Effect of Nitrogen Addition on Continuous Cooling Transformation Behavior of Vanadium Microalloyed Steel: Postprint

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Abstract

The CCT curves of three experimental steels with different vanadium and nitrogen contents were measured using a dilatometer, the microstructures at different cooling rates were observed, the precipitation behavior of vanadium was analyzed, the lattice plane mismatch between various nucleation substrates and ferrite was calculated, and the effect of nitrogen addition on the continuous cooling transformation behavior of vanadium-microalloyed steel was investigated. The results show that nitrogen addition promoted ferrite formation, increased the transformation start temperature of the experimental steels, and also increased the critical cooling rate for the formation of a fully bainitic microstructure; within the cooling rate range of 0.8-1.6℃/s, the microstructure of low-nitrogen steel consisted of granular bainite and lath bainite, whereas a large amount of acicular ferrite was present in the nitrogen-added steel; in low-nitrogen steel, vanadium precipitated mainly before and after transformation, with VC being the predominant precipitate, and increasing vanadium content only increased the precipitation amount but could not change the precipitation temperature or the composition of the precipitates; whereas after nitrogen addition, vanadium precipitated within austenite, predominantly as VN; at 900℃, the planar lattice mismatches of austenite, VC, and VN with ferrite were 6.72%, 3.89%, and 1.55%, respectively, VN had a near-coherent low-energy interface with ferrite, which could serve as a preferential nucleation site for ferrite, effectively promoting ferrite formation.

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Effect of Nitrogen Addition on Continuous Cooling Transformation Behavior of Vanadium Microalloyed Steels

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Abstract

The effect of nitrogen addition on continuous cooling transformation behavior of vanadium microalloyed steels was investigated. CCT curves of three experimental steels with different vanadium and nitrogen content were measured by thermal dilatometer; the microstructural evolution of the steels with varying cooling rates was characterized; their precipitation behavior was tracked, and planar lattice misfit degree of the precipitates with the ferrite matrix was calculated. The results show that ferrite transformation is promoted by nitrogen addition, and the starting temperature of transformation and the critical cooling rate for full bainite transformation are increased as well. For cooling rates in the range of 0.8-1.6℃/s, the microstructure of steels with low nitrogen consists of granular bainite + lath-like bainite, while acicular ferrite also exists. During or after the γ-α transformation, vanadium compounds in low nitrogen steels precipitate mainly as VC, the quantity of which increases with increasing vanadium content. However, for the steel rich in nitrogen, vanadium compounds precipitate as VN in austenite at high temperature. The lattice misfit degree of ferrite with the precipitates of austenite, VC and VN, which occurred at 900℃, are 6.72%, 3.89% and 1.55% respectively. It indicates that VN precipitates act as preferential nucleation sites for ferrites and promote the ferrite transformation.

KEY WORDS metallic materials, vanadium microalloying, continuous cooling transformation, nitrogen addition, planar lattice misfit degree, intragranular ferrite nucleation

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Introduction

Bainitic steels produced by thermo-mechanical controlled processing (TMCP) exhibit good economic efficiency and favorable strength-toughness balance, and are widely used in offshore platforms, pressure vessels, and shipbuilding. However, compared with quenched and tempered steels, the toughness of bainitic steels still needs improvement. Microalloying is an important solution that utilizes precipitation of alloying elements to control microstructure and thereby enhance toughness. Vanadium is one of the most commonly used microalloying elements. Compared with niobium and titanium, vanadium has greater solubility in austenite, and the solubility of VN is lower than that of VC, meaning VN precipitates more readily. This characteristic has promoted the application of vanadium-nitrogen composite microalloying technology.

