

Article

The Effect of Molybdenum on Precipitation Behaviour in Austenite of Strip-Cast Steels Containing Niobium

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Abstract: Two low-C steels microalloyed with niobium (Nb) were fabricated by simulated strip casting, one with molybdenum (Mo) and the other without Mo. Both steels were heat treated to simulate coiling at 900 °C to investigate the effect of Mo on the precipitation behaviour in austenite in low-C strip-cast Nb steels. The mechanical properties results show that during the isothermal holding at 900 °C the hardness of both steels increases and reaches a peak after 3000 s and then decreased after 10,000 s. Additionally, the hardness of the Mo-containing steel is higher than that of the Mo-free steel in all heat-treated conditions. Thermo-Calc predictions suggest that MC-type carbides exist in equilibrium at 900 °C, which are confirmed by transmission electron microscopy (TEM). TEM examination shows that precipitates are formed after 1000 s of isothermal holding in both steels and the size of the particles is refined by the addition of Mo. Energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) reveal that the carbides are enriched in Nb and N. The presence of Mo is also observed in the particles in the Nb-Mo steel during isothermal holding at 900 °C. The concentration of Mo in the precipitates decreases with increasing particle size and isothermal holding time. The precipitates in the Nb-Mo steel provide significant strengthening increments of up to 140 MPa, higher than that in the Nb steel, ~96 MPa. A thermodynamic rationale is given, which explains that the enrichment of Mo in the precipitates reduces the interfacial energy between precipitates and matrix. This is likely to lower the energy barrier for their nucleation and also reduce the coarsening rate, thus leading to finer precipitates during isothermal holding at 900 °C.

Keywords: molybdenum; precipitation; austenite; niobium steels; strip casting

1. Introduction

For the high-strength low-alloy (HSLA) steels containing niobium (Nb) produced by conventional casting techniques, hot deformation in the austenite region usually induces the formation of Nb carbonitrides precipitates [1,2]. The Nb carbonitrides, formed in austenite, are able to provide precipitation strengthening and refine the microstructure by delaying the recrystallization of austenite at high temperatures, improving the strength as a result [2,3]. However, these precipitates can be eventually very coarse after a prolonged isothermal-holding in the austenite region, consequently losing their advantage in the microstructure refinement and precipitation strengthening. In previous literature, trace additions of molybdenum (Mo) were reported to enhance the precipitation strengthening of steels

microalloyed with Nb or/and Ti by suppressing the coarsening of Nb or Ti carbides [4–10]. It was proposed that Mo changes the coarsening resistance of Nb-rich carbonitrides in austenite by lowering interfacial energy [11], and thus refines the precipitates [7,9,11–13]. However, despite the extensive investigations on the effect of Mo on the formation of Nb-rich precipitates in austenite, the mechanisms behind these observations are not well established.

Unlike conventional steel-making processes that usually undergo several controlled hot-rolling passes, direct strip casting (DSC) combines casting and subsequent hot-rolling into a single and continuous route with extremely rapid solidification and high cooling rates [1–3], which reduces cost and saves energy-consumption up to 90%. Dorin et al. [14] studied the formation of Nb (C, N) in strip-cast steels and found that chemically complex Nb-rich precipitates containing C, N, Si, and S were formed in austenite during coiling at a high temperature (850 °C), which provides a significant strength increment of up to ~150 MPa. This early work also emphasized significant differences in the Nb (C, N) precipitates formed in strip-cast materials as compared to the ones formed in conventionally processed steel. One of the main differences is that strip casting produces as-cast samples where the Nb is supersaturated and the precipitates can then be formed during a controlled coiling treatment [15]. Consequently, precipitation occurs in non-deformed austenite. Thus, the mechanism behind the precipitation can be different to the strain-induced precipitation in previous literature. In our previous work [16], the addition of Mo was reported to refine Nb (C, N) precipitates in ferrite of strip-cast steels through increasing dislocation density to enhance the nucleation of precipitation and Mo was absent in the Nb (C, N) precipitates that formed in ferrite, which is quite different to what has been found in steels produced by conventional casting techniques. However, to the best of our knowledge, the effect of Mo on the precipitation of Nb (C, N) in the austenite phase field of strip-cast steels has rarely been studied.

In the present paper, two Nb-containing low-carbon steels were prepared via strip casting with and without Mo. The as-cast samples were then heat treated to simulate coiling in the austenitic region (900 °C was selected using Thermo-Calc software, Figure 1 for different durations and hardness testing was used to monitor the hardening response during heat treatment. Transmission electron microscopy (TEM) was performed to observe the precipitation for different isothermal holding times. Finally, the thermodynamic effects of Mo on Nb-rich precipitates and corresponding precipitation strengthening are also presented.

