Carbide Precipitation Behavior in Nb and Nb-Mo Microalloyed Steels During Heating (Postprint)

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Abstract

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Full Text

Preamble

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Precipitation Behavior of Carbide During Heating Process in Nb and Nb-Mo Micro-Alloyed Steels

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Abstract: The precipitation behavior of carbides in quenched Nb and Nb-Mo micro-alloyed steels during heating was investigated using Gleeble thermal simulation, Vickers hardness testing, SEM, HRTEM, and DSC. The precipitation kinetics of MC-type carbides in the quenched steels were calculated using classical nucleation and growth theory combined with the Avrami equation. The results show that when quenched Nb and Nb-Mo steels were heated at 20 °C/min to various temperatures followed by water quenching, hardness peaks appeared at 300 °C and 700 °C due to the precipitation of ϵ-carbide and MC-type carbide, respectively. MC-type carbides precipitated at approximately 650 °C, causing hardness to increase through precipitation strengthening, which aligns with theoretical calculations showing a nose temperature of about 650 °C for MC-type carbide precipitation. The incorporation of Mo into NbC reduces the lattice mismatch between NbC and the ferrite matrix, thereby decreasing the interfacial energy between the precipitate and ferrite matrix. This accelerates the precipitation kinetics of (Nb, Mo)C, resulting in denser and finer precipitate distributions in Nb-Mo steel and a more pronounced precipitation strengthening effect.

Keywords: carbide, precipitation, Vickers hardness, interfacial energy

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Nb is a strong carbide-forming element that strengthens steel through solid solution or by forming carbonitrides with carbon and nitrogen in the steel matrix [1,2]. For instance, undissolved Nb carbonitrides can inhibit austenite grain growth during high-temperature soaking, dissolved or strain-induced Nb can suppress recrystallization of deformed austenite, and Nb precipitated during subsequent ferrite transformation provides effective precipitation strengthening [3–6]. Consequently, Nb is widely used in engineering machinery, tool and die, and fire-resistant structural steels [7–10]. To enhance the effectiveness of Nb, Nb-Mo composite addition is commonly employed. Cao et al. [11] reported that Nb-Mo composite addition in hot-rolled steel coils provides better precipitation strengthening increments from micro-alloy carbides compared to Nb-Ti composites, thereby improving yield strength. Uemori et al. [12] found that in fire-resistant steels containing Nb and Mo, Mo segregation at NbC/matrix interfaces can inhibit the growth and coarsening of NbC for a period, thus enhancing high-temperature mechanical properties.

In addition to Nb precipitation behavior during post-rolling cooling, researchers have conducted extensive studies on precipitation in Nb-microalloyed martensitic steels during tempering to achieve a good balance of strength and toughness, capitalizing on the secondary hardening effect from extensive dispersion precipitation. Yu et al. [13] and Yang et al. [14] investigated the microstructure, properties, and Nb precipitation in quenched Nb-containing steels at different tempering temperatures. Liu et al. [15–17] further examined the nucleation, growth, and coarsening of cementite and micro-alloy carbides during tempering of quenched martensite using three-dimensional atom probe. However, these studies were based on the same chemical composition at different tempering temperatures, with relatively low Nb content (mass fraction below 0.05%), resulting in less significant secondary hardening effects. Moreover, the mechanism by which Mo influences the precipitation kinetics of NbC in ferrite after Nb-Mo composite addition has not been elaborated in detail.

This work employs an alloy composition system with higher Nb content (0.1 mass fraction) to achieve greater precipitation strengthening increments. Vickers hardness testing and microstructural/precipitate observations were performed on samples heated at a constant rate to various temperatures followed by immediate water quenching after high-temperature quenching. The hardness changes, microstructural evolution, and carbide precipitation behavior in quenched Nb and Nb-Mo steels during heating were investigated. Classical nucleation and growth theory, the Avrami equation, and the precipitation kinetics calculation model for micro-alloy carbides established by Yong Qilong [18] were employed to calculate the precipitation kinetics of Nb precipitates in supersaturated ferrite.