Previous research has primarily focused on precipitation strengthening from V(C,N) precipitation in ferrite. However, recent results demonstrate that nitrogen addition to vanadium microalloyed steels promotes intragranular ferrite transformation, thereby improving toughness. Tsunekage et al. reported that MnS precipitated in austenite can promote intragranular ferrite nucleation, and vanadium precipitation on MnS can enhance this effect. Siwecki et al. showed that increasing nitrogen content promotes V(C,N) precipitation in austenite. Ishikawa proposed that V(C,N) has a Baker-Nutting orientation relationship with ferrite, with low lattice misfit and interfacial energy at the boundary, enabling it to serve as nucleation sites for intragranular ferrite and promote acicular ferrite transformation. Capdevila found that in high-nitrogen vanadium microalloyed steels, acicular ferrite can nucleate on V(C,N) precipitates even without MnS precipitation.

In TMCP production, controlling rolling temperature and cooling rate is essential for optimizing steel microstructure and properties, which requires understanding phase transformation behavior under different cooling rates. This study investigates the effects of vanadium and nitrogen content on the continuous cooling transformation behavior of experimental steels, analyzing vanadium and nitrogen precipitation behavior and the influence of two vanadium precipitates (VC and VN) on transformation to elucidate the role of nitrogen addition in vanadium microalloyed steels.

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1. Experimental Methods

The chemical compositions of the experimental steels are listed in . Steel VM is a base vanadium microalloyed steel containing 0.1% V and 29×10^{-6} N. Steel NH has increased nitrogen content to 210×10^{-6} based on the base composition, while steel VH has increased vanadium content to 0.23% based on the base composition.

The experimental steels were melted in a vacuum induction furnace and cast into 50 kg ingots. After holding at 1200℃ for 2 hours, they were forged into bars with a diameter of 12 mm. The starting forging temperature was 1150℃, and the finishing temperature was above 950℃. The steels were then homogenized at 1200℃ for 1 hour and machined into thermal expansion specimens with a diameter of 3 mm and length of 10 mm. CCT curves were determined using a Formaster-F II automatic phase transformation dilatometer. The austenitizing temperature was 1000℃ with a holding time of 10 minutes, and cooling rates were 40, 16, 8, 4, 1.6, 0.8, 0.28, 0.14, 0.06, and 0.03℃/s. Cross-sections at the thermocouple weld points were prepared by mechanical grinding and polishing, etched with 4% nital solution, and examined using an Olympus GX51 optical microscope. HV5 hardness was measured using a Hengyi VH-5 Vickers hardness tester.

Thermo-Calc software with the TCFE7 database was used to calculate the evolution of precipitate phases with temperature and the site occupancy fractions of carbon and nitrogen in vanadium precipitates for the three experimental steels.

2.1 Effect of Nitrogen Addition on CCT Curves

The CCT curves of the experimental steels are shown in [Figure 1: see original paper]. The volume fractions of various phases at different cooling rates were determined metallographically and are marked on the curves. lists the critical transformation temperatures of the three steels. The Ac_1 temperatures of the three steels are similar. The Ac_3 temperature of the base steel VM is 860℃. The Ac_3 of NH is slightly lower by 5℃ compared to VM, while the Ac_3 of VH is 20℃ higher than VM. The vanadium content in VH is 0.13% higher than in VM. Vanadium is a ferrite-stabilizing element that increases carbon solubility in ferrite and expands the ferrite phase field, thereby raising the temperature at which austenite transformation completes. Additionally, the austenite transformation during heating is a process of nucleation and grain boundary migration. Before transformation completes, vanadium may exist as precipitates or in solution; both the grain boundary pinning effect of precipitates and the solute drag effect of dissolved vanadium atoms can hinder the austenite transformation process.

Thermo-Calc was used to calculate the mass fractions of vanadium precipitates, ferrite, and austenite phases as a function of temperature, as shown in [Figure 2: see original paper]. The mass fractions of vanadium precipitates in VM, NH, and VH are 0.003, 0.001, and 0.008, respectively. The precipitate content in VH with higher vanadium content is significantly higher than in VM and NH. These precipitates pin grain boundaries and hinder austenite transformation, raising the Ac_3 temperature.

The critical cooling rates to obtain fully bainitic microstructure for VM, NH, and VH are 0.8, 1.6, and 0.8℃/s, respectively. The ferrite transformation curve of nitrogen-enriched NH steel shifts leftward, and 7% ferrite still forms at a cooling rate of 0.8℃/s. gives the transformation starting temperatures (Ts) of the experimental steels at different cooling rates. NH shows significantly higher transformation starting temperatures than VM and VH at all cooling rates. This demonstrates that nitrogen addition promotes ferrite formation and increases the transformation starting temperature of the experimental steels.

