grain size) [12]. A series of studies in the authors' laboratories have been undertaken in this area, [eg. 13,14], and Figure 3 presents bending fatigue properties (S-N curves) for three Nb-modified SAE 8620 steels that were vacuum carburized at 1050 °C. The benefit of niobium additions on the low-cycle fatigue life and particularly the endurance limit is clear from the figure, resulting from enhanced austenite grain refinement due to NbC precipitates. More recent work has begun

to explore the potential for enhancing the grain refining effect of niobium during high temperature carburizing by a further addition of Mo, and early results are promising [5,6].

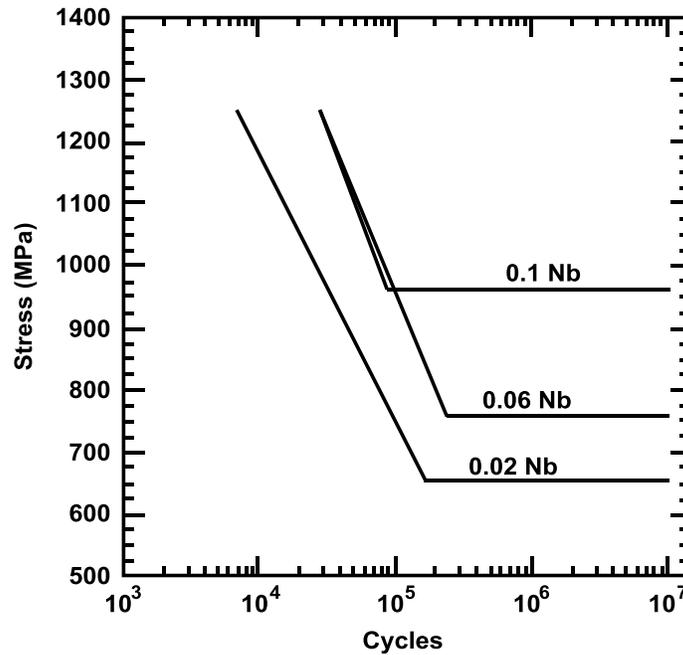


Figure 3. Stress versus cycles to failure in bending fatigue (min./max. stress ratio = +0.1) for Nb-modified SAE 8620 steel, control-rolled, reheated at 114 °C/min to 1050 °C and vacuum carburized [14].

Enloe *et al.* examined NbC precipitation and austenite grain coarsening behavior in a series of SAE 4120 alloys with low (~0.04%) and high (~0.1%) levels of niobium and with or without a molybdenum addition [5,6]. A small titanium addition was also included to provide an additional contribution from TiN pinning [15]. Table I presents the chemical compositions of the modified 4120 alloys investigated by Enloe *et al.* The steels were reheated to 1250 °C, hot-rolled and air cooled to room temperature prior to the simulated carburizing thermal treatment (ie. “pseudocarburizing”) at 1100 °C. The MoLNb alloy was also subjected to a solution treatment at 1250 °C and quenched prior to pseudocarburizing to modify the initial precipitate distribution. Figure 4 shows NbC precipitate size distributions that were measured using transmission electron microscopy (TEM) of extraction replicas, and indicates the precipitate coarsening kinetics at the elevated carburizing temperature. The results are plotted as the cube of the particle radius,  $r$ , versus time, reflecting the well-known LSW (Lifshitz-Slyozov-Wagner) relationship for particle coarsening, where  $r^3$  is proportional to time. A dashed line is superimposed on the figure reflecting LSW kinetics (straight line) with a slope estimated using parameters identified in the literature [5].