Experimental

The experimental Nb and Nb-Mo micro-alloyed steels were melted in a vacuum induction furnace and cast into 50 kg ingots. Their chemical compositions are listed in Table 1 , designated as Nb steel and Nb-Mo steel, respectively, with micro-Ti treatment. After forging and controlled rolling/cooling, 11 mm thick plates were produced. Samples of appropriate size were cut from the plate mid-section, sealed in quartz tubes, soaked at 1200 °C for 5 h, and then water quenched. The microstructure of the quenched samples was observed using an S4300 cold field-emission scanning electron microscope (SEM).

The phase transformation temperatures Ac_1 (pearlite-to-austenite transformation start temperature) and Ac_3 (completion temperature of pro-eutectoid ferrite-to-austenite transformation) for both steels during heating at 20 °C/min were measured using a Formastor-F dilatometer on cylindrical specimens measuring 3 mm in diameter and 10 mm in length. Quenched samples were subjected to thermal cycling experiments on a Gleeble 3800 thermal simulator, heated at 20 °C/min to temperatures between 200–750 °C followed by immedi-

Figure 2

Figure 1: Figure 2

ate water quenching to room temperature, using cylindrical specimens 8 mm in diameter and 12 mm in length. The thermally simulated specimens were then sectioned axially into two halves. From one half, 0.3 mm thick discs were cut, mechanically ground to 35 μm thickness, punched into 3 mm diameter discs, and twin-jet electropolished using a 6% perchloric acid ethanol solution (by volume). The remaining samples were etched with 3% nital solution (by volume) for SEM microstructural observation. The other half was ground, polished, deeply etched with 4% nital solution (by volume), carbon-coated using a HUS-5GB high-vacuum coater, and then carbon extraction replicas containing second-phase particles were collected on Cu grids. Both the twin-jet samples and extraction replicas were examined using a Tecnai F20 field-emission high-resolution transmission electron microscope (HRTEM) for microstructure and precipitate observation, with energy-dispersive spectroscopy (EDS) analysis of precipitates.

Precipitation behavior in the quenched steels was studied using a DSC-60 differential scanning calorimeter (DSC) on small discs 8 mm in diameter and 1 mm thick, heated at 20 °C/min over the temperature range 150–400 °C. Precipitate size distributions were statistically analyzed using Nano Measurer 1.2 software, with no fewer than 200 particles counted per sample. Vickers hardness of both steels after heating to various temperatures and water quenching was measured using an FM-300 digital Vickers hardness tester with a 5 kg load, with the final result taken as the average of five measurements.

2.1 Hardness Testing

Figure 1 [FIGURE:1] shows the Vickers hardness variation with heating peak temperature for Nb and Nb-Mo micro-alloyed steels after soaking at 1200 °C for 5 h, water quenching, heating to different temperatures, and water cooling. The quenched Nb steel exhibited higher hardness than the Nb-Mo steel. Upon heating to 200 °C, the hardness of both steels decreased. At 300 °C, the hardness increased, showing a peak value, after which it decreased again until temperatures exceeded 600 °C, when hardness began to rise once more, reaching another peak at 700 °C. At 750 °C, the hardness decreased again. Throughout the 300–700 °C range, the hardness of Nb-Mo steel remained consistently higher than that of Nb steel.

