

# AN UPDATED PREDICTION MODEL FOR VANADIUM PRECIPITATION STRENGTHENING OF FERRITIC STEELS

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## Abstract

Prediction models for vanadium precipitation strengthening of ferritic steels have been available and used over the course of many years of vanadium microalloying experience. The basis and origin of a newly revised but proven strength prediction model is reviewed and explained. Inherent in the accuracy of the model is the requirement for the assessment of the available carbon and nitrogen to form V(C,N) precipitates. This paper discusses various situations where the amount of nitrogen and carbon in the ferrite may vary substantially, and how the availability of these elements can be significantly altered by the time of precipitation and the presence of other alloy elements, particularly Ti, Nb, and Al. Of these, the effect of the Al content (and prior processing history) seem to be most widely overlooked when evaluating and predicting the expected strengthening of the VN precipitate in polygonal ferrite.

## Introduction

Microalloyed steels for enhanced strength have been common practice for fifty years or more. Strengthening mechanisms have been studied and reported over this time as well. Each microalloy system has their own particular strengthening characteristics evolving out of the inherent differences that each element has on the physical metallurgy involved. Strength and hardness increases from vanadium additions in as-rolled or as-forged products have long been attributed to the precipitation of V(C,N) particles, resulting in dispersion strengthening. Some additional benefits from ferrite grain refinement can also be achieved. Precipitation strengthening with vanadium requires the presence of nitrogen and/or carbon to form V(C,N) particles. This V(C,N) precipitation must occur during or after the austenite to ferrite transformation, resulting in either interphase or general precipitation respectively. Fortunately, there seems to be no significant difference between the strengthening contributions of either type of precipitation. Interphase precipitation may result in larger precipitates (because it occurs at higher temperatures) which could lessen the strengthening effect, but this may be offset by the higher degree of precipitation of the available elements.

V-N strengthening through ferrite grain refinement has been attributed to ferrite formation on VN particles that may precipitate at austenite grain boundaries, resulting in more ferrite grains forming in a given austenite grain. VN precipitation within the austenite grain can also lead to intragranular ferrite formation. Effective use of the ferrite grain refining properties of vanadium in as-rolled applications requires some attention to the chemistry (high V + N contents) and appropriate processing (sufficient deformation and time for VN precipitation in the austenite). But the most effective property of vanadium in grain size control of as-rolled products is the low

solute drag coefficient, allowing the necessary recrystallization of the austenite to occur during the rolling process. Since only recrystallization can cause austenite grain size reduction, and only thermal transformation or mechanical deformation can initiate recrystallization, the greatest benefit of using vanadium is that it allows the natural recrystallization to occur during each rolling pass. The term recrystallization controlled rolling (RCR) is often used to describe this rolling process – multiple recrystallization opportunities with a continuous reduction of austenite grain size.

Because the majority of vanadium strengthening comes from precipitation, and because nitrogen content has a significant role in V(C,N) precipitation, it has always been of interest to the steelmaker to have a predictive model reliably defining the strengthening effects of vanadium and nitrogen. While many have been developed over the years, the original and most widely referenced graphical model is that of Korchynsky and Stewart [1] shown in Fig. 1, and subsequently reproduced by Grozier in MA'75 [2].

One issue with the prediction model in Figure 1 is that it does not predict any strengthening of vanadium at zero nitrogen. This is not likely to be true except in the most extreme cases, as there should be some VC precipitation strengthening even when N is not available. Also, the slope of the strengthening curve for given vanadium additions increases for higher nitrogen levels. At sub-stoichiometric levels of nitrogen, the maximum amount of VN precipitation is controlled by the nitrogen available, not the amount of V. Because of this, V strengthening slopes at different N levels are more likely to be parallel, but starting at different strength levels due to increasing VC precipitation. The VC precipitation strengthening would logically be assumed to be relatively constant for constant V content and processing conditions. Only the nitrogen level is changing. Thus, the strengthening curves at sub-stoichiometric levels of N would be expected to be slightly displaced by higher V contents, but reasonably parallel up to stoichiometric VN levels. As the nitrogen level exceeds stoichiometric V:N, the strengthening effect will be significantly reduced.

