Nitrogen-Enhanced Ferritic Microalloyed Steels

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ABSTRACT

In many ferritic steels, “free” (uncombined) nitrogen is regarded as a harmful impurity, responsible for aging and embrittlement. In making “clean” steel, nitrogen is expected to be below 20 ppm.

In “enhanced-nitrogen” ferritic steels, the amount of nitrogen may be either caused by a high residual content (e.g. up to 110 ppm in electric-arc-furnace (EAF) steels) or intentionally added to levels close to the solubility limit. In the presence of nitrogen binding elements, such as aluminum, titanium, and vanadium, nitrogen is removed from solid solution by forming metal nitrides. The degree of their dispersion affects the microstructure and thus steel properties. The following metallurgical phenomena may be involved -- the grain-coarsening temperature, grain refinement, intragranular ferrite nucleation, optimized precipitation strengthening, and other factors.

An enhanced-nitrogen content particularly benefits vanadium steels, contributing to property improvements and cost reduction.

Key words: Aluminum, vanadium, or titanium nitrides; precipitation; grain refinement; intragranular nucleation; weight reduction

HIGH-NITROGEN AUSTENITIC VS. FERRITIC STEELS

The difference in the solubility of nitrogen in face-centered-cubic austenitic steels compared to body-centered-cubic ferritic steels accounts for different meaning of the term, “high nitrogen.” Depending on chemistry and melting practice, austenitic steels may contain several percent nitrogen. In ferritic steels, the amount of nitrogen is about two orders of magnitude smaller and is used almost exclusively for precipitation of metallic nitrides having different degrees of dispersion. In high-strength, low-alloy (HSLA) steels, the limiting amount of nitrogen is close to 220 ppm but may be greater in higher alloyed steels, such as 9-12% chromium steels. The main nitride-forming elements are aluminum, titanium and vanadium.

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NITROGEN AS A HARMFUL IMPURITY

“Free” nitrogen (dissolved in ferrite) contributes to aging and brittleness. To neutralize these ill effects, it must be removed by scavengers, such as titanium or boron, or by forming metallic-nitride or metallic-carbonitride precipitates having different degrees of dispersion. To counteract the embrittling effect of a precipitation, it should be accompanied by concurrent grain refinement. Nitride precipitation at high temperatures may increase the depth and width of the ductility trough and contribute to cracking during concasting. There is also a deep-seated perception that nitrogen is detrimental to welding, in spite of experimental evidence to the contrary.

Consequently, many standards and specifications severely restrict the permissible amount of nitrogen in ferritic steels. Even in the presence of nitrogen binding elements, restrictions are only partly relaxed, contrary to metallurgical arguments. A revision of these obsolete standards is long overdue.

BENEFICIAL EFFECTS OF ENHANCED NITROGEN

In the presence of nitrogen-binding elements, nitrogen is converted from an impurity into a cost-effective alloy by precipitating as metallic nitrides (MN). The solubility of these compounds in austenite determines their dispersion, stability, and their effect on a variety of metallurgical phenomena:

• Pinning of austenitic-grain boundaries increases the grain-coarsening temperature
• A fine dispersion of stable particles in austenite prevents the growth of recrystallized grains during recrystallization controlled rolling (RCR)
• An increase in the nitrogen content slows down the rate of coarsening of nitrides (Ostwald ripening) by reducing the amount of the substitutional element in solution.

• Enhanced nitrogen increases supersaturation of interstitials in ferrite and promotes nucleation and formation of smaller particles, leading to more effective precipitation strengthening

• Intragranular nucleation of ferrite in austenite is made possible by vanadium-nitride particles

The following examples illustrate the beneficial effect of nitrides in ferritic steels.
• In steels for high-temperature applications, nitrogen improves service life (e.g. boiler tubes) and creep resistance of 9-12% chromium steels
• Hardenability of medium-alloyed steels (e.g. 2% chromium) is increased to a “super-hardenability” level by adding nitrogen.[9]
• Performance of high-speed tool steels is improved by vanadium-nitride precipitation

In this review, we’ll consider mainly enhanced-nitrogen vanadium microalloyed steels and their potential role in large-tonnage applications.

