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Precipitation of MC phase and precipitation strengthening in hot rolled Nb–Mo and Nb–Ti steels

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Abstract Hot rolled Nb–Mo steel of yield strength 600 MPa and Nb–Ti steel of yield strength 525 MPa with polygonal and acicular ferrite microstructure have been developed. Using physicochemical phase analysis, XRD, TEM and EDS, the distribution, morphology, composition, crystal structure and particle size of precipitates were observed and identified in these steels. The results revealed that the steels containing both Nb and Mo exhibited fine and uniformly distributed MC-type carbides, while the carbides were coarse and sparsely distributed in the steels containing Nb and Ti. The physicochemical phase analysis showed MC-type carbides contain both Nb and Mo, and the ratio of Mo/Nb was 0.41. Meanwhile, the mass% of the fine particles (<10 nm in size) of Nb–Mo steel was 58.4%, and higher than that of Nb–Ti steel with 30.0%. Therefore, the results of strengthening mechanisms analysis showed the higher strength of Nb–Mo steel than that of Nb–Ti steel is attributed to its relatively more prominent precipitation strengthening effect. The yield strength increments from precipitation hardening of Nb–Mo steel attained 182.7 MPa and higher than that of Nb–Ti steel.

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Introduction

Precipitation is one of the most important phenomena for controlling the properties of steels [1]. It is well known that Nb, Ti and V have a strong affinity for C and N and that a small addition of these elements to steels yields a significant improvement of mechanical properties due to the formation of fine precipitates. Microstructural control of these precipitates plays an extremely important role in improving the overall property of steels. It is also reported that molybdenum decreases the diffusivity of the carbide-forming species (i.e., Nb and C) and, thus delays the precipitation of MC carbides. These findings strongly suggest that the coexistence of niobium and molybdenum play an important role in significantly enhancing the strength of the HSLA steels. It has been indicated that the HSLA steels containing both niobium and molybdenum exhibited superior strength to the conventional HSLA steels containing niobium or niobium and vanadium [2–5]. In the present work the precipitates and properties of the steel containing Nb–Mo have been investigated and compared with that of steel bearing Nb–Ti. The relations between precipitates and yield strength are discussed.

Materials and experimental procedures

The chemical compositions and Ae_3 temperatures of the investigated steels in this study are shown in Table 1. These steels were melted in a vacuum induction furnace and cast into the ingots. They were hot-rolled to 30 mm thick slabs. After soaking at 1,230 °C for 3.6 ks, they were hot-rolled to 6 mm thick at finishing temperature of 880 °C followed by soaking at 650 °C for 3.6 ks and furnace cooling at a simulation of the hot-coiling.

Table 1 Chemical composition (wt.%) and Ae_3 temperature (°C) of the steels

Steel	C	Mn	Si	*P*	S	Al	Nb	Mo	N	Ti	A_{e3}*
Nb–Ti	0.039	1.10	0.26	<0.001	0.001	–	0.055	–	0.0012	0.015	867
Nb–Mo	0.027	1.11	0.20	0.0092	0.007	<0.005	0.081	0.14	0.0030	–	871

* calculated by the Thermo-Calc program

Micro-hardness results were obtained using MVK-E micro-hardness machine with a load of 100 g. Tensile tests were carried out with those specimens machined from the as-rolled plates along the longitudinal direction. Microstructure and grain size were examined by optical microscope. The ferrite grain sizes were measured by the point-counting method. The precipitation particles were analyzed using physicochemical phase analysis and transmission electron microscopy H-800 TEM analytical and high-resolution transmission electron microscopy with carbon extraction replicas from specimens under as-hot-rolled condition using standard techniques. EDS analysis and quantitative electron diffraction were carried out. Particle size distributions were determined with X-ray diffracto-spectrometer/Kratky small angle scattering goniometer with Co Kα at 30 kV and 30 mA.

Results

Properties

Mechanical properties and micro-hardness of these steels are shown in Table 2. Tensile strength, yield strength and elongation of Nb–Mo steel is higher than that of Nb–Ti steel. Increment of tensile strength and yield strength in Nb–Mo steel against Nb–Ti steel, ΔTS and ΔYS is approximately 45 and 75 MPa, respectively. The elongation of the steel containing Nb and Mo is slightly higher that of the steel containing Nb and Ti. It was revealed that Mo was a more effective element in increasing mechanical properties of the steels containing Nb than Ti.

Optical microstructure micrographs

Optical micrographs of the steels are shown in Fig. 1. The microstructure of Nb–Mo and Nb–Ti steels was composed of polygonal ferrite and acicular ferrite. The difference in microstructure between the steel containing Nb–Mo and the steel containing Nb–Ti is small. The mean ferrite grain size of Nb–Mo steel, about 4.4 μm is smaller than that of Nb–Ti steel, about 4.6 μm.