2.2 Microstructure

Figure 2

Figure 3

Figure 2: Figure 3

Figure 6

Figure 3: Figure 6

presents SEM images of Nb and Nb-Mo micro-alloyed steels after soaking at 1200 °C for 5 h and water quenching. In addition to martensite, numerous elongated or granular bright white structures were distributed in the matrix of both steels, with a higher density in the Nb-Mo steel. Figure 3

shows SEM images of both steels heated at 20 °C/min to 200–700 °C followed by water quenching. When heated to 300 °C, most of the larger bright white structures disappeared, and another phase precipitated within or at the boundaries of ferrite laths (Fig. 3b). This phase gradually grew and coarsened at temperatures above 300 °C (Figs. 3c–f). Figures 4a and 4b show bright-field and dark-field TEM images of the bright white structures in the quenched microstructure of Nb-Mo steel. Diffraction pattern analysis (Fig. 4c) revealed a bcc structure with a different crystallographic orientation from the ferrite matrix. Literature [19] reported similar structures in steels with chemical compositions close to this study under rapid cooling, identifying them as hard-phase martensite/austenite (M/A) islands consisting of martensite and retained austenite [20]. Therefore, these elongated or granular phases are M/A islands. Figures 4d–f show TEM images, diffraction patterns, and EDS analysis of the precipitates at 300 °C. The diffraction pattern indicates a hexagonal structure. Combined with the characteristics of retained austenite decomposition and carbide precipitation in martensite during low-temperature tempering [15,21,22] and the EDS results, this phase was identified as ϵ-carbide, which may evolve into cementite at temperatures above 300 °C [22].

Figure 5 [FIGURE:5] shows TEM images of the two quenched experimental steels heated to 500, 600, and 700 °C followed by immediate water quenching. With increasing temperature, some ferrite lath boundaries in Nb steel became blurred and gradually disappeared, with parallel laths merging into wider ones, and the dislocation density within laths decreased. In contrast, ferrite lath widths in Nb-Mo steel were smaller than those in Nb steel, with most lath boundaries remaining clearly visible even at higher temperatures and significantly higher dislocation densities within laths, indicating that Mo addition suppresses recovery of ferrite laths at elevated temperatures.

After heating to 700 °C and water quenching, the morphology, HRTEM images, and EDS spectra of precipitate particles in both steels are shown in Figure 6

. The precipitate particles in Nb-Mo steel were more densely distributed and finer in size than those in Nb steel. Statistical analysis revealed average precipitate sizes of 2.83 nm and 2.23 nm in Nb steel and Nb-Mo steel, respectively.

EDS analysis showed that the dispersed second-phase particles in Nb steel were NbC, while those in Nb-Mo steel were (Nb, Mo)C, with an average Mo/Nb atomic ratio of 0.56 in the particles, indicating that the Mo site occupancy fraction in NbC reached approximately 30%. The lattice constants of NbC and (Nb,Mo)C in Nb steel and Nb-Mo steel were 0.446 nm and 0.430 nm, respectively. Literature [11,23] precisely measured the lattice constants of (Nb, Mo)C powder samples in hot-rolled Nb-Mo-containing steels using XRD, finding that Mo incorporation reduces the lattice constant of NbC. Jang et al. [24] studied the stability of (Ti, Mo)C in ferrite using first-principles calculations and experiments, discovering that Mo with a smaller atomic radius than Ti partially substitutes Ti atoms in TiC to form (Ti, Mo)C, decreasing the lattice constant. Since NbC and TiC share the same fcc structure and both Nb and Ti have larger atomic radii than Mo, Mo incorporation similarly reduces the lattice constant of NbC.

3.1 Hardness Variations

Due to the relatively low carbon content resulting in insufficient hardenability, the microstructure after quenching consisted of martensite and bainite in both steels. Since Mo promotes bainite transformation, Nb-Mo steel contained more bainite after quenching (Fig. 2), resulting in lower hardness than Nb steel. After heating to 200 °C and water quenching, the hardness of both steels decreased to varying degrees due to carbon atom diffusion during heating, which reduced carbon supersaturation in the matrix and consequently decreased lattice distortion [15]. At 300 °C, M/A islands decomposed [16], forming martensite and ϵ-carbide. The low carbon content and presence of strong carbide-forming elements Nb and Mo inhibited the growth and coarsening of ϵ-carbide [18,25], allowing fine ϵ-carbide to provide some precipitation strengthening. Figure 7 shows the DSC curves for both steels during heating. An exothermic peak near 300 °C, combined with characteristic microstructural changes during martensite tempering [22], confirms ϵ-carbide precipitation, consistent with SEM and TEM observations.