**SPECIFIC ROLE OF NITRIDE-FORMING ELEMENTS**

1. **Aluminum**

The earliest application of nitrides for microstructural control is the use of aluminum nitride (AlN) to produce fine-grained steel.[10] During reheating, AlN that is precipitated in the austenitic-grain boundaries prevents grain growth and contributes, upon transformation, to the fine-ferrite structure. To assure the stability of AlN particles, the Al:N ratio must be close to stoichiometric 2:1.[11] For a higher ratio, the AlN particles may coarsen because of a higher amount of Al in solution, and lose their pinning effectiveness. In the presence of both aluminum and vanadium in steel, the competition for nitrogen is won by more stable AlN, reducing the strengthening potential of vanadium-nitride dispersion. For that reason, the amount of aluminum must be kept to a minimum in normalized hot-rolled sheet and annealed cold-rolled steels.[11, 12]

2. **Vanadium**

Vanadium compounds (VC and VN) have very high solubility in austenite. For that reason, virtually all vanadium is available for precipitation in ferrite, as shown in Figure 1.

**PRECIPITATION HARDENING WITH VANADIUM**

![Figure 1](image1.png)  
*Figure 1 -- In vanadium steels, both carbon and nitrogen increase higher precipitation hardening.[13]*

**EFFECT OF NITROGEN ON VANADIUM-NITRIDE PARTICLES**

![Figure 2](image2.png)  
*Figure 2 -- Enhanced nitrogen increases supersaturation and the rate of nucleation of vanadium-nitride particles. The resulting particles are smaller and closer to each other and their thermal stability is increased because of low vanadium in solution.[13]*

Since nitrogen is more soluble in ferrite than carbon, the amount of nitrogen in ferrite is the same as it is in steel (Figure 2). By contrast, the amount of carbon in ferrite depends on the duration of gamma-to-alpha transformation, i.e., on the carbon content of steel. For a low-carbon steel (0.05-0.07%C), the transformation is rapid and the carbon content in ferrite is close to the ferrite-cementite equilibrium (50 ppm at 600°C). In higher carbon steels, the duration of transformation increases (Figure 3). As long as no cementite is formed, a metastable ferrite-austenite equilibrium persists and the carbon in ferrite may increase five fold to 250 ppm at 600°C (Figure 4).[13]

Because of strong affinity between V and N, vanadium nitride forms first followed by precipitation of V(N,C) or VC. In low-carbon steel, nitrogen is the main partner of vanadium so that VN precipitation in ferrite is the main strengthening contributor.[14]
As the supersaturation in ferrite increases due to nitrogen and carbon interstitials, the driving force for precipitation and nucleation intensity leads to a smaller particle size. The resulting smaller interparticle distance increases the effectiveness of precipitation strengthening. Because of that, the enhanced nitrogen content allows attaining a given yield strength, using up to 40% less vanadium. Increasing the amount of nitrogen above the stoichiometric ratio, further increases the stability of the VN particles. This is of importance in heat-resistant steels, because it delays a loss of strength as temperatures rise.

When austenite is highly supersaturated, VN precipitation may occur at temperatures close to transformation (900°C). The kinetics of VN precipitation is sluggish but can be accelerated by increase in C or N content and by strain. Intragranular nucleation of ferrite on VN particles makes it possible to get fine grains in thick plates, heavy H-shape structurals, and hot-rolled, high-strength seamless pipe.

The nucleation of VN in austenite may be facilitated by the presence of tiny TiN particles in steel containing as little as 40-50 ppm titanium. The TiN nucleus, precipitated below the solidus in the slab, enhances VN precipitation. The (TiV) (NC) particles remain during hot-rolling process. Their function is to prevent grain coarsening between passes of fine, recrystallized austenite. This phenomenon permits the attainment of fine ferrite (4-6 μm) in plates and strip of increasing thickness.

### 3. Titanium

Titanium nitride (TiN) may precipitate near the solidus temperature. To prevent massive TiN formation and to assure fine dispersion of TiN particles, three conditions must be fulfilled -- low titanium, high nitrogen, and rapid cooling (concasting). The presence of stable, finely dispersed TiN particles assures the preservation of the fine-austenite grains during rolling in a high-temperature regime -- recrystallization controlled rolling (RCR).[17] This rolling method is energy friendly, compared to conventional controlled rolling (CCR) below the recrystallization stop temperature. The practice of using TiN dispersion made it possible to process plates and heavy gage strip by RCR.