In NH, nitrogen primarily combines with vanadium, and nitrogen content significantly affects vanadium precipitation behavior. According to the phase calculation results ([Figure 2: see original paper]), V(C,N) in NH begins to precipitate above 1100℃ ([Figure 2: see original paper]b), meaning extensive precipitation occurs in the austenite region. At lower temperatures, the precipitation amount of (Mo,V)C is minimal, and vanadium mainly precipitates as V(C,N). The V(C,N) precipitated in austenite can become nucleation sites for ferrite and promote ferrite transformation, causing transformation to occur at higher temperatures. In contrast, in VM ([Figure 2: see original paper]a) and VH ([Figure 2: see original paper]c), V(C,N) begins to precipitate around 900℃, reaching maximum precipitation amount around 790℃. As temperature continues to decrease, the V(C,N) content drops rapidly, and vanadium mainly precipitates as (Mo,V)C. Considering that the calculation represents thermodynamic equilibrium, actual precipitation should occur at even lower temperatures. Therefore, vanadium precipitation in VM and VH occurs during or after transformation, where precipitation in ferrite only provides precipitation strengthening without affecting ferrite transformation behavior.

2.2 Microstructure

The microstructures of the experimental steels at different cooling rates are shown in [Figure 3: see original paper]. At the same cooling rate, the microstructures of VM and VH are similar. At cooling rates of 1.6 and 0.8℃/s, VM and VH exhibit granular bainite + lath bainite microstructure, with bainite laths nucleating on prior austenite grain boundaries and penetrating through grains in bundles. At a cooling rate of 0.28℃/s, a small amount of ferrite appears, with volume fractions of 4% and 9% in VM and VH, respectively. The microstructure of NH steel shows significant differences: at cooling rates of 1.6 and 0.8℃/s, it consists of granular bainite + acicular ferrite, with acicular ferrite randomly oriented; at 0.28℃/s, it shows ferrite + bainite microstructure with ferrite volume fraction reaching 48%. Nitrogen addition promotes acicular ferrite formation at high cooling rates and ferrite formation at low cooling rates.

The V(C,N) precipitated in austenite has a near-coherent low-energy interface with ferrite and can serve as preferential nucleation sites during ferrite transformation, promoting ferrite formation. However, [Figure 2: see original paper]c shows that although vanadium in VH precipitates at lower temperatures, some precipitation also occurs in austenite, yet these austenitic vanadium precipitates do not promote ferrite transformation. To understand this, the composition of vanadium precipitates in the three steels was analyzed by calculating the carbon and nitrogen site occupancy fractions in vanadium precipitates, as shown in [Figure 4: see original paper]. In NH, nitrogen dominates throughout, indicating precipitation is primarily VN. In VM and VH, the carbon and nitrogen occupancy fractions in V(C,N) precipitates show similar trends. Within the temperature range of 700-900℃, corresponding to the maximum V(C,N) precipitation amount ([Figure 2: see original paper]a,c), carbon occupancy fraction is much higher than nitrogen, indicating precipitation is mainly VC. At lower temperatures, vanadium precipitates as (Mo,V)C. Therefore, vanadium precipitation in low-nitrogen steels is dominated by VC.

Although VN and VC have similar crystal structures, their lattice constants differ, leading to different lattice misfit with ferrite that may affect ferrite formation differently. Turnbull and Vonnegut proposed that heterogeneous nucleation effectiveness depends on lattice misfit between the substrate and nucleating phase, defining a one-dimensional misfit:

$$\delta = \frac{a_s - a_n}{a_n}$$

where δ is the misfit between substrate and nucleating phase, a_n is the lattice constant of the low-index plane of the nucleating phase, and a_s is the lattice constant of the low-index plane of the substrate.

