

## A Review of Vanadium Microalloying in Hot Rolled Steel Sheet Products

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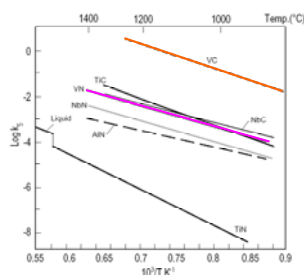
Today I would like to present an overview of the advantages of vanadium as a microalloy addition for hot rolled sheet steel products. Several microalloy systems are available to the sheet metal producer, including niobium, titanium and vanadium. Vanadium has generated renewed interest as a microalloy for sheet products with the advent of the new thin slab direct rolling mills, where processing limitations have highlighted some of vanadium's unique advantages.

### Important Metallurgical Properties of Vanadium In Steel

- High Solubility of V(C,N) in Austenite
- Low Solute Drag Coefficient of V in Austenite
- Nitrogen is the Preferred Element in V(C,N) Precipitation

The important metallurgical properties of vanadium in steel can be grouped into three main categories, with property and processing benefits resulting from each major feature. The first metallurgical property to be discussed is the high solubility of the carbonitrides of vanadium in austenite. Second, the benefits of the low solute drag coefficient of vanadium, often not considered when rolling flat products, will be reviewed. And last, the positive interaction of vanadium with nitrogen which provides an effective use of the residual nitrogen in steel will be discussed.

### Solubility of Microalloy Carbides and Nitrides



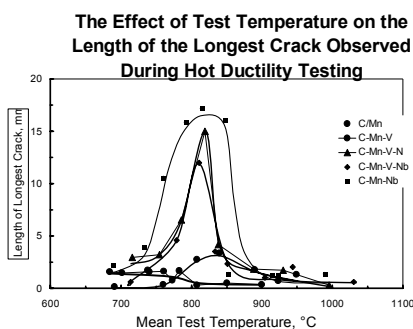
This chart shows the relative solubility of various forms of microalloy carbides and nitrides. First note that for each of the microalloy elements, the carbide form is more soluble than the nitride. The solubility of VC is very high, easily dissolving in austenite, and only precipitating on cooling after the ferrite has formed. TiC, NbC, and VN have very similar solubility, which is interesting because they are by far the most important of the precipitation strengtheners. The difference in solubility between the carbide and nitride forms of each microalloy is much larger for Ti and V than for Nb. Since the solubility of C in austenite is high, the C level in the steel will control the amount of Nb dissolved in the austenite during reheating. The carbon level has virtually no effect on the solubility of vanadium during reheating. For titanium, the nitride form is virtually insoluble at normal reheating

### Benefits of High Solubility of V (C,N) In Austenite

- Excellent Castability
- Reduced Reheat Temperature Requirements
- Predictable Strengthening Over Large Alloy Range

### Benefits of High Solubility of V (C,N) In Austenite

- Excellent Castability
  - Ductility Trough Starts at Lower Temperatures than Niobium Steels
  - Roll Straightening of Slabs can be Accomplished over a Wider Temperature Range Without Transverse Cracking



temperatures. Al does not form a carbide, and the nitride AlN is quite insoluble in austenite, providing it's grain refining characteristics. On cooling after dissolving, however, the kinetics of the AlN formation are quite sluggish, allowing other nitrides like VN to form even though they are more soluble than AlN.

A number of benefits in the steel making process are a result of the high solubility of the V(C,N) compared to other microalloys. These benefits include excellent castability with minimal cracking, reduced reheat temperature requirements, and predictable strengthening over a large alloy range.

Because of the high solubility of VC and VN, there is little or no precipitation at grain boundaries after solidification. As a result, the start of the ductility trough normally associated with microalloyed steels is at a lower temperature compared to Nb steels. This provides a wider temperature in which the slab can be straightened after casting without transverse cracking.