At higher heating temperatures (600 °C), hardness decreased due to matrix recovery and the formation of coarse cementite. However, at elevated tempering temperatures, cementite decomposes and dissolves, releasing carbon atoms that combine with alloying elements to form MC-type micro-alloy carbides, producing precipitation strengthening that counteracts softening from matrix recovery and cementite coarsening, thereby slowing the hardness decrease rate. As temperature continued to rise, the precipitation amount of MC-type carbides increased, and when the precipitation strengthening increment exceeded matrix softening, hardness began to increase. Thus, the hardness increase above 600 °C resulted from micro-alloy carbide precipitation. Since the Ac_1 and Ac_3 temperatures were 735 °C and 915 °C for Nb steel and 715 °C and 905 °C for Nb-Mo steel, respectively, hardness decreased after water quenching from temperatures

above 750 °C because the small amount of austenite formed in the short time after phase transformation could not compensate for ferrite matrix softening from recovery.

Furthermore, Figure 5 shows that Mo addition suppresses substructure recovery in the steel. Although a small amount of Mo co-precipitates with cementite or MC-type carbides, most Mo exists in solid solution due to its high solubility in the matrix [18], which enhances atomic bonding and delays martensite recovery [26]. Additionally, the denser and finer (Nb, Mo)C precipitation pins dislocations [16,26]. Consequently, Nb-Mo steel exhibited higher hardness than Nb steel, with a significant hardness increase at 700 °C due to extensive dispersion strengthening.

3.2 NbC/(Nb, Mo)C Precipitation Kinetics

Classical nucleation and growth theory combined with the Avrami equation is widely used to describe precipitation kinetics of micro-alloy carbonitrides in steel, typically for precipitation during cooling in austenite or ferrite. However, calculations of precipitation kinetics in supersaturated ferrite during heating are rarely reported. After solution treatment above the complete dissolution temperature and water quenching, all Nb can be considered dissolved in the supersaturated ferrite. Rapid heating at a constant rate to a certain temperature induces NbC precipitation. Although the precipitation driving force (supersaturation) is large at low temperatures, diffusion is unfavorable, while at high temperatures, diffusion is favorable but the driving force is low. The combined effect of these two factors should produce C-curve kinetics during heating. Moreover, since the free energy of micro-alloy carbides is lower than that of cementite, micro-alloy carbides are thermodynamically more stable [18]. The higher precipitation temperature of micro-alloy carbides during tempering leads to cementite decomposition and dissolution at elevated temperatures, providing carbon atoms required for micro-alloy carbide precipitation. Therefore, even though cementite may precipitate before micro-alloy carbides during heating, calculations can assume rapid heating to a specific temperature to avoid cementite formation, temporarily neglecting its influence.

Using the calculation method from literature [18], the relationship between critical nucleation work, critical nucleation size, and temperature, as well as precipitation-temperature-time (PTT) curves for micro-alloy carbide precipitation during heating of quenched steels were calculated. To compare the effect of Mo, the compositions used in calculations were 0.042%C-0.1%Nb for Nb steel and 0.042%C-0.1%Nb-0.19%Mo for Nb-Mo steel.