Table 2 Mechanical properties of different materials

Steel	TS (Mpa)	YS (MPa)	EL	Microhardness
Nb–Ti	595.0	525.0	22.8	192
Nb–Mo	640.0	600.0	23.5	220

Precipitates

The results of physicochemical phase analysis show that TiC and NbC was formed in the Nb–Ti steel, and only NbC in the Nb–Mo steel, but Mo_2C could not be found in the Nb–Mo steel. Elements content of MC phases in alloys were shown in Tables 3 and 4. The major constituents of

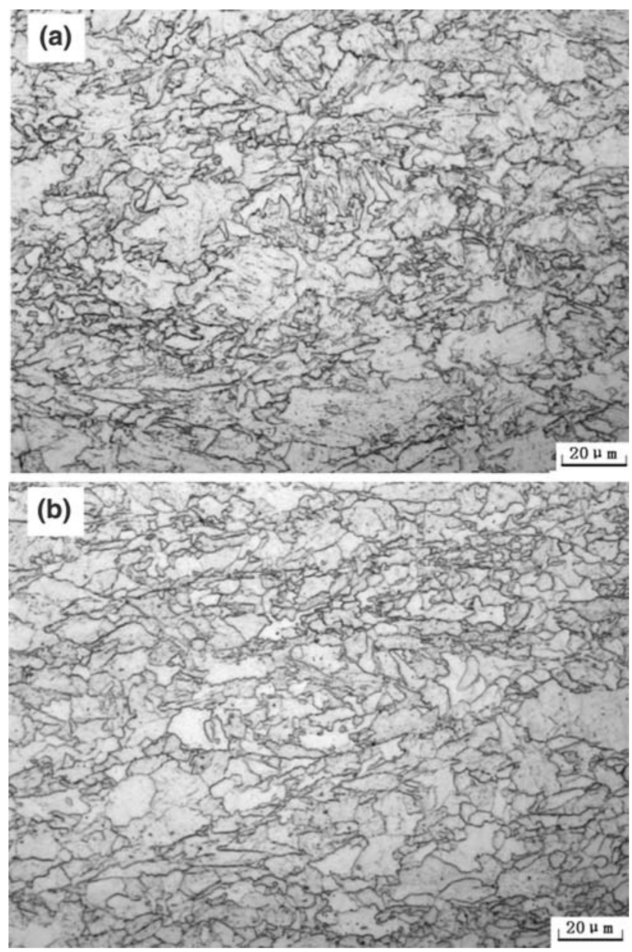

Fig. 1 Optical microstructure micrographs of the Nb–Ti steel (**a**) and the Nb–Mo steel (**b**)

Table 3 Elements content of MC phases in alloys (mass%)

Steel	Nb	Mo	Ti	C	N	∑
Nb–Ti	0.0318	–	0.0138	0.0068	0.0009	0.0533
Nb–Mo	0.0726	0.0308	–	0.0107	0.0030	0.1171

Table 4 Elements content in MC phases (at%)

Steel	Nb	Mo	Ti	C	N	∑
Nb–Ti	27.14	–	22.86	44.92	5.08	100.00
Nb–Mo	35.44	14.56	–	40.29	9.71	100.00

the MC-type carbide of the Nb–Ti steels were identified as Nb and Ti, while those of Nb–Mo steel were identified as Nb and Mo. It was shown that Mo can dissolve in NbC and the ratio of Mo to Nb is 0.41.

In the microalloyed steels, Ti(C,N) precipitates form at high temperatures with a cubical morphology and maintain the shape and chemistry at low temperatures, and TiC and Nb(C,N) precipitates form at relatively lower temperatures with a spheroid morphology in austenite, while NbC or Nb(C,N) form with plate-like morphology in ferrite matrix. Extraction replica TEM photographs of finer precipitate were shown in Fig. 2. It was found that the MC precipitates with plate-like morphology became finer and denser in Nb–Mo steel than in Nb–Ti steel.

Meanwhile, size distribution of precipitation is related to the properties of steels. The distribution of MC-type carbides observed in various steels is shown in Fig. 3. The mass% age of particles whose sizes are less than 10nm, about 58.4%, is higher than that of Nb–Ti steel, about 30.0%. Therefore, the mean particle median size of Nb–Mo steel, about 9.0 nm is smaller than that of Nb–Ti steel, about 74.9 nm. The MC-type carbides found in 0.08Nb–0.14Mo steel were 8.3 times as fine and 2.2 times as dense as those formed in 0.055Nb–0.015Ti steel.