Table I. Chemical Compositions wt.% of Modified 4120 Experimental Alloys [5]

<b>wt.%</b>	<b>C</b>	<b>Mn</b>	<b>Cr</b>	<b>Mo</b>	<b>Ti</b>	<b>Nb</b>	<b>V</b>	<b>Al</b>	<b>N</b>	<b>Ti/N</b>
LNb	0.21	0.89	0.50	0.00	0.015	0.044	-	0.025	0.008	1.9
HNb	0.21	0.83	0.49	0.01	0.012	0.104	-	0.022	0.009	1.3
MoLNb	0.21	0.86	0.50	0.29	0.013	0.043	-	0.024	0.008	1.6
MoHNb	0.21	0.86	0.50	0.30	0.015	0.118	-	0.021	0.008	1.9

L = Low

H = High

The results in Figure 4 suggest some important implications. Most importantly, the molybdenum addition to both the low and high niobium steels reduces the NbC coarsening rate at 1100 °C, as emphasized by the vertically descending arrows in the figure, confirming the benefit of the combined Nb+Mo addition. The higher niobium level is associated with greater coarsening, as expected based on LSW kinetic theory, where the solute concentration of the diffusing species plays an important role, and due to a greater fraction of larger Nb-rich precipitates after hot rolling. Despite the faster particle coarsening kinetics, the high-Nb steel maintains superior grain coarsening resistance due to its increased volume fraction of particles [5,6]. While the coarsening behavior of the solution treated alloy fits the LSW model rather closely, the coarsening rates of the hot-rolled steels are greater than the model predictions. This behavior is attributed to a bi-modal particle size distribution in the hot-rolled condition, due to the presence of coarser particles formed in austenite and finer particles formed in ferrite during cooling after rolling [5]. Grain coarsening studies have confirmed the beneficial influence of adding both niobium and molybdenum [6], and additional studies are needed to verify the corresponding improved fatigue behavior that would be expected.

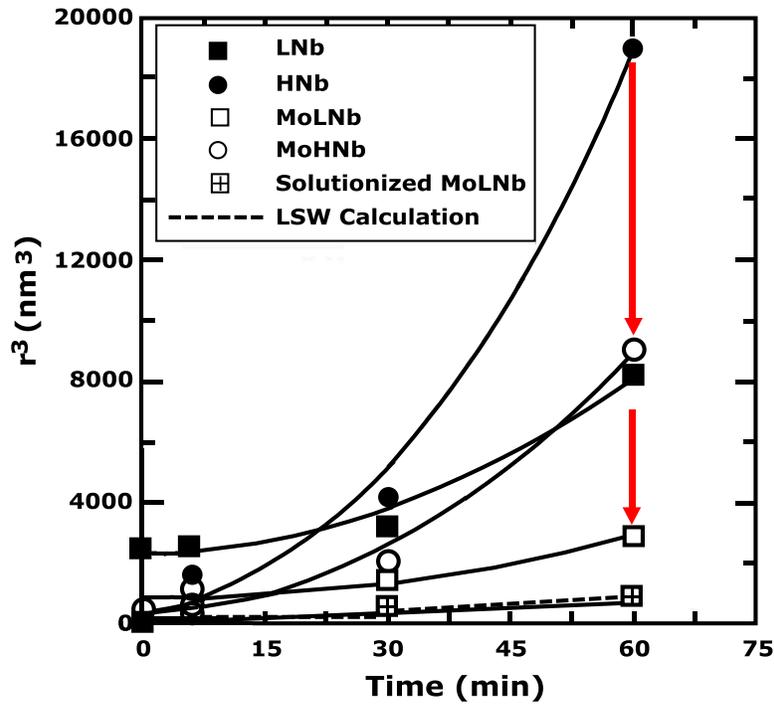


Figure 4. NbC particle radius cubed ( $r^3$ ) vs. holding time at 1100 °C for four hot-rolled experimental steels, and MoLNb steel after 1250 °C solution treatment and quench. Dashed line indicates coarsening rate calculated based on LSW theory [5]. Arrows emphasize the influence of Mo on NbC coarsening kinetics.

