Interphase Precipitation Behavior of Nanocarbides in Nb-Ti Bearing Low-Carbon Microalloyed Steel (Postprint)

Authors: Xiaolin Li, Wang Zhaodong

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Abstract

The effects of isothermal temperature on the microstructure, properties, and precipitation behavior of Nb-Ti microalloyed steel were investigated using thermal dilation experiments, and the precipitation behavior of specimens after isothermal holding at different temperatures was observed and analyzed via transmission electron microscopy (TEM). The results demonstrate that interphase precipitated carbides can be observed in all specimens after isothermal treatment at various temperatures, and decreasing the isothermal temperature significantly refines the interplanar spacing of the planes containing interphase precipitated carbides, the inter-particle spacing within these planes, and the size of the interphase precipitated carbides. The planes containing interphase precipitated carbides with lamellar distribution characteristics exhibit two morphologies: curved and planar. The planar-type planes are parallel to the {011}, {012}, {013}, and {035} planes of ferrite. High-resolution transmission electron microscopy (HRTEM) determination revealed that the interphase precipitated carbides possess an NaCl-type crystal structure with a lattice constant of 0.434 nm, and they obey the Baker-Nutting (B-N) orientation relationship with the ferrite matrix. Energy dispersive spectroscopy (EDS) analysis identified the interphase precipitated carbides as (Nb, Ti)C. The precipitation strengthening contribution was estimated using the Orowan mechanism, and the results indicate that it exceeds 300 MPa at all isothermal temperatures.

Full Text

Interphase Precipitation Behaviors of Nanometer-Sized Carbides in a Nb-Ti-Bearing Low-Carbon Microalloyed Steel

LI Xiaolin, WANG Zhaodong State Key Laboratory of Rolling and Automation, Northeastern University, Shenyang 110819

Abstract: High-strength low-alloy (HSLA) steels utilize low-carbon composition design and are microalloyed with elements such as Nb, V, Ti, Mo, and B. The strength enhancement arises from grain refinement strengthening, solid-solution strengthening, dislocation strengthening, and precipitation hardening, with precipitation hardening having attracted increasing attention. However, detailed investigations on the sheet spacing, inter-particle spacing, crystallography, composition, and nucleation sites of interphase precipitation carbides in Nb-Ti-containing steels remain unreported. This work investigates the microstructure, mechanical properties, and precipitation behaviors of a low-carbon Nb-Ti microalloyed steel using dilatometry and transmission electron microscopy (TEM). The results demonstrate that interphase precipitation occurs across different isothermal temperatures, and decreasing the isothermal temperature significantly refines the sheet spacing, inter-particle spacing, and carbide size. The characteristic sheets of interphase precipitation carbides exhibit both planar and curved morphologies. Planar sheets are found to be parallel to the {011}, {012}, {013}, and {035} planes of ferrite. High-resolution TEM (HRTEM) confirms that the interphase precipitation carbides are (Nb, Ti)C with a NaCl-type crystal structure and a lattice parameter of 0.434 nm, obeying the Baker-Nutting (B-N) orientation relationship with the ferrite matrix. The contribution of interphase precipitation strengthening to the yield strength is estimated to exceed 300 MPa based on the Orowan mechanism.

Keywords: Nb-Ti-bearing microalloyed steel, interphase precipitation, Vickers hardness, HRTEM, orientation relationship, lattice misfit

Microalloyed high-strength low-alloy (HSLA) steels are widely used due to their high strength, high toughness, and excellent weldability. These steels employ low-carbon composition design to ensure good weldability while adding one or more microalloying elements such as Nb, V, Ti, and Mo to achieve strength through grain refinement, solid-solution strengthening, transformation strengthening, and precipitation strengthening. Historically, researchers believed that the primary role of microalloying elements was grain refinement, with precipitation strengthening contributing only marginally.