2. Materials and Methods

The compositions of the steels studied in this work are listed in Table 1. The steels were cast using a lab-scale strip casting simulator, known as a dip tester [17]. The steels were melted in a 75 kW induction furnace using high purity starting elements. The details of the casting process can be found in [18]. The thickness of the lab-scale simulated cast section was ~1 mm. After casting, the samples were immediately transferred into a preheated muffle furnace within 2 s, and within this time the samples did not cool below the heat treatment temperature of 900 °C. The detailed thermal profile and schedule diagram of heat treatment can be found in [18]. Coiling times varied from 100 to 10,000 s, and all samples were air-cooled to room temperature at the end of the heat treatment.

Table 1. Compositions of the studied steels, wt %.

	C	Mn	Si	Al	Nb	Mo	S	N	Fe
Nb steel	0.05	1.45	0.21	0.003	0.05	-	<0.0005	0.01	bal.
Nb-Mo steel	0.05	1.50	0.23	0.004	0.05	0.33	<0.0005	0.01	bal.

Thermo-Calc software (2020b, Thermo-Calc Software, Solna, Sweden) with TCFE 9: Steels/Fe Alloys v9.0 database was used to check to the equilibrium phases at 900 °C for the two steels, as displayed in Figure 1. It can be seen that at 900 °C MC-type carbides can be formed in the austenite region and the theoretical volume fraction of these carbides in equilibrium is ~0.0605%.

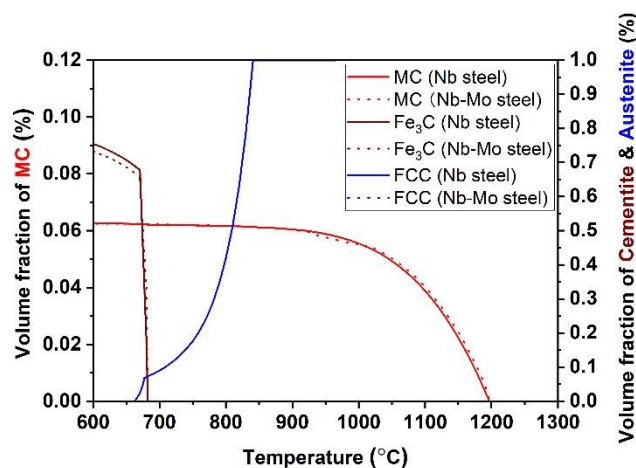


Figure 1. Volume fractions of MC, austenite, and cementite in equilibrium, as predicted by Thermo-Calc software with TCFE 9: Steels/Fe Alloys v9.0 database.

Samples for hardness test and optical microscopy observation were prepared from the central area of the cross-section parallel to the casting direction.

Hardness tests (HWDV-7, TTS Unlimited Inc., Osaka, Japan) were carried out at room temperature to monitor the hardness evolution of both steels heat treated at 900 °C for various times. Average values were generated from at least 7 measurements for each condition.

The specimens for optical microscopy were ground using increasingly finer grades of silicon carbide paper, followed by polishing using diamond particles solutions. Polished samples were etched in 4% nital solution for 10 s. Optical micrographs were taken using Olympus HR DP70 microscope (Olympus, Tokyo, Japan).

TEM foils were electropolished in a solution of 5% perchloric acid in methanol using a twin-jet Tenupol unit, running at 30 V and ~ -35 °C. Carbon layers for TEM carbon replica samples were prepared using a JEOL JEE-420 Vacuum Evaporator (JEOL, Tokyo, Japan) and supported by 300 square mesh copper grids. TEM observation was performed on Philips CM20 instrument (FEI, Hillsboro, OR, USA) with a LaB₆ filament operating at 200 kV. Composition analysis of precipitate particles was carried out using JEOL FEG 2100F TEM with JED-2300T energy dispersive spectroscopy (EDS) detector (JEOL, Tokyo, Japan), operating at 200 kV. Gatan GIF Quantum 965 post column electron energy loss spectroscopy (EELS) (Gatan, Pleasanton, CA, USA) analysis was carried out for fine composition examination using an energy range of 0 to 1000 eV.

3. Results

3.1. Hardness

Hardness measurements were conducted on the two steels for different durations of isothermal holding at 900 °C, as shown in Figure 2. The as-cast hardness of both the Nb and Nb-Mo steels was ~ 201 HV, indicating the minor effect of 0.33 wt % Mo to the Nb steels in the as-cast condition. This has been explained by the very small solid solution strengthening from the addition of Mo in solid solution when the as-cast microstructure of both steels is very similar [19]. As heat treatment progresses, the hardness of both steels evolves in a similar manner. In the early stage (before 100 s), the hardness slowly increases. Afterwards, a more rapid hardening occurs in both steels by reaching the peak hardness after 3000 s at 900 °C. The Nb-steel and Nb-Mo-steel reached peak hardness values of 225 and 245 HV, respectively. However, after 10,000 s isothermal holding, the hardness of both steels drops. Generally, the hardness of the Nb-Mo steel is higher than that of the Nb steel.