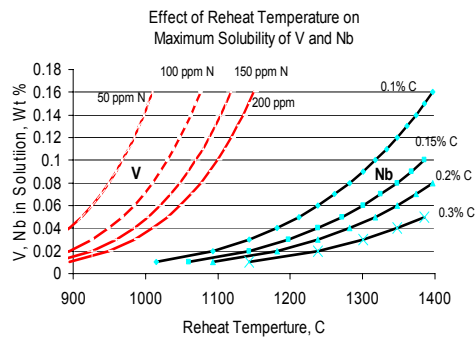
This figure demonstrates the reduced cracking sensitivity of V steels compared to plain carbon and other microalloyed steels. In this case, the quality measurement is the length of the crack produced in an as-cast slab with a fixed bending strain. The C-Mn and the C-Mn-V grades had very little cracking, while the Nb containing grades exhibited significant crack growth. The higher solubility of the V reduced the tendency to precipitate in the grain boundaries, thereby reducing the cracking sensitivity of this grade. The increased cracking tendency of the C-Mn-V-N grade is most likely the result of AlN precipitation, not VN precipitation. For these high nitrogen grades, it is advantageous to minimize the Al content.

### Benefits of High Solubility of V (C,N) In Austenite

- Reduces Minimum Reheat Temperatures Necessary to Dissolve Precipitates
  - Reduces energy requirements
  - Very important in Thin Slab tunnel furnaces

In order for any microalloy to effectively provide strengthening in the as-rolled condition, it must be in solution at the reheat stage. Again, the high solubility of the V(C,N) is a benefit because it reduces the temperature and time required for full solution. This is especially true for thin slab direct rolling operations where the reheat capability of the tunnel furnace is limited.

This is a graph showing the temperatures required to get various amounts of V and Nb in solution during reheating. 1150°C, the typical maximum temperature of a tunnel furnace in a direct rolling operation, is sufficient to get up to 0.15% V in solution in the presence of 200ppm N, while the maximum amount of Nb in solution in a 0.10% carbon steel is around 0.03%. Even when heating to conventional slab reheating temperatures on the order of 1300°C, the amount of Nb in solution is limited, particularly at higher carbon levels.

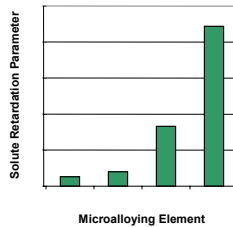


### Benefits of High Solubility of V (C,N) In Austenite

- Provides Predictable Strengthening over Wide Range of V Alloy Content
  - Typical vanadium additions from 0.02% up to 0.15% or higher are soluble at normal reheat temperatures
  - Vanadium strengthening effective at all carbon levels

Also because of the higher solubility of the V(C,N), the strengthening effect of V(C,N) precipitation after transformation is very predictable. As shown in the previous slide, virtually all of the vanadium will be in solution during reheating, regardless of the amount of carbon or nitrogen in the steel. As a result, V additions up to 0.15% can be used for precipitation strengthening providing a near linear increase in yield strength. For alloys such as Nb that are close to the solubility limit at normal reheat temperatures, the amount of alloy in solution will be dependant on reheat temperature and the amount of C and N present, leading to inconsistent strengthening results without careful process control. In addition, V can be used at a full range of carbon levels. Examples of this will be shown in later examples.

### Low Solute Drag Coefficient of V in Austenite



Solute Retardation Parameters for Static Recrystallization

### Benefits of Low Solute Drag Coefficient of V in Austenite

- Allows Recrystallization Controlled Rolling (RCR) Thermal-mechanical Processing
- Minimizes Temperature and Deformation Requirements for Recrystallization
- Reduces Roll Force Requirements

### Benefits of Low Solute Drag Coefficient of V in Austenite

- Allows Recrystallization Controlled Rolling (RCR) Thermal-mechanical Processing
  - Provides Austenite Grain Refinement by Repeated Recrystallization During Rolling Process
  - Results in refined austenite grains without need for low finish rolling temperatures

Vanadium has a relatively low solute drag coefficient relative to other microalloys. This figure shows the vanadium solute drag coefficient and compares to other elements. This solute drag causes a retardation of the recovery and recrystallization of austenite during and after deformation. This property of Nb is what contributes to raising the recrystallization temperature, providing the opportunity for ferrite grain refinement by “pancakeing” of austenite grains prior to transformation. , which in turn will provide some refinement of the final ferrite grains. However, this property of Nb which retards austenite recrystallization also can be detrimental in situations where recrystallization is desired.

The benefits of the low solute drag coefficient of vanadium in austenite include allowing the use of recrystallization controlled rolling (RCR) as a thermal mechanical process for austenite grain refinement, minimizing the temperature and deformation requirements for complete recrystallization during rolling, and reducing the roll force requirements because of the fast recovery and recrystallization of the austenite between roll stands.