Baker calculated the misfit between VC and ferrite, finding only 3% misfit in the [200]VC//[110]α-Fe direction on the α-Fe{100} plane, but 30% misfit in the [001]VC//[001]α-Fe direction. Bramfitt further developed a two-dimensional misfit (planar misfit) for matching between different lattice types:

$$\delta_{(hkl)_n}^{(hkl)_s} = \sum_{i=1}^{3} \frac{|d_{[uvw]_s^i} \cos\theta - d_{[uvw]_n^i}|}{d_{[uvw]_n^i}} \times 100\%$$

where $(hkl)_s$ is a low-index plane of the substrate, $[uvw]_s$ is a low-index direction in plane $(hkl)_s$, $(hkl)_n$ is a low-index plane of the nucleating phase, $[uvw]_n$ is a low-index direction in plane $(hkl)_n$, $d_{[uvw]_s}$ is the atomic spacing along $[uvw]_s$, $d_{[uvw]_n}$ is the atomic spacing along $[uvw]_n$, and θ is the angle between $[uvw]_s$ and $[uvw]_n$.

Equation (2) was used to calculate the planar lattice misfit between austenite, VC, and VN with ferrite. Generally, ferrite and austenite have a K-S orientation relationship during transformation: $\{111\}_\gamma//\{110\}_\alpha$, $\langle 110\rangle_\gamma//\langle 111\rangle_\alpha$. VC and VN have a B-N relationship with ferrite: $\{100\}_{V(C,N)}//\{100\}_\alpha$, $\langle 010\rangle_{V(C,N)}//\langle 011\rangle_\alpha$. Therefore, for calculating misfit between ferrite and austenite, $(111)_\gamma//(110)_\alpha$ was selected as the habit plane, as shown in [Figure 5: see original paper]a. For VC and VN with ferrite, $(100)_{VC,VN}//(100)_\alpha$ was selected, as shown in [Figure 5: see original paper]b and c.

Assuming ferrite nucleation at 900℃, the crystallographic data of each phase are listed in . Lattice constants at 900℃ were extrapolated using the thermal expansion coefficients of the phases. Calculation results show that the planar misfit values of austenite, VC, and VN with ferrite are 6.72%, 3.89%, and 1.55%, respectively. VN has the smallest misfit with ferrite, making it more effective as an intragranular ferrite nucleation site and promoting ferrite transformation.

In nitrogen-enriched NH, vanadium precipitates as VN in austenite, which effectively promotes intragranular ferrite nucleation, forming acicular ferrite microstructure and raising the ferrite transformation starting temperature.

2.3 Hardness

[Figure 6: see original paper] shows the HV5 hardness of experimental steels at various cooling rates. The hardness follows the order VH > VM > NH at all cooling rates. VN precipitation in NH promotes ferrite formation, and even at high cooling rates, some acicular ferrite exists, reducing hardness. At high cooling rates, VM and VH microstructures consist of granular bainite + lath bainite, while at low cooling rates their bainite content is much greater than in NH. Granular bainite contains numerous hard MA islands, and lath bainite has elongated MA constituents distributed on lath boundaries, resulting in higher hardness. Additionally, the vanadium content in VH is 0.13% higher than in VM, producing greater precipitation strengthening, thus VH hardness exceeds that of VM.

Conclusions

1. In vanadium microalloyed steels, increasing nitrogen content promotes ferrite transformation, raises the transformation starting temperature, and increases the critical cooling rate for obtaining fully bainitic microstructure.
2. After nitrogen addition, vanadium precipitates in the austenite region mainly as VN. In low-nitrogen steels, vanadium precipitates during or after the γ-α transformation mainly as VC. Increasing vanadium content can increase the precipitation amount but has little effect on precipitation temperature and precipitate composition.
3. The planar lattice misfit values of austenite, VC, and VN with ferrite are 6.72%, 3.89%, and 1.55%, respectively. VN has the smallest misfit with ferrite and can become preferential nucleation sites for ferrite, promoting ferrite formation.