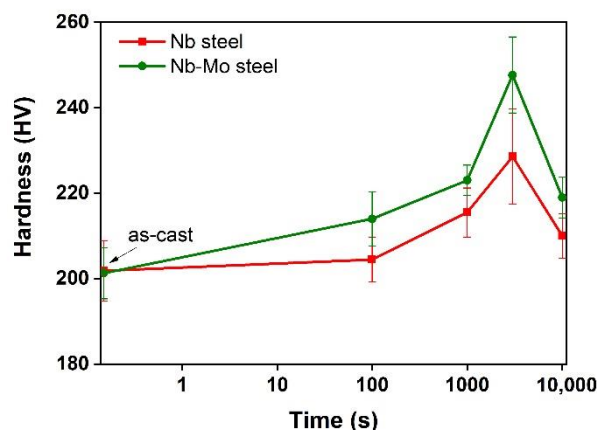


Figure 2. Hardness evolution of the niobium (Nb) and Nb-Mo steels during heat treatment at 900 °C.

3.2. Microstructure

The microstructure of the two steels after isothermal holding at 900 °C for 100, 3000, and 10,000 s were examined and shown in Figure 3. Both microstructures are mainly bainitic, similar to the as-cast microstructure [18], however some grain boundary allotriomorphic ferrite formed in the Nb steel after 10,000 s isothermal holding at 900 °C, but not in the Nb-Mo steel. The formation of allotriomorphic ferrite in strip-cast Nb-steel was already reported in an earlier study [14]. The allotriomorphic ferrite forms during the isothermal treatment at 900 °C, the bainite then forms upon cooling from the isothermal holding temperature. For the case of the Nb-Mo steel, the suppression of the ferrite formation during isothermal holding is due to the solute drag by Mo, which has been discussed in [18].

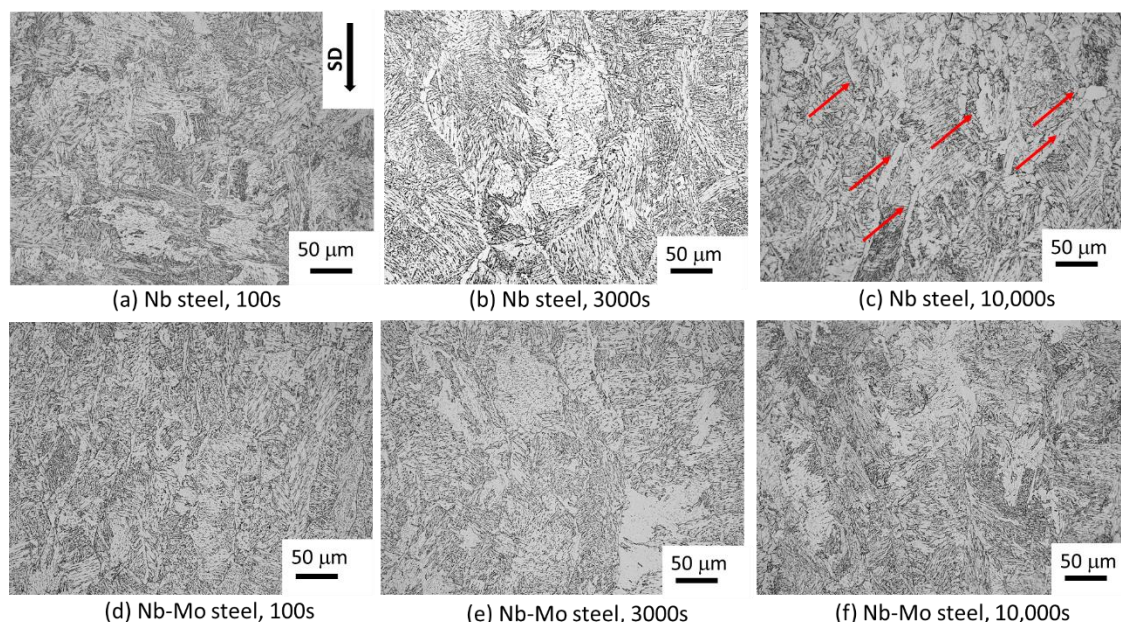


Figure 3. Optical images of the microstructure of the Nb (a–c) and Nb-Mo (d–f) steels after isothermal holding for 100, 3000, and 10,000 s at 900 °C. (Solidification direction (SD) is shown by the black arrow in (a), and allotriomorphic ferrite is shown by the red arrows in (c)).

3.3. TEM

Bright-field (BF) TEM images of carbon replicas produced from the Nb and Nb-Mo steels heat treated at 900 °C for various times are shown in Figure 4. Precipitation does not occur after isothermal holding for 100 s and only some coarse spherical particles around 250 nm in diameter are observed in

both steels (Figure 4a,e). After 1000 s of isothermal holding at 900 °C, precipitates are formed. From the Thermo-Calc calculation in Figure 1, these precipitates are MC-type carbides. The size of the carbides in both steels increases as a function of isothermal holding time, Figure 5. Generally, the particle size in the steel containing Mo is smaller than that in the Mo-free steel.