### Precipitation of Mixed (Nb,Mo)C

The influence of molybdenum on microalloy carbide coarsening has been ascribed to a variety of potential factors including, (1) Mo-segregation to the particle/matrix interface, reducing interfacial energy, (2) reduced misfit strains at the interface, due to effects of molybdenum on lattice parameters, or (3) reduced niobium diffusivity due to the presence of solute molybdenum [4,5,16,17]. Evolution of the mixed (NbMo) carbide precipitates was examined in the Nb-Mo modified SAE 4120 alloys discussed above, using TEM/STEM (with energy dispersive characteristic X-ray spectroscopic chemical analysis, EDS) and 3-D atom probe tomography (APT). These recent studies have contributed new understanding of (Nb,Mo) carbide precipitation behavior, and a few highlights are included below.

Figure 5(a) shows a composition profile for niobium, molybdenum and titanium determined using STEM-EDS from the surface toward the center of a small carbide on an extraction replica shown in an annular dark field STEM image (Figure 5(b)) for the hot-rolled and air cooled MoHNb specimen. The results indicate the presence of niobium, molybdenum and titanium in the precipitate, with molybdenum enrichment near the surface, and titanium present near the center. The increased X-ray counts for these elements near the center are due to the increased interaction volume in this location. The molybdenum enrichment near the surface could be due to segregation to the interface, or low-temperature precipitation during cooling.

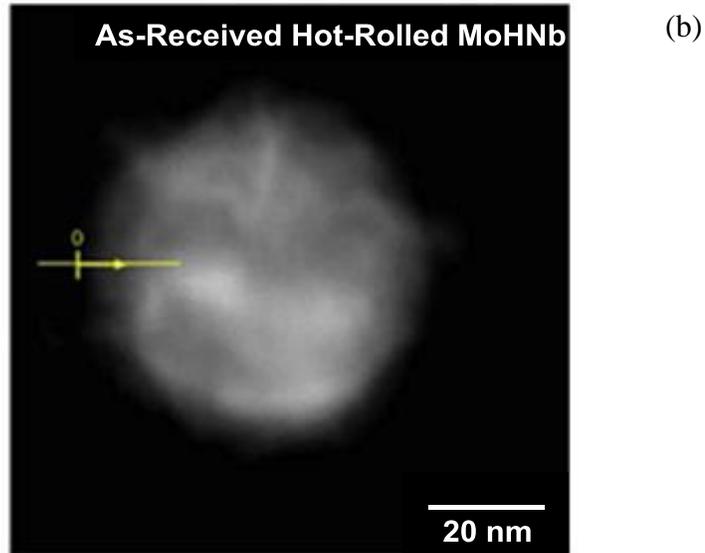
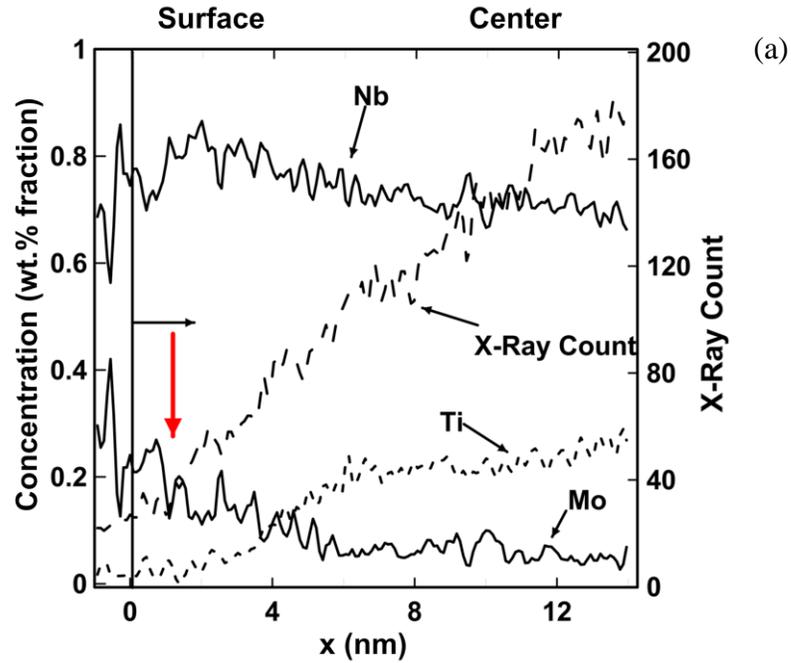


Figure 5. STEM EDS composition profiles (a) for niobium, molybdenum and titanium for microalloy carbide with reference location shown in the dark field STEM image in (b), for hot-rolled steel MoHNb [4]. Mo enrichment near the particle/matrix interface is highlighted by the red arrow in (a).