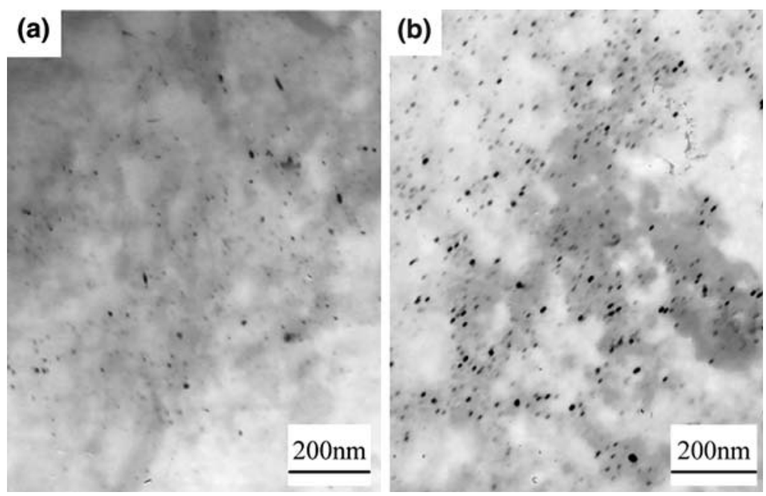

Fig. 2 Extraction replica TEM photographs of fine precipitate of Nb–Ti steel (**a**) and Nb–Mo steel (**b**)

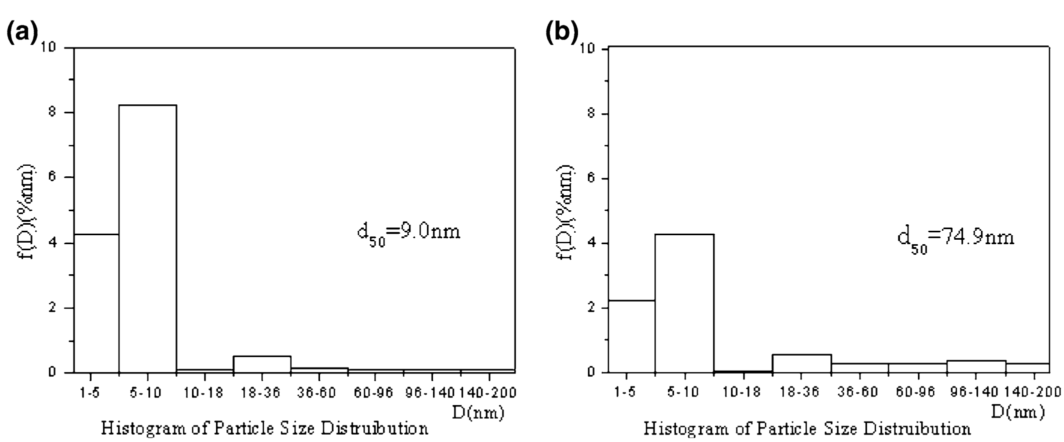

Fig. 3 Distribution of particle size of MC particles of Nb–Mo steel (**a**) and Nb–Ti steel (**b**)

Table 5 Results of calculation and chemical analysis of C element in the steels

Steel	C in Alloy	C in MC	C in Fe_3C	C in residual
Nb–Ti	0.039	0.0069	0.0176	0.0145
Nb–Mo	0.027	0.0115	0.0056	0.0099

Discussion

From quantitative metallurgy [6], the contributions from different strengthening mechanisms to the YS can be dissociated according to the following equation:

$$YS = \sigma_0 + \sigma_{ss} + K \cdot d^{-1/2} + \sigma_d + \sigma_{ppt} \quad (1)$$

where d is the average grain size of ferrite and K represents the difficulty of transmitting slip across grain boundaries and is around 17.4 MPa $\sqrt{mm}$; σ_0 is the intrinsic strength of ferrite lattice and is around 53 MPa; and σ_{ss} is the contribution to strength from solid solution hardening which can be calculated from the equation

$$\sigma_{ss}(\mathrm{MPa}) = 4570[C] + 37[\mathrm{Mn}] + 83[\mathrm{Si}] \quad (2)$$

where the carbon element in residual of the steels were shown in Table 5.

Since the first four terms in Eq. (1) are normally known and the strengthening from dislocation hardening σ_d is negligibly small as the finishing rolling temperature is above the Ar_3 transformation temperature, Eq. (1) can be used to determine the contribution to strength from precipitation hardening, σ_{ppt}.

$$\sigma_{ppt} = YS - \sigma_0 - \sigma_{ss} - K \cdot d^{-1/2} \quad (3)$$

Precipitation strengthening is an effective strengthening method. The yield stresses of microalloyed steels contain a contribution from the precipitation strengthening which is also described quantitatively by the Ashby-Orowan equation. According to Ashby-Orowan relationship [7]

$$\sigma_p = (0.538Gbf^{1/2}/X)\ln(X/2b) \quad (4)$$

where σ_p is the increase in yield strength (MPa), G is the shear modulus (MPa), b is the Burgers vector (mm), f is the volume fraction of particles, and X is the real (spatial) diameter of the particles (mm).