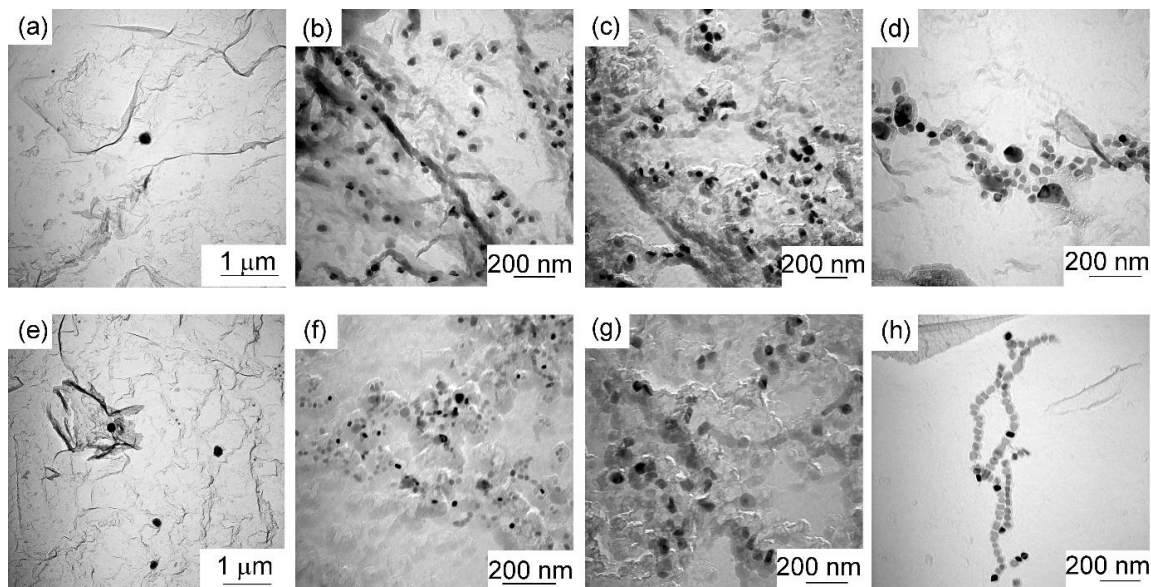


Figure 4. Bright-field (BF) Transmission electron microscopy (TEM) images of the carbon replicas of the Nb (a–d) and Nb-Mo (e–h) steels heat treated at 900 °C for 100 s, 1000 s, 3000 s, and 10,000 s, from left to right. Note scale bar changes.

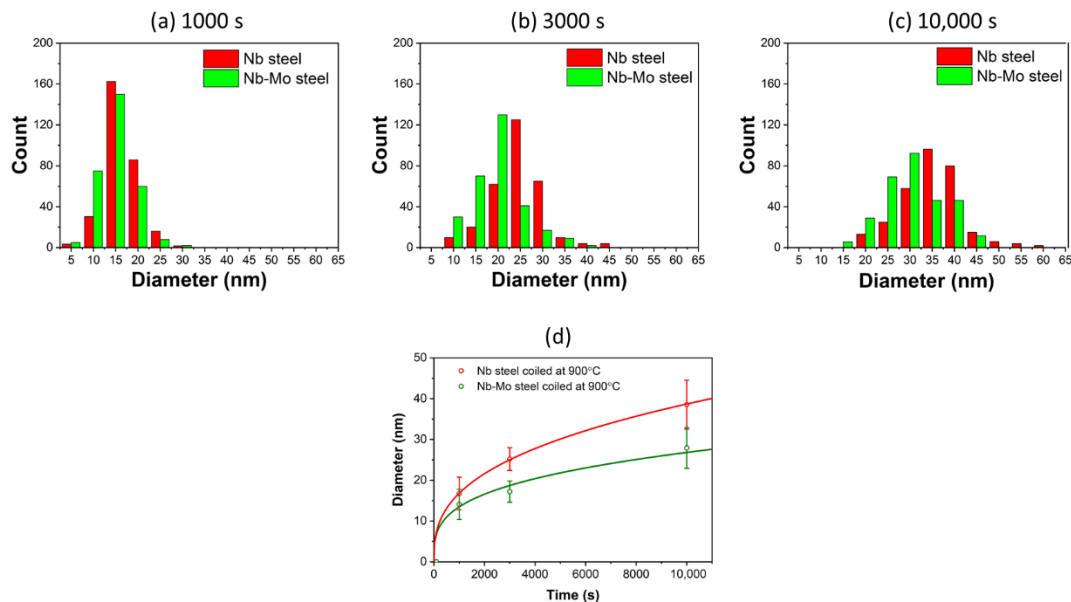


Figure 5. Size distributions (a–c) of the carbides in the Nb and Nb-Mo steels heat treated at 900 °C for 1000 s, 3000 s, and 10,000 s, respectively. (d) is the average particle size evolution of the two steels during isothermal holding at 900 °C.