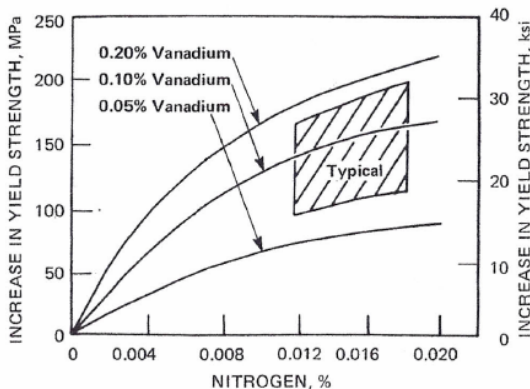


Figure 1. Increase in yield strength from nitrogen and vanadium as a result of the precipitation of vanadium nitride. Control-cooled coil product, with a coiling temperature of 593 C. [2]

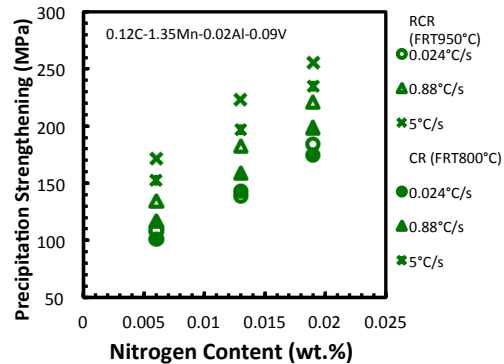


Figure 2. Effect of nitrogen on precipitation strengthening. [3]

In 1981, Siwecki et.al. published results of a precipitation study verifying the consistent strengthening potential of sub-stoichiometric additions of N to a V containing steel [3]. Figure 2 shows the contribution of V-N precipitation strengthening to a 0.12% C, 1.35% Mn, 0.09% V steel produced by either control rolling (CR) or recrystallization controlled rolling (RCR). For all processing conditions, the contribution of additional nitrogen was linear, consistently at 6-7 MPa for every additional 10 ppm of nitrogen. For these nitrogen levels, the nitrogen is sub-stoichiometric to the vanadium level, so the linear nitrogen response is expected and consistent with the logic that the amount of additional VN precipitation strengthening is controlled by the N available. The V is available for precipitation as all V(C,N) is dissolved during the prior reheat, and VN will form preferentially over the VC.

### **Rational for a Revised Graphical Model**

To better represent the V-N strengthening potential, a method was needed to generate a descriptive graphical model that would have a visual impact demonstrating the incremental strengthening potential of the VN precipitation, and yet also reflect the strengthening contributed by VC precipitation. As shown in Figure 2, there will always be the possibility of different base levels of strength from processing variations, but the incremental strength from enhanced VN precipitation is consistent. An empirical fit to a mechanical property data set from multiple production mills was chosen as the basis for the model. Next, for functionality and for ease of visual recognition, it was decided to use incremental yield strength as the Y axis, and vanadium content, the controlled alloy addition, as the x axis. Different but fixed nitrogen levels would be represented by multiple curves on this graphical representation.

What is required to build this kind of graphical model is the strength contribution of three different situations. First, the effect of interstitial or free nitrogen is needed to predict the starting points. Second, the strengthening rate for V additions must be determined when there is a hyper-stoichiometric level of nitrogen available and VN precipitation is predominant. Third, the strengthening rate for V additions when no nitrogen is available (hyper-stoichiometric additions of V to N) must also be determined. It is presumed that VC will form at this time and be the primary precipitate for strengthening.

For the base data set, a previously published compilation of test results from three different thin-slab direct-rolled strip mills was used [4]. As described in a previous publication [5] a simplified version of linear regression was chosen to represent the strengthening effects of V and N as follows:

$$\text{Predicted YS (MPa)} = 226 + 40(\% \text{Mn}) + 742(\% \text{V}) + 8440(\% \text{N}) \quad (1)$$

A brief review of the literature to estimate a value of the strengthening coefficient for interstitial or “free” nitrogen suggested that the effect is quite small. In MA’75, Pickering [6] reported a typical value of 350 MPa per 1% N, based on a survey of several different authors. Compared to the N coefficient in V steels, this value is small, but not zero. This value is used to determine the starting (0% V) point of the different strength curves representing different nitrogen levels, providing separation in the initial portion of the graph. Other authors have suggested higher values of interstitial nitrogen strengthening, which may be true and would separate these curves to a greater degree.