### NITROGEN-ENHANCED VANADIUM STEELS

The benefits resulting from enhanced nitrogen in vanadium-microalloyed steels may be summarized as follows:

- Ferrite grain refinement indicated by a higher austenite-to-ferrite transformation ratio
- Optimized precipitation strengthening with higher volume fractions and smaller size of VN particles
- An increase in the kinetics of VN precipitation in austenite, facilitating intragranular nucleation of ferrite
- A decrease in the V:N ratio, reducing the vanadium content in solution and improving the thermal stability of VN particles
- Processing by the energy-friendly RCR practice, made possible by fine dispersion of (TiV) (NC) particles
  - The low recrystallization-stop temperature of vanadium steel is not affected by the enhanced nitrogen and is ideal for processing by direct charging.[18]
  - The weight-reducing potential of V-N steels allows better utilization of resources and energy conservation compared to carbon-manganese steels.

The above advantages, made possible by enhancing the nitrogen content in vanadium-microalloyed steels, are being exploited in a variety of products: hot and cold rolled strip, plates, wire rod and rebars, forging steels, seamless tubes, heavy structural H-shapes, hot-rolled and roll-formed structural components.

The weight-reducing potential of nitrogen-enhanced, vanadium microalloyed steels is achieved thanks to changes in the microstructure during hot-rolling and subsequent cooling. The low cost of high strength (500-600 MPa yield strength) makes these steels economically attractive as a substitute for low-performance carbon-manganese steels. Examples of the chemistry and tensile properties of nitrogen-enhanced vanadium steels are shown in Table 1.
Effect of Nitrogen

Niobium
Vanadium
Solubility of M(C, N) in austenite Low High
Propensity for concast cracking High Low
Recrystallization-stop temperature High Low
Ease of recrystallization Low High
Preferred rolling practice CCR RCR
Compatibility with nitrogen Negative Positive
Effect on grain refinement Strong Strong
Effect on precipitation strengthening Weak Strong
Effect of N on precipitation in austenite Intensive Limited
Effect of N on precipitation in ferrite Negligible Positive
Nitrogen-binding capacity Weak Strong

TABLE 1 -- EXAMPLES OF NITROGEN-ENHANCED VANADIUM-MICROALLOYED STEELS

<table>
<thead>
<tr>
<th>Gage, mm</th>
<th>Process</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>V</th>
<th>Nb</th>
<th>Ti</th>
<th>N</th>
<th>YS*</th>
<th>UTS*</th>
<th>% El</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strip, 6.5</td>
<td>Conv. HSM</td>
<td>0.15</td>
<td>1.4</td>
<td>0.3</td>
<td>0.03</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>585</td>
<td>710</td>
<td>25</td>
<td>[21]</td>
</tr>
<tr>
<td>Strip, 8.0</td>
<td>Conv. HSM</td>
<td>0.09</td>
<td>1.65</td>
<td>0.25</td>
<td>0.025</td>
<td>0.14</td>
<td>0.02</td>
<td>-</td>
<td>0.015</td>
<td>640</td>
<td>780</td>
<td>12</td>
<td>[22]</td>
</tr>
<tr>
<td>Strip, 6.5</td>
<td>CSP</td>
<td>0.05</td>
<td>1.5</td>
<td>0.3</td>
<td>-</td>
<td>0.12</td>
<td>0.02</td>
<td>-</td>
<td>0.02</td>
<td>530</td>
<td>635</td>
<td>26</td>
<td>[23]</td>
</tr>
<tr>
<td>Strip, 6.3</td>
<td>CSP</td>
<td>0.05</td>
<td>1.5</td>
<td>0.20</td>
<td>0.03</td>
<td>0.12</td>
<td>-</td>
<td>0.005</td>
<td>0.024</td>
<td>610</td>
<td>675</td>
<td>28</td>
<td>[27]</td>
</tr>
<tr>
<td>Plate, 20</td>
<td>RCR &amp; ACC</td>
<td>0.09</td>
<td>1.4</td>
<td>0.25</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
<td>0.01</td>
<td>0.013</td>
<td>445</td>
<td>565</td>
<td>(20)</td>
<td>[17]</td>
</tr>
<tr>
<td>Rebar, 25</td>
<td>Hot-Rolled</td>
<td>0.21</td>
<td>1.4</td>
<td>0.60</td>
<td>-</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
<td>0.015</td>
<td>550</td>
<td>695</td>
<td>21</td>
<td>[24]</td>
</tr>
</tbody>
</table>

*MPa

HARMFUL EFFECTS OF ENHANCED NITROGEN

It should be noted that not all microalloyed steels benefit from nitrogen enhancement. Titanium, when present in sufficient quantities, acts as a scavenger forming massive TiN particles at high temperatures which may be detrimental to fatigue and toughness.[19] In the presence of nitrogen and sulfur, a greater difference between the total and effective titanium content is needed for precipitation as TiC. Similarly, in niobium-microalloyed steel, enhanced nitrogen promotes wasteful precipitation of Nb(CN) in austenite and necessitates a larger niobium addition to achieve suppression of recrystallization and eventual precipitation in ferrite.[20] The effect of enhanced nitrogen content is very different for V and and Nb steels, as shown in Table 2.