The compositions of carbides formed in both steels after isothermal holding at 900 °C for 10,000 s were analysed by TEM-EDS, as shown in Figure 6. The carbides in both steels are enriched in Nb and N. In the Nb-Mo steel, the carbides also contain Mo, however, the Nb (L) (2.169 keV), Mo (L) (2.292 keV) and S (K) (2.309 keV) peaks overlap in EDS spectrum, which presents difficulty for accurate

compositional analysis of the carbides. Therefore, EELS was utilised to confirm the presence of Nb, Mo and S in the carbides, as shown in Figure 7. The carbides in the Nb-Mo steel simulated coiled at 900 °C are clearly enriched in Nb and Mo, though S is not identified to be present. As we can also see from Figure 7, there were some distortion of carbon film around precipitates, which may happen during carbon-replica preparation. This may be the reason of why the intensity of carbon is higher around particles.

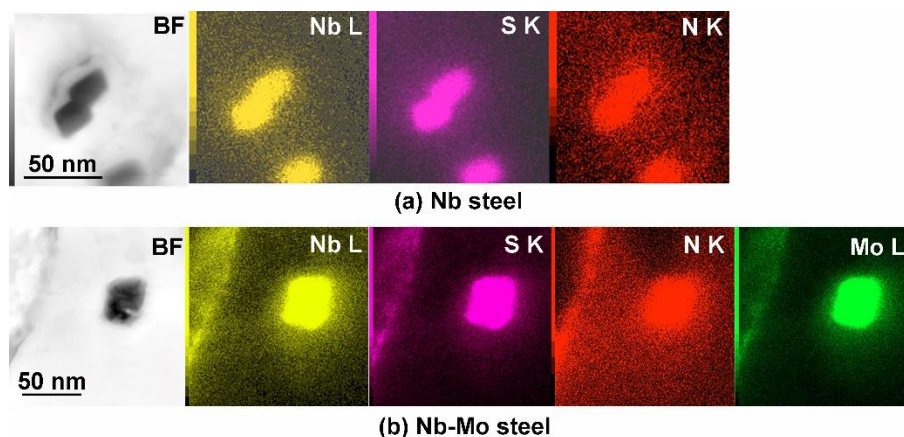


Figure 6. Bright-field (BF) TEM image and corresponding energy dispersive spectroscopy (EDS) chemical maps for the carbon replicas of precipitates in the (a) Nb and (b) Nb-Mo steels heat treated at 900 °C for 10,000 s.

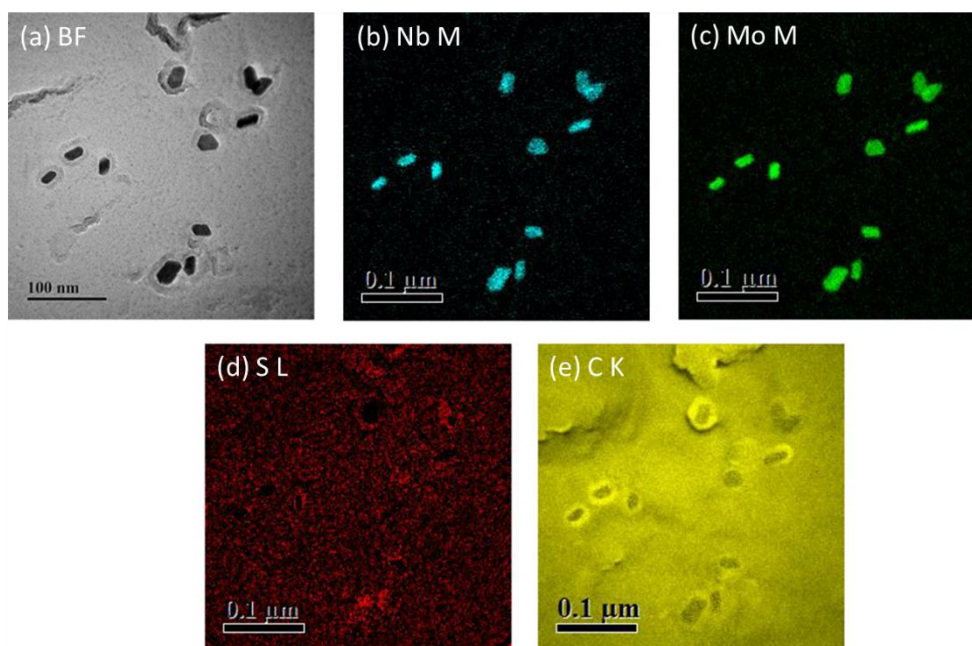


Figure 7. Electron energy loss spectroscopy (EELS) examination of the carbon replicas for the chemistry of the precipitates in the Nb-Mo steel after isothermal holding at 900 °C for 3000 s: (a) BF TEM image; (b) Nb; (c) Mo; (d) S; (e) C.