The initial section of each strengthening curve would represent the initial V addition, which would by necessity be nitrogen rich assuming a starting N level of at least 50 ppm. The N coefficient is used to represent the N contribution to strength, therefore predicting the VN precipitation strengthening. In line with that assumption, the V coefficient is assumed to represent the V strengthening due to VC precipitation. While these assumptions are tenuous at best, the end results proved to be very credible.

Finally, we know that only precipitation in the ferrite during or after transformation provides strength. We also know that VN precipitation takes precedence over VC precipitation. Therefore, for the purposes of this model it is assumed that all VC precipitation takes place in the ferrite after transformation. The maximum solubility of carbon in ferrite immediately after transformation is considered to be about 0.02% C, and decreases rapidly as it cools further. That means the maximum VC precipitation that can be expected is that which forms from a maximum of 0.02% C, which stoichiometrically translates to 0.085% V. (V:C = 4.24:1) Vanadium added above the amount needed to form VN and VC from all of the N and C available will not contribute to precipitation strengthening directly except to help drive the VC and VN precipitation to completion.

The result is a strength prediction curve for increasing V additions consisting of three lines with three distinct slopes – the first line having a higher slope with N available for VN precipitation, and the second line representing VC precipitation having a smaller slope when V is added beyond the stoichiometric V:N ratio (3.64:1). After the available C in ferrite is consumed, presumed to be a maximum of 0.02% C, the strengthening slope for vanadium additions approaches zero. The first inflection point of the Strength-Vanadium curve is at a V level of 3.64 x N content. The second inflection point is .085 V above the first break point, where all C in the ferrite is consumed. The result is as shown in Figure 4.

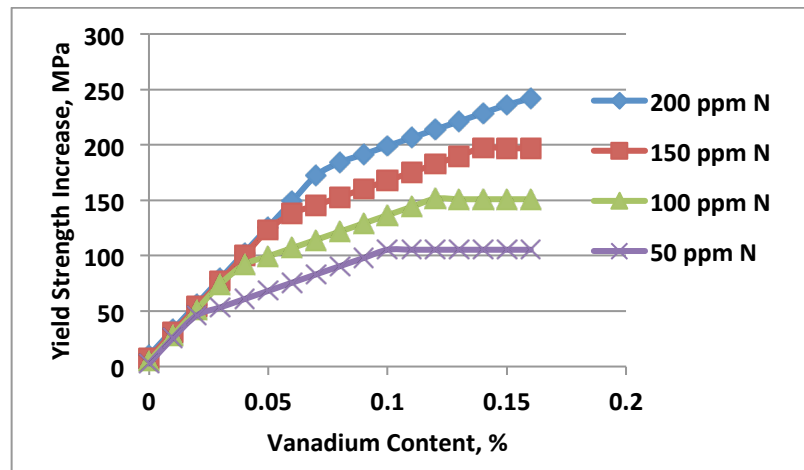


Figure 3. Linear representation of strengthening model of ferritic steels with V and N

Since the assumption is that all available nitrogen and all available carbon in the ferrite are consumed, there are no interstitial elements left to form strengthening vanadium precipitates. The microalloying (precipitation strengthening) effect of vanadium has been exhausted because of the consumption of the available interstitial elements in the ferrite.

## Consideration of Possible Mitigating Factors

The relationship of yield strength increase with vanadium addition can be affected by a number of variables. First, all VC and VN (or V[C,N]) must be in solution in the austenite prior to the final transformation to ferrite. This usually limits this analysis to either as-rolled or as-forged products. Second, there should be no re-precipitation in the austenite during rolling or forging. At high levels of vanadium and nitrogen, this is likely to be some deformation-induced precipitation which, while it can contribute to intragranular ferrite formation, does not contribute directly to strength.

Secondly, most or all of the V should be precipitated in the ferrite, but we know that is not always true. The strengthening shown in Figure 4 is not likely to contain all of the potential vanadium precipitation, but it does represent strength achieved in a variety of actual hot strip mill production processes. Since the VC precipitation is the last vanadium precipitation to occur and at a slower rate than the VN precipitation, it is subject to more dependence on process variation. Strengthening can be significantly less when an accelerated cooling practice is used well beyond the austenite to ferrite transformation temperature. For these situations where VC precipitation is limited, it is expected that the vanadium strengthening rate (slope of the line) in the intermediate (VC) region can be significantly less.