The use of RCR rolling provides repeated austenite grain refinement through the recrystallization process during rolling. Each roll pass results in new austenite grains, each refined in size from the previous grains. Because the recrystallization process itself provides the refinement of the austenite grain, there is no need to lower the finish rolling temperatures below the recrystallization stop temperature. Rapid cooling after the final rolling pass using lamellar cooling on the run-out table of a hot strip mill will minimize austenite grain growth after transformation. Rapid cooling also lowers the transformation temperature to insure extremely fine ferrite grain size.

### Benefits of Low Solute Drag Coefficient of V in Austenite

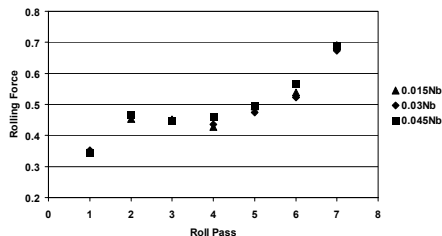
- Minimizes Temperature and Deformation Requirements for Recrystallization
  - Promotes uniformity of grain size from surface to center of product
  - Important for uniform through thickness recrystallization of as-cast austenite grains in Thin Slab - Direct Rolling process

### Benefits of Low Solute Drag Coefficient of V in Austenite

- Reduces Roll Force Requirements
  - RCR Rolling allows higher finish rolling temperatures
  - Rapid recrystallization eliminates retained deformation strengthening between rolls
  - Limited precipitation in austenite minimizes strengthening during rolling

### Effects of Low Solute Drag Coefficient of V in Austenite

Rolling force per unit width  
Niobium bearing heats

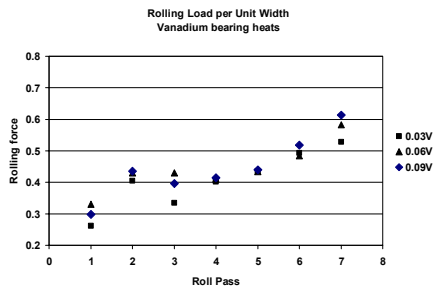


Because the austenite recrystallization is not retarded, it is easier to get complete recrystallization of the austenite through the thickness of the slab during rolling, even though the deformation strains may vary. As a result, the austenite grains are more uniform in size from surface to center, resulting in more uniform mechanical properties. This ease of austenite recrystallization is especially important in thin slab direct rolling production of strip, since it is sometimes difficult to complete the necessary recrystallization of the as-cast grains that enter the rolling process. The limited reheat temperatures and the minimal total deformation of the thin slab contribute to the difficulty of getting complete recrystallization through the thickness.

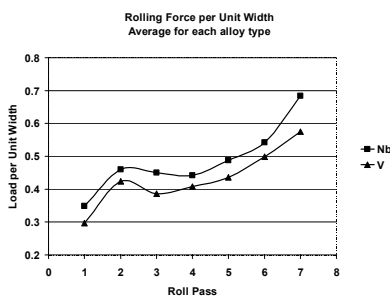
The use of RCR rolling with higher finish temperatures, along with the rapid recrystallization and recovery of the austenite, results in reduced roll force requirements. In addition, the limited precipitation of V(C,N) in the austenite minimizes strengthening during rolling, also contributing to reduced roll force requirements.

The next three graphs show the results from work presented by Clare Wynn from the University of Wales at the 2004 MS&T conference in New Orleans. Included in this work were the roll force per unit width measurements for a series of Nb and V bearing low carbon steels. This graph shows the roll force requirements for each roll pass for a series of Nb levels from 0.015% to 0.045%. As shown, there were only slight differences by Nb content, but increasing roll force with each rolling pass.

### Effects of Low Solute Drag Coefficient of V in Austenite



### Effects of Low Solute Drag Coefficient of V in Austenite



### Benefits of Nitrogen as the Preferred Element in V(C,N) Precipitation

- Transforms Nitrogen From Unwanted Residual to a Useful Part of the Alloy System
- Management of N Level Maximizes the Precipitation Strengthening of a Given Vanadium Alloy Addition
- Potential for Nitrogen Strain Aging is Minimized with Vanadium Additions

This next graph shows similar data for a series of V bearing steels, from 0.03% to 0.08% V. Again, there is little difference between the different V levels, but there was generally increasing roll force required with each rolling pass. The question is, what was the difference between the alloy systems.