Based on TEM-EDS analysis, the Mo/(Nb + Mo) composition ratio of the carbides in the Nb-Mo steel isothermal holding at 900 °C are presented in Figure 8. It can be seen that the ratio significantly decreases with increasing coiling time and particle size, which is similar to previous work on Ti-Mo steels [8,20,21]. For instance, during isothermal holding at 925 °C from 100 to 3000 s on a Ti-Mo steel [21], Wang et al. report a reduction of the Mo/(Ti + Mo) composition ratio of the (Ti, Mo)C

precipitates with increasing holding time, from 0.24 to 0.062, which is quite similar to the result in Figure 8. The incorporation of Mo into Nb(C, N) precipitates indicates that Mo plays an important role during the nucleation at the early stages of the precipitation kinetics at 900 °C. As the precipitates coarsen, however, they are mainly enriched in Nb given the decrease in the Mo/(Nb + Mo) ratio as a function of coiling time. This growth mechanism can be rationalized by the difference in diffusivities between Nb (1.12×10^{-12} cm²/s) and Mo (0.74×10^{-12} cm²/s) [22–24].

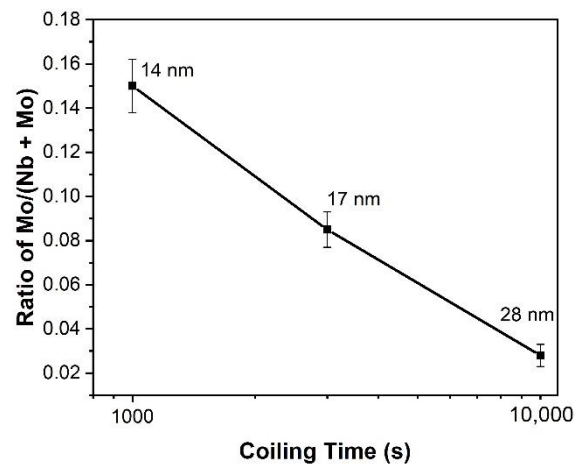


Figure 8. Mo/(Nb + Mo) ratio of carbides formed in the Nb-Mo steel heat treated at 900 °C for various times.

4. Discussion

4.1. The Effect of Mo on the Thermodynamics of Precipitation

In the austenite region, the solid solubility products of NbC, NbN, and MoC are obtained from [12,25]:

$$\log[\text{Nb}][\text{C}] = 5.43 - 10960/T \quad (1)$$

$$\log[\text{Nb}][\text{N}] = 6.163 - 7583/T \quad (2)$$

$$\log[\text{Mo}][\text{C}] = 4.96 - 12230/T \quad (3)$$

where $[M]$ is the weight percentage of element M in solid solution. As (Nb, Mo) (C, N) carbonitride can be treated as a solution that is composed of NbC, NbN and MoC and having NaCl-type structure, the $(\text{Nb}_{k1+m1}, \text{Mo}_{k2})(\text{C}_{k1+k2}, \text{N}_{m1})$ formula was used in the present work for the thermodynamic and kinetic discussion. Here, $k1$, $k2$ and $m1$ are the mole fractions for NbC, MoC and NbN and $k1 + k2 + m1 = 1$. Through calculation, the equilibrium ratio of Mo/(Nb+Mo) at 900 °C is 0.00177, which indicates that the precipitates observed in this work did not have an equilibrium composition, as shown in Figure 8.

It is well-known that microalloyed carbonitrides formed in the austenite matrix typically keep a cube-on-cube orientation relationship with the matrix [25]. Therefore, the lattice misfit can be calculated as:

$$\delta = \left| \frac{a_{M(\text{C}, \text{N})} - a_{\gamma}}{a_{M(\text{C}, \text{N})}} \right| \quad (4)$$

where, $a_{M(\text{C}, \text{N})}$ and a_{γ} are the lattice parameters for carbonitrides M (C, N) and austenite, respectively. From the literature [25,26], the austenite lattice parameter is taken here to be 0.36615 nm, and the lattice parameter for $(\text{Nb}_{k1+m1}, \text{Mo}_{k2})(\text{C}_{k1+k2}, \text{N}_{m1})$ can be obtained by using the linear interpolation method [12]. The interfacial energy can be calculated as:

$$\alpha = \frac{E \times a_{\alpha}}{4 \times \pi \times (1 - \nu^2)} f(\delta) \quad (5)$$

where E is the elastic modulus (208.2 GPa [26]), ν is the Poisson's ratio (0.32 [27]) and

$$f(\delta) = \delta \times \left[\frac{2}{1 + \frac{1}{4 \times \delta^2}} - \ln(2 \times \delta) \right] \quad (6)$$

Figure 9 shows the interfacial energy between the precipitates and the austenite matrix as a function of temperature. It can be seen that the precipitates in the Nb-Mo steel have a lower interfacial energy than in the Nb steel when heat treated at 900 °C, which suggests that the incorporation of Mo in Nb (C, N) precipitates can lead to a lower interfacial energy. This has been previously reported in the Nb-containing steels produced by conventional methods [28]. Similar results have also been observed in the Ti-Mo steels [20,21]. The Mo in TiC has been reported to decrease the misfit strain between TiC precipitates and iron matrix at the early stage of precipitation, resulting in a lower interfacial energy between TiC and matrix.