On the other hand, Zajac [7] has proposed that the precipitation strengthening of VC can be enhanced at intermediate C levels by super-saturation of metastable C in the ferrite. Deduced values of precipitation strengthening for isothermally transformed 0.12% V steels at 650°C indicated a strong carbon effect. However, the N effect on enhancing VN strengthening was equally strong at all carbon levels. The effect of super-saturation of C in the ferrite is to extend the VC strengthening portion of the curve to higher V levels, but does not replace the enhanced strengthening of VN.

And finally, the rate of precipitation of VN and VC are controlled by various time-temperature parameters (solubility, diffusion and precipitation). As a result, different degrees of precipitation completion would be expected as process conditions changed. Besides affecting the actual amount of incremental strengthening, it would also cause difficulty in verifying with production data any of the inflection points suggested in Figure 3. Perhaps a better representation would be much more of a continuous curve. To reflect this reality, the model was modified as shown in Figure 4. Many years of experience has proven the model to be very useful in predicting the trade-off in V and N content in the final strength level. Because of the process dependence of the relationship, it is only an estimate of the actual strength achieved. So while quantitatively, the actual strength increments can be variable, there is always a qualitative relationship of the type shown in Figure 4.

Even with the qualifications just mentioned, and the indirect derivation of the initial coefficients, this prediction of precipitation strengthening has proven to be very useful. In particular, an increase of yield strength by 7 MPa for each 10 ppm nitrogen added (when N is less than stoichiometric V:N) has been extremely consistent over a wide range of carbon content as reported by multiple investigators.

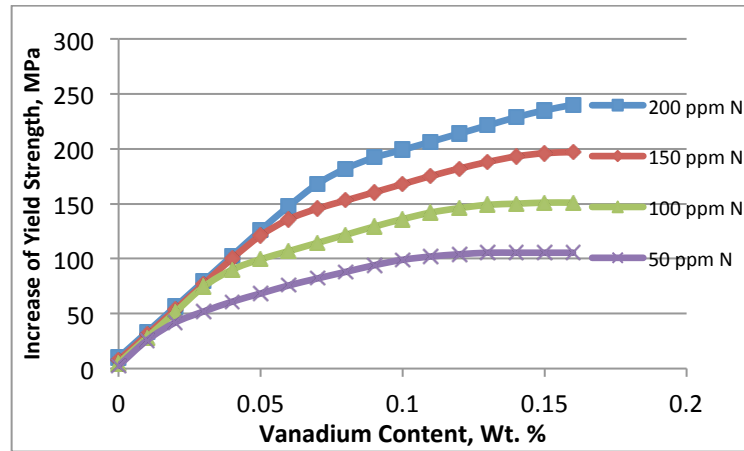


Figure 4. Modified strengthening model of ferritic steel with vanadium and nitrogen

### Effective Nitrogen

With the understanding that the effectiveness of precipitation strengthening with vanadium is largely controlled by the available nitrogen, it is important to review the concept of “effective nitrogen”. From the previous discussion, it is apparent the VN precipitation in ferrite will occur in preference to VC precipitation. There may be some co-precipitation of V(C,N), but most investigators have found that the first to form is VN, then followed by VC precipitation around the VN particle. So the effectiveness of the vanadium addition is primarily a function of the nitrogen available. The problem is that, even if the nitrogen is in the steel, it may not be available for VN precipitation in the ferrite. Any nitride former that has a thermodynamic “preference” for nitrogen is capable of reducing the beneficial strengthening effect of VN precipitation. The “Effective” nitrogen, as defined as the nitrogen available for formation of VN precipitates, may be much less than the total nitrogen reported by standard analysis.

The first, and most well know of the nitrogen scavengers, is titanium. TiN will form at very high temperatures, even before solidification, and will not typically dissolve to any significant extent during the reheat operation. So it can be assumed that for any Ti addition to the steel, a stoichiometric amount of nitrogen will be removed from availability.

Niobium additions can also complicate the issue. NbN is usually in solution during conventional reheating, but in CSP mills the reduced reheat temperatures may be insufficient to fully dissolve NbN. Also, because of the lower solubility of NbN vs. VN, the possibility of NbN precipitation during rolling is much higher than VN precipitation. Add to this the possibility that a Nb bearing steel is likely to be finish rolled at lower temperatures to take advantage of the higher recrystallization stop temperature. The combination creates a real problem in designing a V-Nb alloy system that takes advantage of the austenite conditioning properties of niobium while allowing the maximum VN precipitation.