METHODS OF ADDING NITROGEN

In general, nitrogen is added in the form of nitrided steel additives like Mn, Cr, or V. Since nitrogen is concentrated on the surface of these additives, recovery is lower than when a V(NC) compound is used. This product is the result of vanadium-oxide reduction by carbon in the presence of nitrogen. Frequently, the addition is made during tapping. In a ladle furnace, stirring is helpful in increasing the nitrogen recovery. In a vacuum furnace, an addition under atmospheric nitrogen pressure is recommended. Nitrided calcium carbide (calcium cyanamide, Ca CN₂) can be used when a simultaneous increase in the carbon content can be tolerated. In all instances, the nitrogen recovery can be improved by using cored-wire feeding.

Nitrogen can also be added during steelmaking or when using nitrogen for shrouding of the steel stream during tapping. However, reproducibility may present a problem with this technique.

FUTURE TRENDS

The beginning of the 21st century witnessed an acceleration of the emancipation drive among developing nations. Their desire to improve living standards through industrialization resulted in an explosive growth of steel production and consumption. The surging steel demand contributed to shortages of resources and price increases. Since this situation is not a cyclic phenomenon and may persist for many decades, various measures have been considered to achieve a “sustainable” rate of growth. Among many approaches, immediate results can be obtained by satisfying engineering needs.

TABLE 2 -- EFFECT OF ENHANCED NITROGEN IN NIOBIUM- AND VANADIUM-MICROALLOYED STEELS

<table>
<thead>
<tr>
<th>Effect of Nitrogen</th>
<th>Niobium</th>
<th>Vanadium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility of M(C, N) in austenite</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Propensity for concast cracking</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Recrystallization-stop temperature</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Ease of recrystallization</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Preferred rolling practice</td>
<td>CCR</td>
<td>RCR</td>
</tr>
<tr>
<td>Compatibility with nitrogen</td>
<td>Negative</td>
<td>Positive</td>
</tr>
<tr>
<td>Effect on grain refinement</td>
<td>Strong</td>
<td>Strong</td>
</tr>
<tr>
<td>Effect on precipitation strengthening</td>
<td>Weak</td>
<td>Strong</td>
</tr>
<tr>
<td>Effect of N on precipitation in austenite</td>
<td>Intensive</td>
<td>Limited</td>
</tr>
<tr>
<td>Effect of N on precipitation in ferrite</td>
<td>Negligible</td>
<td>Positive</td>
</tr>
<tr>
<td>Nitrogen-binding capacity</td>
<td>Weak</td>
<td>Strong</td>
</tr>
</tbody>
</table>
with less steel of better (stronger) quality.\textsuperscript{25} This concept is incorporated in the “Steel Industry Development Policy” in China. Steel producers are encouraged to develop economical, resource-saving high-strength steels to achieve weight reduction by replacing low-strength carbon-manganese steels.\textsuperscript{26} To be economically viable, the weight reducing potential of stronger steel must be obtained at low cost. Microalloyed steels meet this prerequisite as a substitute for commodity-grade carbon steels.

In microalloyed steels, a 2- to 3-fold increase in the yield strength compared to hot-rolled C-Mn steels is achieved by microstructural changes during hot-rolling and subsequent cooling. The interaction of the microalloying element with plastic deformation contributes to the grain refinement of austenite. As the austenite transforms to fine ferrite, precipitation hardening takes place. These two strengthening mechanisms account for about 70\% of the yield strength, as shown in Figure 5. No costly alloying or heat treatment is required.

Among the microalloying elements (Nb, Ti, and V), vanadium steels benefit most from the enhancement of nitrogen. The advantages of V-N steels include: intensive grain refinement, grain refinement in heavy section by intragranular nucleation, optimized precipitation hardening, energy friendly hot-rolling process (RCR), ease of austenite recrystallization ideal for direct charging, and abundance of vanadium-bearing iron ores.

The development and perfection of microalloyed steels is rated as the key metallurgical development of the past century. In the new century, vanadium-nitrogen microalloyed steels may not only reduce dangerous supply-demand strains, they may also be economically beneficial to both steel producers and users, contribute to national wealth formation and reduce the effects of pollution to the environment. This is a unique “win-win” situation for both steel producers and steel users.

REFERENCES