It has been previously reported that an increase in Gibbs free energy occurs from the addition of Mo to MC precipitates [7,13]. According to the classic theory of nucleation [25,26,29], the increase of Gibbs free energy (absolute value) reduces the driving force for precipitation, while the decrease of interfacial energy is beneficial for precipitation. Thus, there is a competition between the effect that Mo has on the Gibbs free energy and on the interfacial energy.

Theoretical calculations in previous work [28] suggests that the incorporation of Mo into Nb (C, N) precipitates can accelerate the precipitation kinetics of Nb (C, N) carbonitrides by lowering the interfacial energy due to the smaller lattice misfit between precipitates and matrix. This explains the high concentration of Mo in the precipitates at the early stages of precipitation and also the smaller size of the precipitates in the Mo-containing steel.

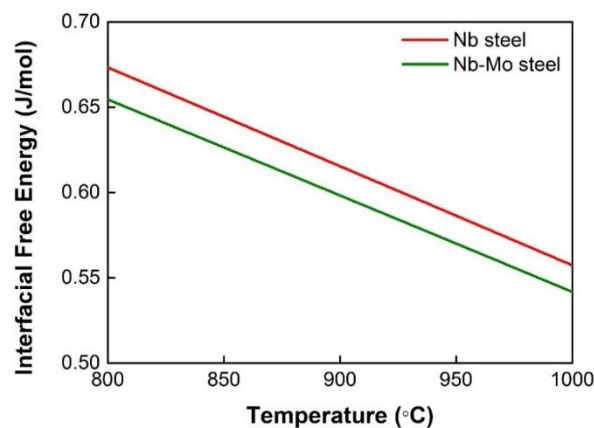


Figure 9. Interfacial free energy of the precipitates formed in austenite for the two steels.

4.2. The Effect of Mo on the Coarsening Kinetics of Precipitation

The influence of Mo in the Ostwald ripening stage of precipitation was quantified using Lifshitz-Slyozov-Wanger (LSW) theory [30,31], which predicts the average size of particles when the volume fraction of precipitation is small:

$$\bar{r}_t = \bar{r}_0 \times (1 + k \times \sigma \times D \times c_0 \times t)^{1/3} \quad (7)$$

where $\bar{r}_t$ and $\bar{r}_0$ are the average particle radius and nucleus radius, respectively. D and c_0 are the diffusivity and mole concentration of the controlling element respectively, t is the isothermal holding

time, and k is a constant parameter. The controlling element can be determined by the value of the product $D \times c_0$. At 900 °C, $D \times c_{0-Nb} = 9.9 \times 10^{-17}$ is smaller than $D \times c_{0-Mo} = 4.3 \times 10^{-16}$ [24,25]. Thus, Nb is the rate-limiting element in both steels. Therefore, the coarsening of the precipitates in both steels when isothermal holding at 900 °C is dependent on the interfacial energy σ , which was lower in the Nb-Mo steel than in the Nb steel. Consequently, the coarsening rate of precipitates in the Nb-Mo steel heat treated at 900 °C is smaller than that in the Nb steel, leading to a smaller particle size (Figure 5). Additionally, as mentioned above, the diffusion of Mo between precipitates and matrix also slows the growth and coarsening of particles.

4.3. Precipitation Hardening

A simple yield strength model was used to better understand the strengthening contribution from the precipitates. As shown in Figure 3, the bulk microstructure of both steels is very similar and mainly consists of bainite. For simplicity, we consider that the strength increment observed during isothermal holding comes mainly from the precipitates. The equivalent yield strength is obtained by converting the hardness values as per the equation ($\sigma_y = 3.06 \times H_v$) in [32]. After isothermal holding for 100 s at 900 °C, the strength of the Nb-Mo steel increases by ~25 MPa, but no obvious change in the strength of the Nb steel occurs, which suggests that a small amount of very fine precipitates is formed, likely due to the lower interfacial energy from Mo (Figure 9) that reduces the energy barrier to nucleation. However, no Nb-rich carbonitrides are seen in the Nb-Mo steel after isothermal holding at 900 °C for 100 s using the carbon replica sample preparation method (Figure 4). This is probably due to the low extraction capability of carbon replica for the particles with diameters <10 nm.

In recent work by Dorin et al. [14], the shearing to by-passing of the Nb-carbonitrides formed in the austenite was found to occur for a radius of ~6 nm. In the present work, the precipitates formed at 900 °C are always larger and we hence assume that they will be by-passed by moving dislocations. As a result, the Friedel's statistical model for Orowan looping [33] can be used to estimate the strength increment from the precipitates:

$$\sigma_p = 0.7 \times M \times G \times b \frac{\sqrt{f}}{R} \quad (8)$$

where M is the Taylor factor (~3), G is the shear modulus of ferritic matrix (~80 GPa [26]), b is the Burgers vector (~0.25 nm [26]), f and R are the volume fraction and the radius of precipitates. The radius of precipitates can be obtained from the TEM results in Figure 5. In this work, the maximum precipitation hardening at each isothermal holding time at 900 °C was calculated using the theoretical volume fraction of Nb carbonitrides under equilibrium calculated by Thermo-Calc software with TCFE 9: Steels/Fe Alloys v9.0 database, 0.0605%, as shown in Table 2.