3.2.1 Effect of Mo on Interfacial Energy During NbC Precipitation

During nucleation of alloy carbides, interfacial energy between the precipitate and Fe matrix impedes nucleation. Interfacial energy comprises structural and chemical components, with structural energy typically exceeding chemical en-

Figure 9

Figure 4: Figure 9

ergy by more than an order of magnitude for semi-coherent interfaces [18]; therefore, only structural interfacial energy was considered for NbC precipitation. According to Vegard' s law [28], when both MoC and NbC have cubic crystal structures, the lattice parameter of the composite precipitate (NbxMo1-x)C (0 $\leq$ x $\leq$ 1) varies linearly with Mo atomic occupancy fraction [29]. Using lattice constants of 0.4477 nm for NbC [24] and 0.4277 nm for MoC [30], the variation of (NbxMo1-x)C lattice parameter with Mo occupancy fraction is shown in Figure 8 [FIGURE:8]. As Mo occupancy fraction increases, the lattice parameter of (NbxMo1-x)C decreases.

MC-type micro-alloy carbides (NbxMo1-x)C with NaCl crystal structure typically have a Baker-Nutting orientation relationship with the ferrite matrix [18]: (001)(NbxMo1-x)C//(001)α, 010C//[110]α. The mismatch d in the 100C//[110]α and (001)(NbxMo1-x)C//(001)α directions can be calculated by [18]:

d = (a(NbxMo1-x)C - $\sqrt{2}$aα) / a(NbxMo1-x)C

where a(NbxMo1-x)C and aα are the lattice parameters of (NbxMo1-x)C and ferrite, respectively.

Since the lattice parameter of (NbxMo1-x)C varies with Mo occupancy fraction, its mismatch with ferrite also changes accordingly. Based on the semi-coherent dislocation theory for (NbxMo1-x)C/ferrite [18], the interfacial energy between (NbxMo1-x)C and ferrite matrix can be calculated. The results are shown in Figure 9

for x values ranging from 0.5 to 1. As Mo occupancy fraction increases, the interfacial energy between (NbxMo1-x)C and ferrite decreases. Additionally, the interfacial energy between (NbxMo1-x)C and the matrix in this work varies with temperature, primarily due to the temperature dependence of the ferrite matrix elastic modulus [18].

3.2.2 Critical Nucleation Size and Energy of (NbxMo1-x)C

The free energy change for forming a nucleus of diameter d of (NbxMo1-x)C on a dislocation line in ferrite is:

$$\Delta G = \Delta Gchem \cdot V + \Delta GV \cdot V + \pi d^2 \sigma int + \Delta Gd$$

where ΔGchem is the molar free energy change of precipitation, ΔGV is the volume free energy change, σint is the interfacial energy between precipitate and matrix, ΔGd is the dislocation core energy, V is the molar volume of (NbxMo1-x)C, and ΔGV can be calculated from the solubility product of the precipitate in ferrite [18].

Setting $\partial\Delta G/\partial d = 0$ yields the critical nucleation size dc and critical nucleation energy ΔGc:

dc = -2σint / ΔGV $\cdot$[1 - (1 + A)^(1/2)] ΔGc = 16$\pi\sigma$int^3 / (3ΔGV^2) $\cdot$f(A)

where A = Gb^2 / [4π(1 - ν)] $\cdot$(ln(dc/b) + 1) / (σint$\cdot$dc), G is the shear modulus of ferrite matrix, b is the magnitude of the Burgers vector, and ν is Poisson' s ratio.

3.2.3 Nucleation Rate of (NbxMo1-x)C

When (NbxMo1-x)C nucleates on dislocation lines and the nucleation rate rapidly decays to zero, the nucleation rate I can be expressed as:

I = K $\cdot$ (T/σint)^(1/2) $\cdot$ exp(-ΔGc/kT) $\cdot$ ρ

where K is a temperature-independent constant, T is thermodynamic temperature, k is Boltzmann constant, ρ is matrix dislocation density, and Q is the diffusion activation energy of Nb. Taking logarithms of both sides gives:

ln I = ln(πKρ) + (1/2)ln T - ln σint - ΔGc/kT - Q/kT

3.2.4 Precipitation-Temperature-Time (PTT) Curves of (NbxMo1-x)C

Assuming the time $t_{0\cdot05}$ when (NbxMo1-x)C precipitation reaches 5% mass fraction represents the precipitation start time, the PTT equation for (NbxMo1-x)C is:

ln $t_{0\cdot05}$ = ln t_0 - 1.28994 - 2 ln σint + (5/3)ln T + ΔGc/kT + Q/kT

where n is the precipitation kinetic time exponent. When the nucleation rate of micro-alloy carbides rapidly decays to zero, n = 1, and t_0 is a time-independent constant [18].