However, Funakawa et al. recently developed a high-strength steel with excellent hole expansion properties based on Ti-Mo microalloyed steel, commercially named "NANOHITEN." This steel is characterized by numerous interphase-precipitated (Ti, Mo)C carbides approximately 3 nm in size distributed in the ferrite matrix, contributing up to 300 MPa to the yield strength. This breakthrough fundamentally changed researchers' understanding of microalloying elements. Subsequent studies have reported on the crystal structure, orientation relationships, and strengthening effects of interphase precipitation carbides in various microalloyed systems including Ti, Nb, V, Ti-Mo, V-Ti, and Nb-V-Ti. These investigations consistently show that interphase precipitation carbides possess a NaCl-type crystal structure and follow either the Baker-Nutting (B-N) or Nishiyama-Wassermann (N-W) orientation relationship with the matrix, with calculated precipitation strengthening contributions exceeding 300 MPa via the Orowan mechanism.

Beyond crystal structure and strengthening effects, the distribution morphology of interphase precipitation carbides has received considerable attention. Smith and Dunne classified the distribution morphologies in different microalloyed steels into two types: (1) planar interphase precipitation (PIP), where the carbide sheets are planar, and (2) curved interphase precipitation (CIP), where the carbide sheets are curved. Honeycombe proposed a "ledge mechanism" to explain PIP in Fe-0.15C-0.75V steel, where the carbide sheets are parallel to the partially coherent interface $\{110\}\alpha//\{111\}\gamma$. Ricks and Howell and Bhadeshia proposed a "quasi-ledge mechanism" and "bowing mechanism," respectively, to explain CIP in Fe-0.2C-10Cr steel, where the carbide sheets are parallel to the incoherent interface. Okamoto et al. observed interphase precipitation carbides parallel to {112}, {114}, and {116} ferrite planes in Nb-bearing low-carbon microalloyed steel, while Yen et al. observed carbides parallel to {210}, {211}, and {111} ferrite planes in Ti-Mo-bearing low-carbon microalloyed steel. These observations contradict the "ledge mechanism," and the underlying mechanisms require further investigation.

This work focuses on the underexplored Nb-Ti microalloyed system, employing HRTEM to investigate the crystal structure, lattice parameter, and orientation relationship of interphase precipitation carbides after isothermal quenching, and utilizes lattice misfit principles to determine the specific nucleation sites of these carbides.

1. Experimental Methods

The experimental Nb-Ti microalloyed steel had a chemical composition (mass fraction, %) of: C 0.15, Si 0.26, Mn 0.98, Nb 0.03, Ti 0.07, P 0.016, S 0.004, N 0.0026, and Fe balance. The steel was melted in a 150 kg vacuum induction furnace and cast into ingots. After removing the shrinkage cavity, the ingots were forged into 100 mm × 100 mm × 120 mm billets. The billets were reheated to 1250 °C for 2 h and hot-rolled in seven passes on a 450 mm two-high reversible experimental mill to a final thickness of approximately 12 mm. The 12 mm thick plates were then held at 1250 °C for 72 h to dissolve carbides completely into the matrix before quenching to room temperature. Standard dilatometric specimens with a diameter of 3 mm and length of 10 mm were machined from the treated plates.

Heat treatment experiments were conducted on a Formaster-FII dilatometer following the schematic shown in [Figure 1: see original paper]. Specimens were heated to 1250 °C at 10 °C/s and held for 3 min for austenitization, then rapidly cooled at 50 °C/s to 690, 660, 630, and 600 °C and isothermally held for 20 min to induce ferrite transformation before final helium gas quenching to room temperature.

The dilatometric specimens were sectioned approximately 1 mm below the thermocouple using wire electrical discharge machining. After mechanical grinding and polishing, the samples were etched with 4% (volume fraction) nital for approximately 15 s. Microstructures were examined using a LEICA DMIRM optical microscope (OM). Vickers microhardness of ferrite was measured using an HV-50 microhardness tester with a 25 g load and 10 s dwell time, with 20 measurements averaged per specimen.