Table 2. Calculated precipitation hardening (MPa) by Orowan mechanism for the Nb and Nb-Mo steels after isothermal holding at 900 °C.

Ageing Time	Nb Steel	Nb-Mo Steel
1000 s	144	171
3000 s	96	140
10,000 s	63	87

The change in yield strength between the as-cast and heat treated samples provides a direct measurement of the precipitate hardening for each sample. Figure 10 compares the measured precipitation hardening with the calculated precipitation hardening shown in Table 2. It can be seen that for both steels the calculated and measured precipitation hardening at 3000 s are very close. For simulated coiling times less than 3000 s the measured yield strength is lower than the calculated yield strength, and this is probably because the volume fraction is lower than the maximum. This means that there is still solute available after 1000 s of isothermal holding at 900 °C. After 3000 s, the Friedel's statistical model for Orowan looping prediction agrees reasonably well with the experimental strength

determined from the hardness measurements. For the longest isothermal holding time, the precipitation hardening reduces, which is due to the growth and coarsening of precipitates. Additionally, at 10,000 s, the measured yield strength is slightly lower than the calculated yield strength, probably because after a long time isothermal holding the concentration of carbon in solid solution decreases due to precipitation, resulting in lower solid solution strengthening. Furthermore, the coarsening of austenite grains and the formation of allotriomorph ferrite (Figure 3) after a long time isothermal holding may also contribute to the drop in the measured yield strength. Therefore, to conclude, the increase in the hardness of both steels after isothermal holding at 900 °C until 3000 s (Figure 2) mainly derives from the increasing precipitation hardening. At 3000 s, the maximum precipitation hardening is achieved. However, further simulated coiling to 10,000 s decreases the hardness of both steels, which is due to the coarsening of precipitates and the microstructure softening.

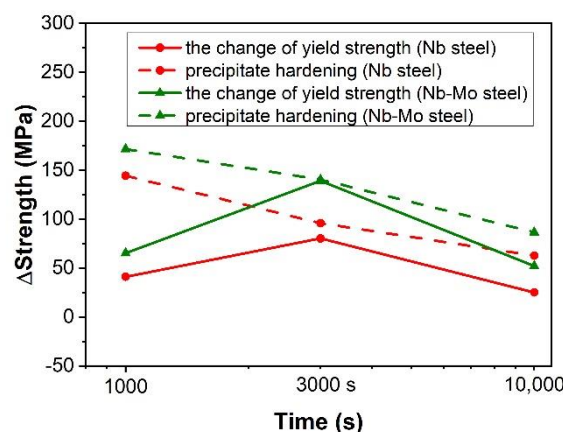


Figure 10. Comparison of the precipitation hardening using the maximum theoretical volume fraction and the change of yield strength for both steels after isothermal holding at 900 °C.

5. Conclusions

In the present study, the effect of Mo on the precipitation behaviour in austenite in low-carbon strip-cast steels containing Nb has been investigated. The key conclusions are as follows:

- (1) The hardness values of both as-cast steels were similar. During isothermal holding at 900 °C, the hardness of the two steels increased and reached the peak at 3000 s, then decreased after 10,000 s isothermal holding. Generally, the Nb-Mo steel had higher hardness than the Nb steel at all isothermal holding times.
- (2) The microstructures of both steels after isothermal holding at 900 °C were bainite, only some grain boundary allotriomorph (GBA) were formed in the Nb steels heat treated for 10,000 s at 900 °C.
- (3) Nb-carbonitrides precipitated in both steels after isothermal holding for 1000 s at 900 °C, and the size of the particles in the Nb-Mo steel was finer than that in the Nb steel. In the Mo-containing steel, Mo also participated in the precipitation, and the concentration of Mo in Nb-rich carbonitrides decreased with increasing particle size and isothermal holding time.
- (4) The enrichment of Mo in the Nb-rich carbonitrides reduces the interfacial energy between precipitates and the matrix, which lowers the nucleation energy barrier and the precipitate coarsening rate.
- (5) Strength modelling suggests that precipitation reached maximum volume fraction (0.0605%) after isothermal holding at 900 °C for 3000 s. The precipitates in the Nb-Mo steel imparted an increase in yield strength up to ~140 MPa, which was higher than that in the Nb steel, ~96 MPa. Further strengthening contributions of the precipitates in both steels decreased after 10,000 s isothermal holding at 900 °C due to the coarsening of the particles.

Author Contributions: Conceptualization, L.J. and N.S.; methodology, L.J., T.D. and N.S.; software, X.S.; investigation, L.J.; data curation, L.J. and H.Y.; writing—original draft, L.J.; writing—review & editing, R.K.W.M., T.D. and N.S.; supervision, R.K.W.M., T.D., P.D.H. and N.S.; project administration, N.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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