This graph shows the average values for the Nb and the V grades shown in the previous two graphs. The roll force requirements for the V grades were consistently less than that of the Nb grades, with the difference particularly high at the final rolling pass. For this demonstration, identical reductions per pass and rolling temperatures were used. It is apparent that the rapid recrystallization of the austenite, along with the absence of any precipitation in the austenite, resulted in significantly lower roll force requirements for the V containing low carbon strip steel.

The third metallurgical property of vanadium microalloyed steels is the preference for nitrogen in the V(C,N) precipitate. As shown in the solubility chart, the VC is much more soluble than the VN, resulting in the driving force for V precipitation to be much stronger with N present. As a result, nitrogen changes from an unwanted residual element to an important part of the alloy system. Management of the nitrogen level maximizes the strengthening of the vanadium addition, and the preferred precipitation with N minimizes the risks of nitrogen strain aging.

### Benefits of Nitrogen as the Preferred Element in V(C,N) Precipitation

- Transforms Nitrogen From Unwanted Residual to a Useful Part of the Alloy System
  - Utilizes the residual nitrogen content of all steels
  - Particularly useful in EAF steels

### Benefits of Nitrogen as the Preferred Element in V(C,N) Precipitation

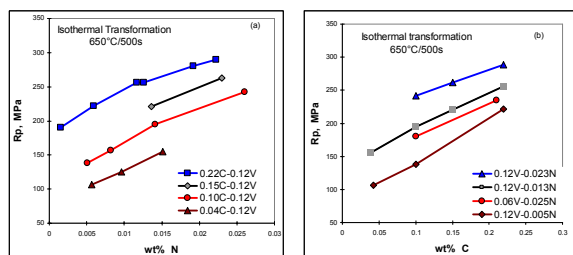
- Management of N Level Maximizes the Precipitation Strengthening of a Given Vanadium Alloy Addition
  - Vanadium is the only microalloy that effectively strengthens steel as a nitride precipitate
  - Managing the nitrogen level will maximize the cost effectiveness of vanadium alloying

The transformation of nitrogen from an unwanted residual to a useful part of the alloy system provides effective utilization of the residual nitrogen that is normally in all steels. In particular, the higher nitrogen levels normally associated with electric arc furnace operations are no longer a problem, but become an advantage.

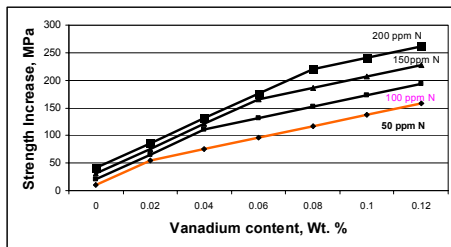
Vanadium is the only microalloy that effectively strengthens steel as a nitride precipitate. Because of the finer and more complete precipitation of vanadium in the presence of nitrogen, managing the nitrogen level appropriate to the vanadium level will maximize the cost effectiveness of the vanadium alloy addition.

These figures illustrate that the nitrogen enhancement of vanadium precipitation strengthening is effective at different carbon levels. The rate of strengthening with enhanced nitrogen is typically about 7 MPa for every 10ppm of additional nitrogen, independent of the carbon level. Additional carbon increases the yield strength, but does not change the strengthening contribution of the added nitrogen.

### Effect of C and N on Yield Strength



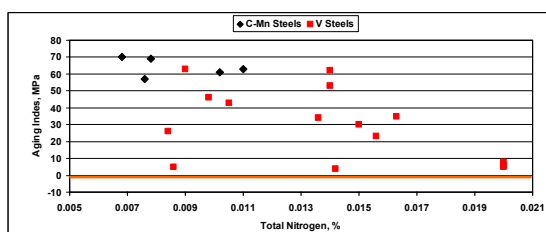
### Effects of Nitrogen as the Preferred Element in V(C,N) Precipitation



### Benefits of Nitrogen as the Preferred Element in V(C,N) Precipitation

- Potential for Nitrogen Strain Aging is Minimized with Vanadium Additions
  - “Free” nitrogen is minimized
  - Processing designed to complete the VN precipitation will provide the most strength while eliminating strain aging

