Effect of Nanoscale Carbides and Low-Angle Boundary Density on the Fire Resistance of Fe-C-Mo-M(M=Nb, V or Ti) Series Steels Postprint

Authors: Zhang Zhengyan, Sun Xinjun, Li Zhaodong, Wang Xiaojiang, Yong Qilong, Guodong Wang

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Abstract

Through a microalloying design featuring high Nb, V, or Ti (~0.1%) and low Mo ($ $0.2%), the failure temperatures of Fe-C-M-Mo (M = Nb, V, or Ti) series alloy steels were measured via constant-load tensile testing following TMCP processing. The interface density in post-TMCP samples was analyzed by EBSD, while nano-precipitates in samples after constant-load tensile testing were characterized using TEM. The results show that: the addition of approximately 0.2% Mo to Fe-C-V/Nb steel increased its failure temperature by approximately 40°C during the constant-load tensile heating process at 280 MPa. Low-angle interfaces provide favorable nucleation sites for MC-type precipitates, thereby accelerating MC phase precipitation; the nucleation and precipitation of fine, dispersed MC phase at low-angle interfaces during heating exerted effective high-temperature precipitation strengthening, thereby enhancing the failure temperature of fire-resistant steel. Mo-containing Ti-Mo steel exhibits a relatively high low-angle interface density, resulting in more rapid precipitation of MC-type precipitates and consequently the highest failure temperature; Nb-Mo steel ranks second; V-Mo steel, possessing the lowest low-angle interface density, exhibits retarded kinetics of MC phase precipitation at elevated temperatures, thus yielding the lowest failure temperature.

Full Text

Preamble

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Effect of Nanometer-Sized Carbides and Low-Angle Grain Boundary Density on Fire Resistance of Fe-C-Mo-M (M=Nb, V or Ti) Steels

ZHANG Zhengyan[1,2], SUN Xinjun[1], LI Zhaodong[1], WANG Xiaojiang[3], YONG Qilong[1**], WANG Guodong[2]

[1] Department of Structural Steels, Central Iron and Steel Research Institute, Beijing 100081, China
[2] School of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

Abstract
Fe-C-Mo-M steels (where M is Nb, V or Ti at ~0.1%, and Mo at 0.2%) were produced by thermal mechanical control processing (TMCP). Their fire resistance performance was characterized in terms of failure temperature through constant-load tensile tests conducted while heating from ambient temperature to 800°C at a rate of 28°C/min under a constant load of 280 MPa. The grain boundary misorientation distributions after TMCP were examined by electron backscattered diffraction (EBSD), and MC-type carbide precipitates were characterized by transmission electron microscopy (TEM). The results show that adding approximately 0.2% Mo to Fe-C-Nb/V steels increases the failure temperature by about 40°C. Low-angle grain boundaries provide favorable nucleation sites for MC-type carbides, accelerating their precipitation. During heating, fine and dispersed MC carbides precipitating at low-angle grain boundaries produce effective high-temperature precipitation strengthening, thereby improving the fire resistance of the steels. Among the tested steels, Ti-Mo steel exhibits the highest failure temperature due to its highest low-angle grain boundary density, which leads to rapid precipitation of MC-type carbides. Nb-Mo steel ranks second, while V-Mo steel shows the lowest failure temperature because its lowest low-angle grain boundary density slows down the precipitation kinetics of MC carbides at elevated temperatures.

Keywords: metallic materials, intelligent fire-resistant steel, failure temperature, precipitation strengthening, low-angle grain boundary density, nanometer-sized carbides

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Introduction

As a novel structural steel for building construction, fire-resistant steel offers advantages such as lower cost and greater usable floor area compared with conventional structural steels that require fireproof coating, while enhancing building safety. Consequently, fire-resistant steels have found widespread application. Fire-resistant steels developed in the 1980s containing alloying elements such as Mo, Cr, and Nb have been widely adopted due to their excellent high-temperature properties and compliance with stringent fire-resistance standards. During the 1990s, steel companies including Ma Steel, Ben Steel, and Wu Steel also developed fire-resistant steels with specific compositions for use in high-rise buildings. Early fire-resistant steels typically contained relatively high Mo content (~0.5%) to enhance high-temperature performance through solid solution and precipitation strengthening. However, high Mo content significantly increases alloy costs. In recent years, researchers have proposed replacing Mo with Nb or V. For instance, some studies have suggested alloy designs with low or ultra-low Mo content. Other researchers have substituted Nb or V for Mo, but these approaches either introduced other precious elements or utilized insufficient alloying additions, resulting in insignificant precipitation strengthening increments. Furthermore, the high-temperature strengthening mechanisms of fire-resistant steels require deeper investigation.