References

1. N. Tsunekage, K. Kobayashi, H. Tsubakino, Influence of sulphur and vanadium additions on toughness of bainitic steels, *Materials Science and Technology*, 17(7), 847(2001)

2. Rune Lagneborg, Tadeusz Siwecki, Stanislaw Zajac, Bevis Hutchinson, *The Role of Vanadium in Microalloyed Steels* (Stockholm, The Scandinavian Journal of Metallurgy, 1999) p.15
3. K. Nakai, T. Sakamoto, R. Asakura, Y. Kotani, N. Isomura, S. Kobayashi, M. Hamada, Y. Komizo, Nucleation of bainite at small angle dislocation network in austenite and its effects on mechanical properties in steels, *ISIJ International*, 51(2), 274(2011)
4. Dragomir Glisic, Nenad Radovic, Ankica Koprivica, Abdunnaser Fadel, Djordje Drobnjak, Influence of reheating temperature and vanadium content on transformation behavior and mechanical properties of medium carbon forging steels, *ISIJ International*, 50(4), 601(2010)
5. Tadeusz SIWECKI, Vanadium microalloyed bainitic hot strip steels, *ISIJ International*, 50(5), 760(2010)
6. F. Ishikawa, T. Takahashi, T Ochi, Intragranular ferrite nucleation in medium-carbon vanadium steels, *Metallurgical and Materials Transactions A*, 25A(5), 929(1994)
7. F. Ishikawa, T. Takahashi, The formation of intragranular ferrite plates in medium-carbon steels for hot-forging and its effect on the toughness, *ISIJ International*, 35(9), 1128(1995)
8. C. Capdevila, C. Garcia-mateo, J. Chao, F. G. Caballero, Effect of V and N precipitation on acicular ferrite formation in sulfur-lean vanadium steels, *Metallurgical and Materials Transactions A*, 40A(3), 522(2009)
9. M. J. Crooks, A. J. Garrett-Reed, J. B. Vander Sande, W. S. Owen, The isothermal austenite-ferrite transformation in some deformed vanadium steels, *Metallurgical Transactions A*, 13(8), 1347(1982)
10. A. T. Davenport, L. C. Brossard, R. E. Miner, Precipitation in microalloyed high-strength low-alloy steels, *Journal of Metals*, 27(6), 21(1975)
11. S. Yamamoto, C. Ouchi, T. Osuka, The effect of microalloying elements on the recovery and recrystallization in deformed austenite, in: *Conf. Proc. Thermomechanical Processing of Microalloyed Austenite*, edited by A. J. DeArdo, G. A. Ratz and P. J. Wray (Pittsburgh, The Metallurgical Society of AIME, 1982) p. 613
12. J. J. Jonas, I. Weiss, Effect of precipitation on recrystallization in microalloyed steels, *Metal Science*, 13, 238(1979)
13. B. Bramfitt, The effect of carbide and nitride additions on the heterogeneous nucleation behavior of liquid iron, *Metallurgical Transactions*, 1(7), 1987(1970)
14. T. N. Baker, Processes, microstructure and properties of vanadium microalloyed steels, *Materials Science and Technology*, 25(9), 1083(2009)

15. N. Tsunekage, K. Kobayashi, H. Tsubakino, Influence of sulphur and vanadium additions on toughness of bainitic steels, *Materials Science and Technology*, 17(7), 847(2001)

16. K. Nakai, T. Sakamoto, R. Asakura, Y. Kotani, N. Isomura, S. Kobayashi, M. Hamada, Y. Komizo, Nucleation of bainite at small angle dislocation network in austenite and its effects on mechanical properties in steels, *ISIJ International*, 51(2), 274(2011)

17. XU Zuyao, GU Wengui, YU Xuejie, Superledges and carbides in bainite, *Acta Metallurgica Sinica*, 19(1), 12(1983)

18. YONG Qilong, YAN Shenggong, PEI Hezhong, TIAN Jianguo, YANG Wenyong, Physical metallurgical data of vanadium in steel, *Journal of Iron and Steel Research*, 10(5), 63(1998)

19. YONG Qilong, *Second Phases in Structural Steels* (Beijing, Metallurgical Industry Press, 2006) p.275

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