Calculations of particle compositions in mixed  $(\text{Nb}_x\text{Mo}_{1-x})\text{C}$  have been made for these steels using a regular solution model enabled by the MoC solubility product expressions recently made available from Pavlina *et al.*, as discussed above [3,4,18]. Figure 6 shows predicted molybdenum atom fractions on the metallic sublattice for alloys containing 0.2%C, 0.3%Mo, and 0.043 or 0.118%Nb, corresponding to the nominal MoLNb and MoHNb alloy compositions. The figure indicates that substantial molybdenum incorporation into the niobium carbides is expected at temperatures in the ferritic regime, and much less so in austenite. As expected, the molybdenum fractions are also reduced when the overall niobium concentration is increased in the alloy.

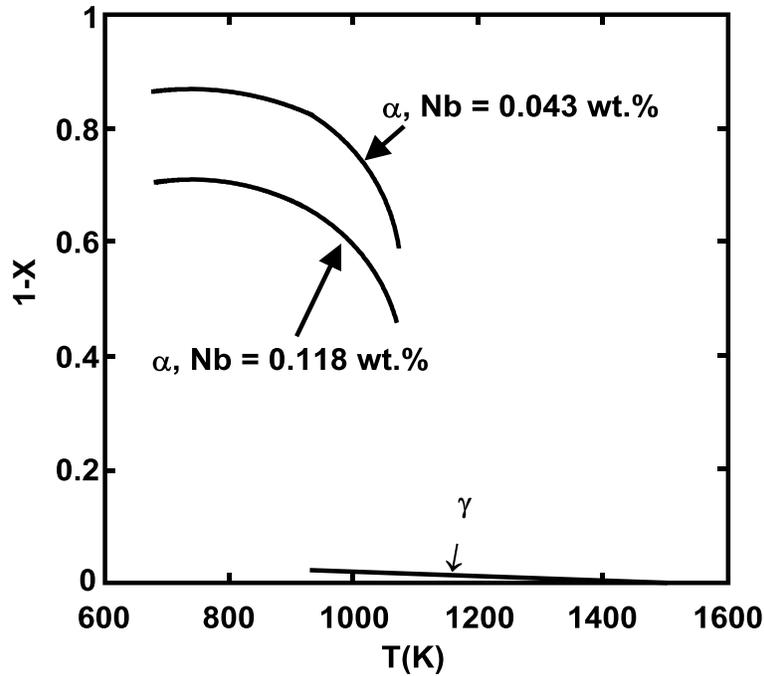


Figure 6. Predicted Mo concentrations in  $(\text{Nb}_x\text{Mo}_{1-x})\text{C}$  for 0.2%C, 0.3%Mo steels in ferrite and austenite at various temperatures [4].

Particle compositions in specimens heated to a low temperature (900 °C) within the austenite regime (and quenched) retain a mixed character, and are found to be dependent on alloy composition and particle size, as shown in Figure 7 for the MoLNb and MoHNb. The smaller particles contain greater molybdenum fractions, while larger particles contain higher titanium concentrations, particularly in the lower-Nb steel. Presumably, the finer particles may have formed at lower temperature (with greater molybdenum enrichment expected, as per Figure 6), or may have been influenced by re-precipitation during quenching from the austenite.