### Aging Index in Al killed Sheet Steels As Rolled

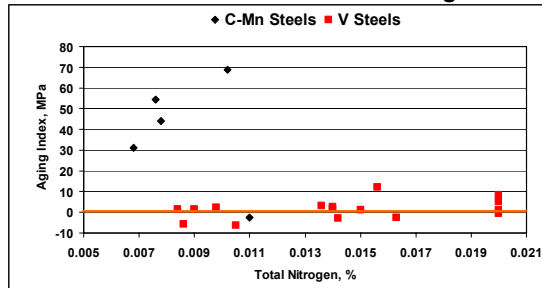


This graph shows the relative strength increase of vanadium additions, as affected by the nitrogen level. Once the vanadium addition exceeds the stoichiometric level (V:N = 3.7:1), the rate of strengthening of the vanadium will be reduced. Only carbon is available for precipitation strengthening after the nitrogen is no longer available. The effectiveness of VC precipitation is limited, and can be affected by processing parameters such as cooling rates. As shown in the graph, a 150MPa strength increase with 50ppm N would require over 0.10% V. However, if 150ppm N were available, the same strength increment of 150MPa could be achieved with only a 0.06% V addition.

Because of the preference of vanadium for nitrogen, free nitrogen is minimized with the addition of vanadium. As a result, processing designed to complete the VN precipitation will provide both the most effective strengthening, while eliminating nitrogen strain aging.

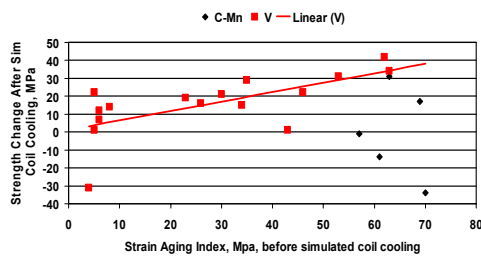
This graph shows the results of 100°C strain aging tests for a series of carbon and vanadium steels with a range of nitrogen levels. The samples were from strip steel rolled on CSP mills, some samples taken prior to the coil cooling step. Because of the absence of the coil cooling step after rolling, there was definite scatter in the aging index results, although a trend to lower aging index with high nitrogen levels in the vanadium steels was apparent. To complete the VN precipitation that would be expected with a good coil cooling process, duplicate samples were reheated to 600°C and slow cooled to simulate the coil cooling process.

### Aging Index in Al killed Sheet Steels 600 C Simulated Coil Cooling



This graph shows the strain aging index results after the 600°C simulated coil cooling of the samples. As shown, nitrogen strain aging was eliminated in all of the V bearing steels, but the C-Mn steels still had reduced but significant strain aging. All of these steels contained Al and some of the reduction of free nitrogen could have been a result of the formation of AlN. AlN formation is the only possibility for reduction of strain aging in the C-Mn steels. However, AlN precipitation would not strengthen the steels, while VN precipitation would be expected to increase the strength of the steels.

### Strengthening of V Sheet Steels from 600 C Simulated Coil Cooling



This slide shows the yield strength change of the test samples after the 600°C simulated coil cooling. The C-Mn steels showed, on the average, no strength change after the simulated coil cooling step. The vanadium steels, however, showed a consistent strength increase, which appears proportional to the level of the strain aging index prior to the simulated coil cooling step. This confirms that, even in the presence of Al, the coil cooling step is critical to achieving the maximum strengthening of a given V addition, as well as insuring that free nitrogen is minimized.

## SUMMARY

- The solubility of V(C,N) in steel is ideal for allowing processing at normal carbon steel practices and providing predictable precipitation strengthening of the ferrite over a large alloy addition range
- The low solute drag coefficient promotes necessary austenite recrystallization during rolling, leading to low rolling forces and uniformly fine ferrite grains
- Nitrogen is used effectively as part of the vanadium alloy system, providing maximum strengthening while eliminating strain aging

In summary, we have shown that the solubility of V(C,N) in steel is ideal for allowing processing at normal carbon steel practices and providing predictable precipitation strengthening of the ferrite over a large alloy addition range. The low solute drag coefficient promotes necessary austenite recrystallization during rolling, leading to low rolling forces and uniformly fine ferrite grains. Nitrogen is required for effective use of vanadium and becomes part of the vanadium alloy system, providing maximum strengthening while eliminating strain aging.