To characterize precipitation behavior after different isothermal treatments, 300 m thick discs were sliced from the dilatometric specimens and mechanically thinned to 50 m. Final thinning was performed using a twin-jet electropolisher with 9% (volume fraction) perchloric acid alcohol solution at 30–35 V and –20 °C. Precipitate size, morphology, and distribution were examined using a Tecnai G2 F20 field-emission transmission electron microscope (TEM). HRTEM was employed to determine crystal structure, lattice parameter, and orientation relationship with the ferrite matrix, while energy-dispersive spectroscopy (EDS) was used to determine chemical composition.

2. Results

2.1 Microstructure

The dilatometric curves for specimens isothermally treated at different temperatures are shown in [Figure 2: see original paper]. The ferrite transformation follows a "C-curve" behavior, with the specimen held at 630 °C exhibiting the maximum dilation. This occurs because decreasing the isothermal temperature increases the transformation driving force and ferrite transformation rate; however, further temperature reduction suppresses carbon diffusion, thereby decreasing the transformation rate.

Optical micrographs of specimens after isothermal treatment are presented in [Figure 3: see original paper]. All specimens consist of ferrite and martensite, where the white-contrast phase is ferrite formed during isothermal holding and the black-contrast phase is martensite formed from untransformed austenite during subsequent helium quenching. The measured ferrite volume fractions are 29%, 64%, 92%, and 79% after isothermal holding at 690, 660, 630, and 600 °C, respectively. The ferrite volume fraction initially increases then decreases with decreasing temperature, reaching a maximum at 630 °C, consistent with the dilatometric results.

2.2 Precipitation Behavior

The layered arrangement characteristic of interphase precipitation carbides in microalloyed steels is difficult to observe because when carbide sizes (<10 nm) are much smaller than the TEM foil thickness (~100 nm), the ferrite grains must be tilted to specific orientations to reveal the layered features. Therefore, proper observation methodology is essential. [Figure 4: see original paper] schematically illustrates the TEM observation geometry. Different morphologies appear when viewed along different zone axes. Assuming the electron beam direction is [u, v, w] and the interphase precipitation plane is parallel to {h, k, l}, the layered characteristics are only visible when $hu + kv + lw = 0$; when $hu + kv + lw \neq 0$, the layered features disappear and the carbides appear randomly distributed. In this study, specimens were tilted to align the zone axis of the interphase precipitation plane with the electron beam direction to observe precipitation behavior after different isothermal treatments.

TEM images of interphase precipitation carbides after isothermal treatment at various temperatures are shown in [Figure 5: see original paper]. After holding at 690 °C, the carbides exhibit curved interphase precipitation (CIP) with irregular sheet spacing. At 660 °C, the carbides show CIP with regular sheet spacing. At 630 °C, a mixture of planar interphase precipitation (PIP) and CIP with regular sheet spacing is observed. At 600 °C, only PIP is present. Thus, decreasing the isothermal temperature gradually transforms the precipitation morphology from CIP to PIP.

From TEM analysis, the sheet spacing (L1) and inter-particle spacing (L2) can be determined. L1 is measured directly from TEM images, while L2 is calculated using the formula with parameters t (foil thickness) and n (number of carbides per unit length L within a sheet). The measured and calculated values show that L1 and L2 decrease with decreasing isothermal temperature: L1 = 26.1, 19.2, 15.3, and 12.6 nm, and L2 = 52.6, 48.3, 46.0, and 42.1 nm at 690, 660, 630, and 600 °C, respectively. This trend agrees with literature reports.

For PIP, interphase precipitation carbides within a single ferrite grain can form on multiple crystallographic planes with different indices, as shown in [Figure 6: see original paper]. TEM images and corresponding selected-area electron diffraction (SAED) patterns reveal that after holding at 630 °C, the carbide sheets are parallel to ferrite {011} planes, while at 600 °C they are parallel to {011}, {012}, and {013} planes.