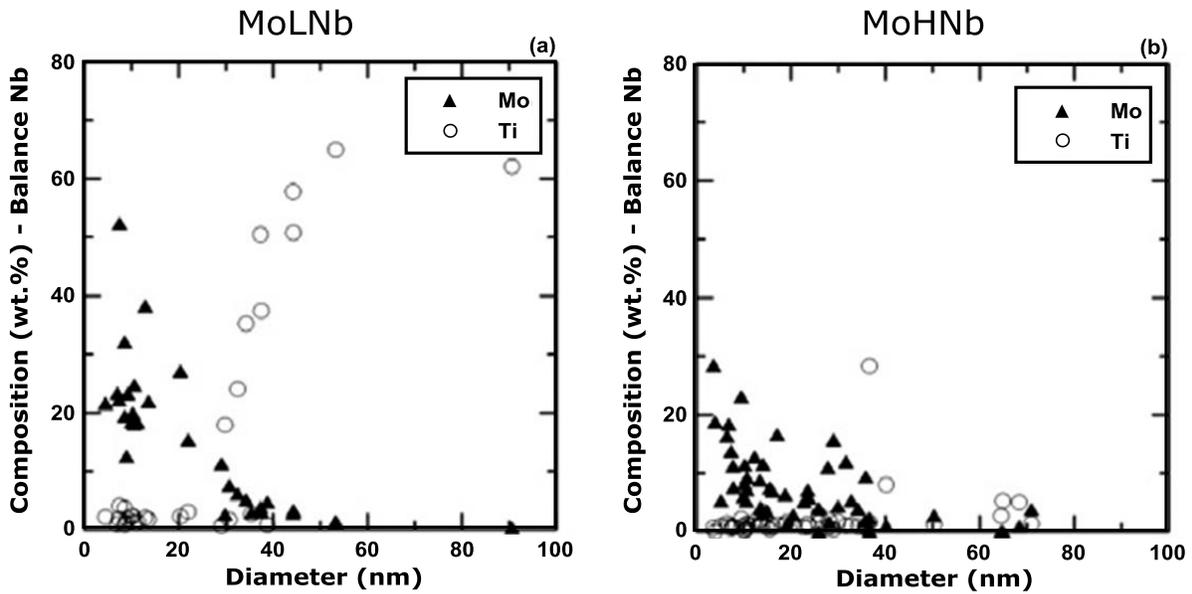


Figure 7. Molybdenum and titanium metallic sublattice compositions (balance niobium) versus particle diameter determined by STEM EDS in mixed carbides for MoLNb (a) and MoHNb (b) steels hot-rolled, reheated to 900 °C and water quenched [4].

As the STEM-EDS results are unable to distinguish molybdenum enrichment near the surface from segregation at the interface, 3-D APT, (atom probe tomography), with high spatial resolution, was used to examine small precipitates in specimens quenched from austenite. Figure 8(a) shows a 3-D reconstructed image of the specimen tip in the MoHNb sample heated to 900 °C and water quenched (with red dots indicating individual carbon atoms, and blue dots indicating areas of niobium atoms), and Figure 8(b) shows a corresponding composite profile or “proximity histogram” (a profile of local atomic concentration as a function of proximity to an interface [19]) centred on the 10% niobium iso-concentration surfaces (blue surfaces in Figure 8(a)) for four particles in the reconstruction. The profile shows molybdenum incorporation in the carbide, but does not indicate any substantial enrichment of the interface with molybdenum. This result does not support the hypothesis that molybdenum’s contribution to NbC coarsening resistance in austenite results from segregation to the interface, but does not preclude the possibility that such a mechanism may operate in ferrite.