Building upon previous research and aiming to further reduce alloy costs, this study employs a microalloying design featuring low Mo (0.2%) and high Nb, V, or Ti (~0.1%). Through thermomechanical control processing (TMCP), we obtained "intelligent" fire-resistant steels in which microalloy carbides do not readily precipitate during rolling but form abundant nanometer-sized precipitates during fire exposure, thereby achieving effective precipitation strengthening. From the perspective of high-temperature strengthening mechanisms, this paper comparatively analyzes the reasons for different failure temperatures in Fe-C-M-Mo (M=Nb, V or Ti) steels during constant-load heating, and explains their high-temperature strengthening behavior based on microstructural characteristics and nanometer-sized microalloy carbide precipitation features.

Experimental Methods

The experimental steels were vacuum induction melted and then subjected to two-stage controlled rolling (recrystallization and non-recrystallization regions) with a finish rolling temperature of 800°C. After rolling, the steels were cooled by laminar flow to approximately 400°C followed by air cooling, yielding alloy steels of different compositions in both Fe-C-M and Fe-C-M-Mo (M=Nb, V or Ti) systems. The chemical compositions are listed in .

Constant-load tensile tests were performed on a Gleeble 3800 thermal simulator to determine the failure temperature of the steels. The test procedure involved heating specimens from room temperature to elevated temperature (800°C in this study) under a constant load below the steel' s room-temperature yield strength. A constant load of 280 MPa was applied with a heating rate of 28°C/min from room temperature to 800°C. The strain-temperature curve was recorded during heating, and the failure temperature was defined as the temperature at which strain suddenly increased in the strain-temperature curve.

Rolled specimens were ground, polished, and etched with 3% nital (volume fraction) for microstructural observation using an S-4300 cold field-emission scanning electron microscope (SEM). For EBSD analysis, rolled specimens were ground, polished, and electropolished in 6% perchloric acid alcohol solution (volume fraction) at 20 V for 10 s. EBSD was conducted to determine the distribution and density of low-angle and high-angle grain boundaries. The EBSD scan area was 100$×100μm^{2}$ with a step size of 0.2 m. Following literature reports, grain boundary density was defined as the total interface length per unit area.

Thermo-Calc software (TCFE 6 database) was used to calculate the equilibrium volume fractions of MC-type precipitates in the experimental steels with different compositions. Carbon extraction replicas were prepared from both as-rolled and constant-load tensile tested specimens. Precipitate morphology was observed using a Tecnai F20 field-emission transmission electron microscope (TEM), and particle number density was statistically analyzed from more than five TEM fields of view with no fewer than 100 particles counted.

Results and Discussion

2.1 Failure Temperature of Experimental Steels Under 280 MPa Constant Load

presents the failure temperatures of steels with different compositions. The strain-temperature curves obtained from constant-load tensile tests are shown in [Figure 1: see original paper]. Different steel compositions exhibit varying failure temperatures. Steels with combined additions of Nb, V, or Ti with Mo demonstrate higher failure temperatures. Ti-Mo steel shows the highest failure temperature at 714°C, which is 8°C and 22°C higher than that of Nb-Mo and V-Mo steels, respectively. Moreover, both Nb-Mo and V-Mo steels exhibit failure temperatures approximately 45°C higher than their Mo-free counterparts. Regardless of Mo addition, Nb-containing steels consistently show higher failure temperatures than V-containing steels (19°C higher without Mo, 14°C higher with Mo). Additionally, Low-Nb-Mo steel with lower Nb content exhibits a failure temperature of 675°C, which falls between those of Nb-Mo and V-Mo steels.

2.2 Microstructural Morphology

[Figure 2: see original paper] shows SEM images of the experimental steels. The microstructures of V steel ([Figure 2: see original paper]a) and Nb steel ([Figure 2: see original paper]c) consist of granular bainite (GB), quasi-polygonal ferrite (QF), and minor pearlite (P). Since Mo inhibits pearlite transformation to some extent, V-Mo ([Figure 2: see original paper]b) and Nb-Mo ([Figure 2: see original paper]d) steels exhibit microstructures composed of GB and minor QF. Both Ti-Mo and Low-Nb-Mo steels show fully GB microstructures. Furthermore, Nb steel exhibits finer and more flattened microstructures compared with V steel, and this effect becomes more pronounced with Mo addition. This indicates that ferrite grain sizes in Nb-containing steels are finer than those in V-containing steels, whether added alone or in combination. This can be attributed to two factors: First, Nb atoms have a larger atomic size mismatch with Fe atoms (~15%) compared with V, and they segregate to austenite grain boundaries, exerting a strong solute drag effect on recrystallization of deformed austenite. Second, NbC has lower solubility in iron matrix than VC, making it more prone to strain-induced precipitation during rolling and forming finely dispersed NbC particles that more significantly inhibit austenite recrystallization. Consequently, Nb-containing steels show more flattened microstructures after rolling and finer grains after transformation. The microstructure becomes even finer with Mo addition, indicating that Mo enhances the recrystallization inhibition effect of Nb and V. Literature also reports that Mo addition suppresses recrystallization of deformed austenite in Ti-microalloyed steels.