Equations (2)-(7) show that precipitation kinetics are influenced by two factors: precipitation free energy (driving force) and interfacial energy. Mo has minimal effect on the precipitation driving force of NbC in ferrite [18]. Jang et al. [24] and Wang et al. [31] experimentally found that the Mo occupancy fraction decreases as TiC grows and coarsens in the Fe matrix. Liu et al. [16,17] observed using atom probe that Mo diffuses out of (Nb, V, Mo)C carbides during tempering, gradually being replaced by Nb and V carbides, indicating that Mo is thermodynamically unstable in MC-type carbides and only has high occupancy fraction during early nucleation stages. As MC-type carbides grow and coarsen and precipitation kinetics approach equilibrium, the Mo occupancy fraction decreases. Since the precipitation free energy considered in calculations approaches equilibrium values at a given temperature, Mo incorporation is assumed to have negligible effect on the precipitation free energy of NbC during early nucleation stages.

Figure 10

Figure 5: Figure 10

Figure 11

Figure 6: Figure 11

Based on these calculations, the critical nucleation work and critical nucleation size for (NbxMo1-x)C precipitation in ferrite are shown in Figure 10

. At the same precipitation temperature, both critical nucleation work and critical nucleation size decrease with increasing Mo occupancy fraction, indicating that (Nb, Mo)C precipitates more readily in Nb-Mo steel. This aligns with TEM observations showing denser and finer precipitate distributions in Nb-Mo steel.

Similarly, the precipitation-temperature-time (PTT) kinetics curves for (NbxMo1-x)C precipitation in ferrite during heating were calculated, as shown in Figure 11

. Mo incorporation reduces the mismatch between NbC and ferrite matrix, thereby decreasing interfacial energy and shifting the precipitation kinetics curve upward and leftward, indicating accelerated precipitation kinetics. The nose temperature for fastest precipitation increases from 600 °C to 650 °C with increasing Mo occupancy fraction, which agrees well with the experimental precipitation start temperature of approximately 650 °C obtained from hardness testing.

Conclusions

(1) When quenched Nb and Nb-Mo micro-alloyed steels were heated at 20 °C/min to various temperatures followed by water quenching, hardness peaks appeared at 300 °C and 700 °C. The peak at 300 °C resulted from decomposition of martensite/austenite (M/A) islands into ϵ-carbide, while the peak at 700 °C was caused by precipitation strengthening from nanometer-scale MC-type carbides.

(2) The hardness decrease in quenched Nb and Nb-Mo micro-alloyed steels heated at 20 °C/min to 300–600 °C followed by water quenching resulted from matrix recovery and cementite coarsening, with no MC-type carbide precipitation below 600 °C. When temperature exceeded 600 °C, nanometer-scale MC-type carbides precipitated, causing precipitation strengthening and hardness increase. Theoretical calculations yielded C-shaped PTT curves for MC-type carbide precipitation during heating with a nose temperature of approximately 650 °C, consistent with

experimental results.

(3) Mo incorporation into NbC reduces the lattice mismatch between NbC and ferrite matrix, thereby decreasing interfacial energy between precipitates and ferrite matrix. This accelerates the precipitation kinetics of (Nb, Mo)C in ferrite, resulting in denser, finer precipitate particles and more effective precipitation strengthening in Nb-Mo steel.

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Figure 13

Figure 7: Figure 13

Figure 14

Figure 8: Figure 14

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Figures