Table 6 Dissociated strength contribution from various strengthening mechanisms

Steel	Solid solution (MPa)	Grain refinement (MPa)	Precipitation by Eq. (3) (MPa)	Precipitation by Eq. (4) (MPa)
Nb–Ti	128.5	256.5	86.9	87.4
Nb–Mo	102.9	262.3	181.8	182.7

The results of strength analysis for Nb–Ti and Nb–Mo steels are listed in Table 6. The data in Table 6 indicate that the difference of grain refinement strengthening effect in two steels is obviously smaller than that of precipitation strengthening effect in the two steels. The smaller difference of the effect of grain size on the strength in the two steels is mainly due to the smaller difference of the mean ferrite grain size of Nb–Mo steel, about 4.4 μm and Nb–Ti steel, about 4.6 μm.

It can be found that the higher strength of Nb–Mo steel than that of Nb–Ti steel is attributed to its relatively more prominent precipitation strengthening effect. The measured microhardness of the ferrite matrix listed in the last column in Table 2 also indicates that the ferrite matrix strength of Nb–Mo steel is higher than that of the Nb–Ti steel owing to the more prominent precipitation strengthening effect. The contributions from precipitation strengthening to the yield strength of Nb–Mo steel attained 182.7 MPa and higher than that of Nb–Ti steel, 87.4 MPa by Eq. (4).

Yield strength increments from precipitation hardening by Eq. (3) is in good agreement with the result by Eq. (4). Therefore, the Eq. (3) is believed to be applicable to describe yield strength increments from precipitation hardening. It is suggested that finer and denser MC carbides less than 10 nm causes a major precipitate-hardening effect.

The HSLA steels containing Nb and Mo exhibit higher strength in comparison to the conventional HSLA steels containing Nb and Ti. According to the prior analysis, finer and denser the MC carbides observed in steels containing Nb and Mo caused a major precipitate-hardening effect.

In fact, the Mo addition influences the precipitation kinetics of MC carbides. Wada et al. [8, 9] showed that molybdenum decreases the activity coefficient of carbon. Akben [2] also reported that molybdenum can retard the precipitation of MC carbides. Other investigators have reported that molybdenum can reduce precipitation of niobium in austenite [4, 5]. This is probably related to an increase in solubility resulting from a decrease in carbon activity influenced by molybdenum. With less precipitation in austenite, more numerous precipitates could form in ferrite resulting in enhanced strength. These results are quite coincident with the experimental result that fine MC carbides were mainly in the ferrite region, as shown in Fig. 2. It is concluded that molybdenum increases the degree of precipitation hardening which can be obtained from the microalloying elements.

Unlike the relative precipitation strength, the maximum precipitation-strength contribution does strongly depend on the microalloy content. In general, there is an increase in strength as the microalloy addition increases. The data in Table 3 show that the volume fraction of precipitate are enhanced by precipitating of Mo with Nb. Meanwhile, the lattice parameter of (Nb,Mo)C of Nb–Mo steel is 0.44482 nm and less than that of NbC, 0.44699 nm. Thus, the observed presence of molybdenum in the precipitates may also increase their strengthening effectiveness by increasing coherency strains and by increasing volume fraction of precipitates.

Therefore, it is believed that the enhanced yield strength of the steels containing both Nb and Mo results from the precipitation hardening caused by finer and denser MC carbides, which resulted from increasing solubility of MC type carbides in austenite by Mo and increasing coherency strains and volume fraction of precipitates by precipitating of Mo with Nb.

Conclusions

1. High strength hot rolled Nb–Mo steel with a yield strength of 600 MPa and Nb–Ti steel with a yield strength of 525 MPa with polygonal and acicular ferrite microstructure have been developed.
2. Mechanical properties of Nb–Mo steels were higher than those of Nb–Ti steel. Higher strength levels can be obtained by the addition of Nb+Mo than by addition of Nb+Ti.
3. The Nb–Mo steel exhibits larger contributions from precipitation strengthening than the Nb–Ti steel.
4. Qualitative analysis of the carbonitride particles indicates that MC phases of Nb–Mo steel contain Nb and Mo, and Nb:Mo is 2.43.
5. In Nb–Mo steel, the mean size of (Nb,Mo)precipitates was 9 nm and the mass% of the fine particles less than 10 nm in size were 58.4%, which caused a major precipitate-hardening effect.
6. The enhanced yield strength of the steels containing both Nb and Mo results from the precipitation hardening caused by finer and denser precipitates than those of the steels containing Nb–Ti.

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