HRTEM images in [Figure 7: see original paper] show that the carbides are fully embedded in the ferrite matrix, with clear Moiré fringes resulting from superposition effects. The carbide dimensions measured parallel and perpendicular to the Moiré fringes are 10.8 nm × 6.9 nm at 660 °C and 5.4 nm × 3.9 nm at 600 °C. Multiple measurements confirm that carbide size decreases with decreasing isothermal temperature.

The crystal structure and orientation relationship were determined by Fourier transform analysis. Both 660 °C and 600 °C specimens contain interphase precipitation carbides with a NaCl-type crystal structure following the B-N orientation relationship: [100]ferrite//[110]carbide, (001)ferrite//(001)carbide, and $(0\bar{1}0)$ferrite//$(0\bar{1}1)$carbide. EDS analysis confirms the carbides as (Nb, Ti)C.

2.3 Microhardness

Since all specimens exhibit a ferrite-martensite duplex structure, where martensite affects the surrounding ferrite hardness and grain boundary strengthening occurs near interfaces, Vickers hardness measurements were performed in the centers of large ferrite grains. [Figure 8: see original paper] shows that Vickers hardness increases from 197 HV to 263 HV as isothermal temperature decreases, primarily due to precipitation strengthening.

3. Discussion

3.1 Precipitation Strengthening

The interaction between carbides and dislocations follows the Orowan mechanism, where gliding dislocations are impeded by carbides, causing them to bow out. When the applied stress exceeds the critical stress required for dislocations to bypass the carbides, the dislocation line loops around them, leaving a series of dislocation loops. The precipitation strengthening increment can be calculated using the Orowan equation. The calculated contributions to yield strength are 380, 414, 434, and 475 MPa for specimens isothermally held at 690, 660, 630, and 600 °C, respectively, all exceeding 300 MPa. The precipitation strengthening increases significantly with decreasing isothermal temperature.

3.2 Nucleation Site of Interphase Precipitation

All previous studies have concluded that interphase precipitation carbides nucleate at the ferrite-austenite interface. To determine whether nucleation occurs in ferrite near the interface or in austenite, this work calculated the lattice misfit between (Nb, Ti)C and both ferrite and austenite. The lattice parameter of (Nb, Ti)C was determined from the measured (002) plane spacing of 0.217 nm using the cubic crystal formula, yielding a = 0.434 nm. The misfit $ $1 between (Nb, Ti)C and ferrite (a = 0.286 nm) is calculated as 6.8%. If carbides nucleated in austenite, they would initially follow a cube-cube orientation relationship with $ $2 = 18% (using a_{austenite} = 0.356 nm). The significantly smaller misfit for ferrite nucleation indicates that interphase precipitation carbides nucleate and grow in ferrite near the austenite-ferrite interface to produce the characteristic layered arrangement.

Conclusions

1. Isothermal quenching at different temperatures produced ferrite-martensite duplex structures. The ferrite volume fraction first increased

then decreased with decreasing temperature, reaching a maximum at 630 °C, consistent with dilatometric results.

2. Interphase precipitation carbides were observed at all isothermal temperatures. Decreasing temperature significantly refined the sheet spacing, inter-particle spacing, and carbide size. The layered carbide sheets exhibited both curved and planar morphologies, with the distribution gradually evolving from CIP to PIP as temperature decreased.
3. HRTEM confirmed that interphase precipitation carbides have a NaCl-type crystal structure with a lattice parameter of 0.434 nm, following the B-N orientation relationship with the ferrite matrix. EDS analysis identified the carbides as (Nb, Ti)C. Lattice misfit calculations determined that carbides nucleate in ferrite near the austenite-ferrite interface.
4. Orowan mechanism calculations estimated precipitation strengthening contributions exceeding 300 MPa for all conditions, with strengthening increasing significantly as isothermal temperature decreased.

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