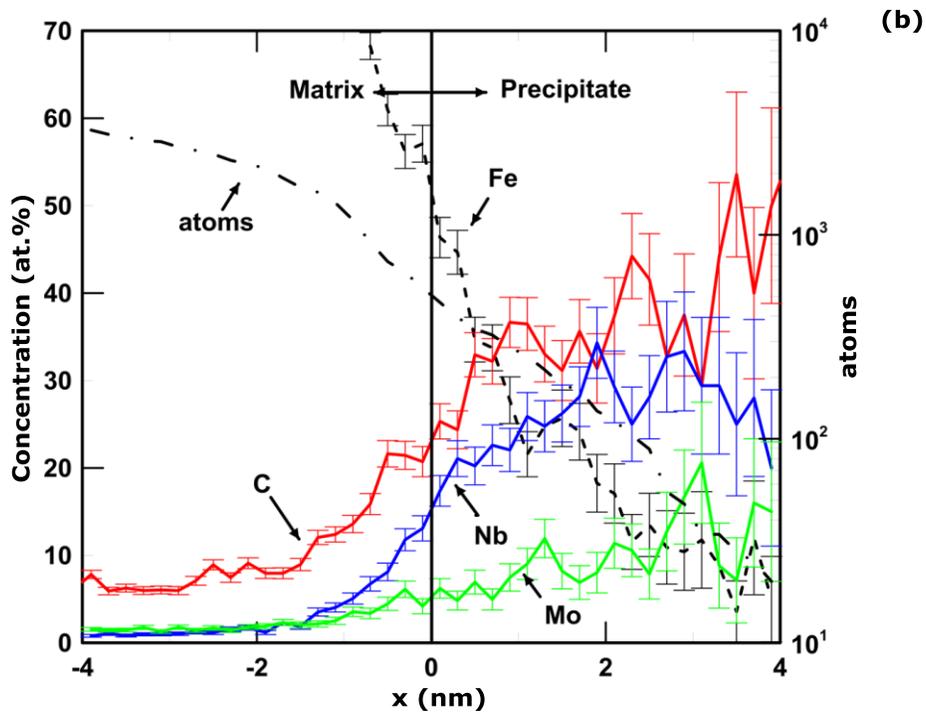
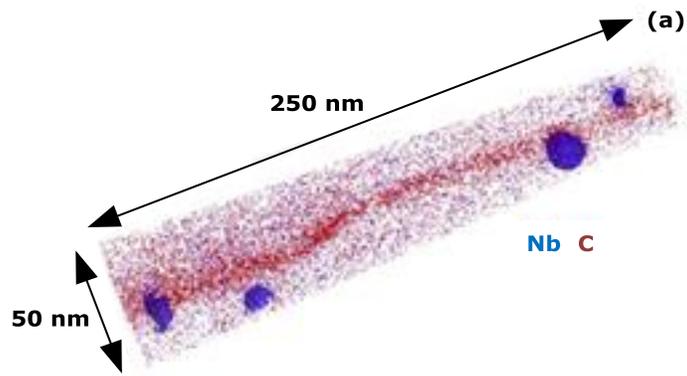


Figure 8. Three dimensional atom-map reconstruction (a) of hot-rolled MoHNb sample heated to 900 °C and water quenched. Proximity histogram (b) for the four particles showing atom count and atomic concentrations of Fe, C, Nb and Mo as a function of distance from a 10 at.% Nb iso-concentration surface [4].

## Summary

Niobium and molybdenum are important elements in many steels due to their specific individual effects: predominantly grain refinement and precipitation in the case of Nb-microalloyed HSLA steels, and predominantly hardenability and temper resistance in Mo-added structural steels. When added in combination, some additional synergy is also possible from a contribution of molybdenum to reduced NbC coarsening kinetics. The understanding of the associated mechanism remains incomplete, however. Precipitate coarsening resistance enhances precipitation strengthening in ferrite in some applications, and has been shown recently to provide austenite refinement during high temperature carburizing simulations. Molybdenum is incorporated in the microalloy carbides, particularly at lower temperature, and recent analysis of Mo-carbide solubility has provided solubility products for MoC and Mo<sub>2</sub>C in ferrite and austenite enabling better understanding of the mixed (Nb,Mo)C carbides. Atom probe tomography has not confirmed enrichment of the particle/matrix interface for small particles quenched from austenite, although this mechanism cannot be ruled out in ferrite.

## Acknowledgements

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