Additionally, literature suggests that B is often added to fire-resistant steels to enhance high-temperature properties, as free B segregating to grain boundaries improves hardenability, thereby facilitating formation of high-strength low-temperature bainite. When steels contain high Ti or Al contents, N preferentially combines with Ti and Al to form primary or secondary TiN and AlN at high temperatures, leaving B free to segregate to grain boundaries and promote bainite formation. Therefore, Ti-Mo steel and Low-Nb-Mo steel with higher Ti and Al contents exhibit fully granular bainite microstructures ([Figure 2: see original paper]e, f) with fine martensite-austenite (M/A) islands dispersed in the matrix.

[Figure 3: see original paper] presents EBSD grain boundary distribution maps of the experimental steels, where black thick lines represent high-angle grain boundaries (misorientation >15°) and red thin lines represent low-angle grain boundaries (misorientation 2-15°). Ti-Mo and Low-Nb-Mo steels with fully granular bainite microstructures contain more low-angle grain boundaries than other steels with mixed microstructures of granular bainite and equiaxed/polygonal ferrite. In steels composed of ferrite and granular bainite, equiaxed or polygonal ferrite contains few or no low-angle grain boundaries, whereas bainitic ferrite contains numerous low-angle grain boundaries.

From [Figure 3: see original paper] and the definition of grain boundary density, we obtained the relationship between grain boundary density and misorientation angle for the experimental steels ([Figure 4: see original paper]). The misorientation angle range is 0-61° with a step of 5°, while the inserted figure shows 0-15° with a step of 2°. The results demonstrate that Mo addition to Nb and V steels increases low-angle grain boundary (2-15°) density. The specific densities of low-angle grain boundaries (2-15°) are listed in . Analysis of [Figure 3: see original paper] indicates that these low-angle grain boundaries primarily exist in bainitic ferrite. According to the dislocation model of low-angle grain boundaries, higher low-angle grain boundary density corresponds to higher dislocation density. This suggests that Mo addition promotes bainite transformation, resulting in more bainitic ferrite with higher dislocation density. Moreover, Nb-containing steels (with or without Mo) exhibit higher low-angle grain boundary densities than V-containing steels. Ti-Mo steel with granular bainite microstructure shows the highest low-angle grain boundary density at 1.23 m^{-2}, while Low-Nb-Mo steel has a density of 1.15 m^{-2}, ranking second.

Discussion

The room-temperature strengthening mechanisms of steels include solid solution strengthening, grain boundary strengthening, precipitation strengthening, and dislocation strengthening. The effectiveness of each strengthening mechanism depends on the steel' s elastic modulus, which decreases with increasing temperature, particularly significantly above 600°C. Therefore, when analyzing high-temperature strengthening mechanisms, the temperature dependence of elastic modulus must be considered. Researchers have attributed the strength degradation of steels at elevated temperatures to several factors: (1) dislocation motion (slip and climb) at high temperatures causing plastic deformation; (2) grain growth, carbide spheroidization, and precipitate coarsening facilitating dislocation motion; (3) α/γ phase transformation causing softening at temperatures above 700°C; and (4) grain boundary sliding. Literature also suggests that grain refinement strengthening becomes ineffective above 600°C, which exceeds the equicohesive temperature of steels. Currently, solid solution strengthening and second-phase precipitation strengthening are considered the primary mechanisms for improving high-temperature strength. Since all experimental steels in this study failed above 600°C, grain boundary strengthening is no longer effective. Dislocation strengthening is also insignificant at high temperatures. With the characteristic of low Mo and high Nb, V, or Ti additions, the solid solution strengthening effect of small Mo amounts is limited. Consequently, precipitation strengthening from Nb, V, and Ti microalloying becomes particularly important.