### Aluminum Content

This leaves one more nitride forming element that is often overlooked, but almost always present. Aluminum is routinely added to steels for deoxidation and for grain refinement. The soluble Al, that amount that is not oxidized, can form AlN. Aluminum does not form AlC. The

solubility of AlN is lower than VN, making it a competitor to V for the available N. Grozier recognized this problem, and discussed it at length [2]. He pointed out that when vanadium-nitrogen heats are produced with high aluminum contents, adequate reheating temperatures must be maintained to avoid a reduction in strength properties. Numerous other authors have identified the same issues. Similar problems exist with the new thin-slab direct-roll mills that use tunnel furnaces with limited heating capability.

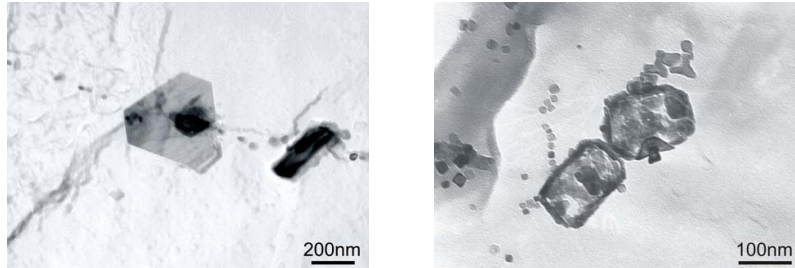


Figure 5. TEM micrograph showing AlN + MnS in a V-N steel (left), and complex particles containing Al in a V-Ti-N steel (right) after equalization at 1050°C [8].

Fortunately, even with the low solubility of AlN, it is kinetically very sluggish to precipitate during the cooling cycle. As long as the temperature is in a decreasing mode in normal production processing cycles, AlN precipitation is minimized. Any reheating, however, can cause rapid precipitation. Problem areas include the traditional slab/billet reheating as discussed. One place where this reheating can occur is at the surface during casting, where discontinuous but repeating water sprays can create repeated thermal cycling. These cool and reheat cycles are ideal for precipitating AlN. While these AlN precipitates may be re-dissolved during conventional reheat cycles, they can cause hot short issues at the caster, resulting in cracking problems [9].

Very recent work reported by Rothleutner and Van Tyne[10] demonstrated the problem of Al effects in V-N microalloyed air-cooled forging steels. Again, the problem is getting the AlN in solution during the reheat cycle for forging. Air-cooled forging alloys rely heavily on VN precipitation, so the amount of effective nitrogen available is critical. His work demonstrated a loss of 50 MPa when reducing the forging reheat temperature from 1200 to 1100°C in a 0.37% C, 0.088% V, 0.031% Al, 153 ppm N steel.

Modern steelmaking practices are capable of adequately deoxidizing steels with substantially less Al than in the past. Clean steel practices using reducing slag and other techniques are now widely used. There is little need to maintain high Al contents to minimize steel reoxidation from high oxygen slags.

While fine ferrite grain size is a desirable trait for microalloyed steels, the method to achieve these fine grains in an as-rolled or as-forged microstructure is completely independent of the presence of aluminum. Rolling and cooling practices primarily determine the final grain size in microalloyed steels. Aluminum additions to meet specification grain size requirements are of no value in as-rolled steels. Neither is the reheat testing of these steels for subsequent austenite grain size. Since the as-rolled product will not be heat treated, the austenite grain size achieved on reheating is irrelevant to the performance of the steel in the as-rolled condition.

## Summary

A graphical model showing the interactions of V and N on the precipitation strengthening of polygonal ferrite/ pearlite steel is developed using a combination of empirical data and expected thermal-mechanical response. The resulting model has been shown to be very useful in predicting the effects of nitrogen on V(C,N) precipitation strengthening. The importance of the effective nitrogen level is developed, considering the possible competing effects of the presence of alternate nitride forming elements. In particular, the importance of considering the competition of aluminum and vanadium for the nitrogen content is reviewed. When using the vanadium-nitrogen alloying system, it is highly recommended that the aluminum additions be limited to that necessary for the desired metallurgical function required of the aluminum addition. Since microalloyed steels were designed to be used in the as-rolled or as-forged condition, the presence of aluminum has no bearing on the grain size of the steel as used.

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