[Figure 5: see original paper] shows TEM images of precipitate distribution and morphology in Nb-Mo, V-Mo, and Ti-Mo steels. [Figure 5: see original paper]a, c, and e correspond to as-rolled samples, revealing sparse precipitate distribution with most particles approximately 10 nm in size, likely formed through strain-induced precipitation in austenite. V-Mo steel exhibits the lowest precipitate number density compared with Nb-Mo and Ti-Mo steels, which can be attributed to the higher solubility product of V carbides in steel, making strain-induced precipitation more difficult. Additionally, the relatively fast laminar cooling rate after rolling suppressed extensive precipitation in ferrite. [Figure 5: see original paper]b, d, and f show precipitate morphologies after constant-load tensile testing, demonstrating dense dispersion of microalloy carbides much more numerous than in the as-rolled condition, with sizes smaller than 10 nm, indicating precipitation from ferrite. This characteristic—limited precipitation during rolling but abundant nanometer-sized carbide dispersion during heating—embodies the "intelligent" fire-resistant feature of these steels. EDS analysis identified these nanometer-sized carbides as (Nb, Mo)C, (V, Mo)C, and (Ti, Mo)C. The statistical results of particle number density are shown in [Figure 6: see original paper]. The average precipitate size in different steels is similar at approximately 6 nm, while the number densities are 1417 m^{-2}, 925 m^{-2}, and

1657 m^{-2} for Nb-Mo, V-Mo, and Ti-Mo steels, respectively. Ti-Mo steel shows the highest precipitate number density, followed by Nb-Mo steel, with V-Mo steel having the lowest.

The equilibrium volume fractions of different microalloy carbides in steel matrix vary due to differences in ideal stoichiometry, density, solubility product, and alloying element activity. lists the volume fractions of MC phase at 600°C (a typical testing and precipitation temperature for fire-resistant steels) calculated using Thermo-Calc (TCFE 6 database). Under equilibrium conditions, V-Mo steel shows the highest precipitation amount, while Nb-Mo and Ti-Mo steels have lower amounts, with Nb-Mo steel slightly higher than Ti-Mo steel. Previous research on Fe-C-Mn-Nb steels found that higher grain boundary density leads to higher failure temperature. The improvement in failure temperature results from increased grain boundary density, as low-angle grain boundaries necessarily provide favorable nucleation sites for MC precipitation. Therefore, although V-Mo steel has the highest equilibrium precipitation amount at 600°C, its lower low-angle grain boundary density cannot provide sufficient nucleation sites, resulting in slower precipitation kinetics and consequently lower failure temperature under non-equilibrium conditions. In contrast, Ti-Mo and Nb-Mo steels, despite having lower equilibrium precipitation amounts, possess higher low-angle grain boundary densities that provide abundant nucleation sites and faster precipitation kinetics, leading to higher failure temperatures.

Furthermore, Nb-Mo steel shows higher precipitate number density than Nb steel. This can be explained by two factors: First, Nb-Mo steel has higher low-angle grain boundary density, providing more nucleation sites for precipitates. Second, Mo incorporation into NbC to form (Nb, Mo)C reduces the lattice misfit with the iron matrix, decreasing interfacial energy and nucleation barrier. Consequently, Nb-Mo steel exhibits greater precipitation strengthening increment and higher failure temperature at elevated temperatures. Similar analysis applies to the higher failure temperature of V-Mo steel compared with V steel. Although Low-Nb-Mo steel has numerous low-angle grain boundaries that could provide ample nucleation sites for MC precipitation, its overall precipitation amount is lower than that of Nb-Mo steel, preventing it from achieving the highest failure temperature.

These findings demonstrate that to improve the failure temperature of "intelligent" fire-resistant steels through high-temperature nanometer-sized microalloy carbide precipitation strengthening, both the as-rolled microstructure (particularly increasing low-angle grain boundary density to provide nucleation sites) and rational alloying additions must be considered. The synergistic effect of these two factors enables "intelligent" fire-resistant steels to achieve excellent high-temperature fire resistance.

Conclusions

1. Through TMCP processing with high M (M=Nb, V, Ti) and low Mo microalloying, low-cost intelligent fire-resistant steels can be designed. Adding approximately 0.2% Mo to Fe-C-V/Nb steels increases the failure temperature by about 40°C during constant-load tensile heating at 280 MPa.
2. In steels with granular bainite microstructure, low-angle grain boundaries provide favorable nucleation sites for MC-type precipitates. The dispersion of nanometer-sized MC carbides precipitating at low-angle grain boundaries during heating produces effective high-temperature precipitation strengthening, thereby improving the failure temperature of fire-resistant steels.
3. The high-temperature precipitation phases in Ti-Mo, Nb-Mo, and V-Mo steels are all (M, Mo)C (M=Ti, Nb, V). Ti-Mo steel exhibits the highest failure temperature due to its highest low-angle grain boundary density and high MC-type precipitation amount. Nb-Mo steel ranks second, while V-Mo steel shows the lowest failure temperature because its lowest low-angle grain boundary density slows MC precipitation kinetics at high temperatures.

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Note: Figure translations are in progress. See original paper for figures.