

Vanadium in Cold-rolled Sheet Steels

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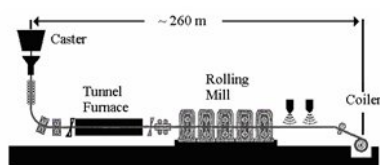
Scope

- **PART 1:** Review some background related to vanadium in cold-rolled sheet steels.
- **PART 2:** Discuss some highlights of a recent project related to HSLA sheet produced by thin-slab casting.

Background: HSLA Sheet

- Vanadium is extensively used in hot-rolled HSLA sheet products.
- V can be especially important in thin-slab cast products

Thin-Slab Casting (CSP)



K. Wronenberg and K. Schwenkfer, 1995.

- CSP Tunnel furnace temperatures are lower than conventional slab reheat temperatures (<1150 vs 1300°C)

The presentation is divided into two parts. First, some background and prior work related to the use of vanadium in cold-rolled sheet steels will be reviewed briefly. Then some new results will be presented, related to a project that included vanadium-containing HSLA sheet produced by thin-slab casting (CSP or compact strip production).

In hot rolled products, which are the subject of other presentations here, vanadium has been used for many years in high strength products, often in combination with other microalloying additions such as niobium or titanium. Vanadium can provide important contributions via both precipitation strengthening and ferrite grain refinement (due to austenite conditioning during thermomechanical processing).

Because of unique interactions between characteristics of vanadium and characteristics of the thin-slab CSP process, vanadium has received special interest in products manufactured via this route. These characteristics will be discussed further in the next few slides.

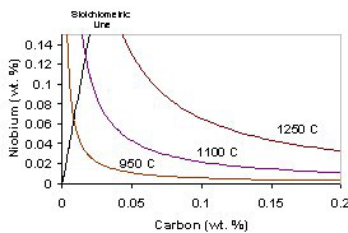
The Compact Strip Production (CSP) process involves near net shape casting (2" slab) and hot direct rolling (HDR) to streamline the steelmaking process. Some metallurgical characteristics of this process are as follows:

- There is no γ - α - γ phase change prior to soaking.
- The soaking temperature is lower than in conventional hot strip mills (1150°C vs. 1300°C).
- All hot-rolling is accomplished in the finishing stands (no roughing).

The relevance of soaking temperature will be discussed further, in the context of microalloy precipitate solubility.

Microalloy Solubility

- Solubility at the reheat temperature prior to hot-rolling defines the maximum additions of Nb, Ti



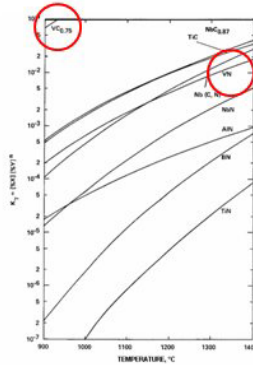
For any microalloying addition to be used most effectively, it must be dissolved during processing, and then precipitate at some lower temperature in the fashion desired. Solubility is therefore an important subject in any microalloying context, and is influenced by steel chemical composition and temperature. The diagram here shows the NbC solubility product in austenite at three temperatures consistent with the following expression:

$$\log_{10}[\text{Nb}][\text{C}] = 2.26 - (6770/T_K)$$

The curves represent combinations of Nb and C dissolved in austenite, such that the austenite is in equilibrium with NbC. The diagram shows that about 0.04Nb can be dissolved at a reheat temperature of 1100oC in a 0.05% carbon steel, while higher levels are soluble at higher temperature. The solubility of TiC is somewhat similar to NbC.

Vanadium Solubility in Austenite

- Reheat temperature is not of consequence



Here, solubility products in austenite are shown vs. temperature for a number of compounds. Where higher microalloying additions are desired, vanadium plays a key role because of its greater solubility. VC solubility is much greater than TiC or NbC, and VC is soluble during reheating to any austenitic rolling temperatures for carbon levels typical of sheet steel products. As a consequence, VC is not usually considered an important microalloy precipitate in austenite. While VN is less soluble than VC, the levels of nitrogen are low enough that VN solubility is also not of concern during reheating. Reheat temperature before rolling is usually not an important variable in the context of optimizing vanadium levels based on solubility, and so vanadium has attracted special interest for processes with low reheating temperatures.

What about Cold-Rolled Sheet ?

- While vanadium is extensively used in hot-rolled HSLA sheet products, it is not as widely used in cold-rolled and annealed HSLA grades.
- Strengthening effects are less efficient than in hot-rolled products...

While vanadium is used extensively in hot-rolled HSLA products as discussed in the previous few slides, it is not as widely used in cold-rolled HSLA sheet products. The conventional view held in the technical literature is that the strengthening effect of vanadium is somewhat less efficient in comparison to other microalloying species, when comparing the relative behavior of the hot-rolled and cold-rolled conditions.

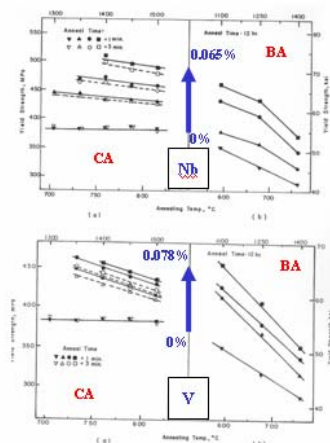
Why?

- The coarsening rate of vanadium carbides (during annealing) is reportedly greater than niobium or titanium carbides...
- So the V-contribution to strengthening is diminished by annealing

The reason that vanadium is less effective in cold-rolled, compared to hot-rolled products, is that the strengthening precipitates, such as vanadium carbide, are considered to coarsen more readily during annealing, than other precipitates such as niobium carbide. The increased coarsening rate of vanadium carbide is considered to arise because of its greater solubility. Coarsening increases their size, and reduces their strengthening contribution, so the microalloying contribution can be diminished during the annealing process, especially in the case of vanadium.

The effects mentioned above are shown here with an example from work of Pradhan in 1982, showing the yield strength of a series of Nb and V microalloyed sheet steels, after simulated batch or continuous annealing. When compared to a plain-carbon steel, both Nb and V provide strengthening in the hot-rolled condition (not shown here), and after both continuous and batch annealing. The data here relate to conditions where recrystallization is complete at the temperatures of interest. The strength is reduced during annealing of both series of steels (due primarily to microalloy carbonitride coarsening), especially for the batch-annealed situation. The slope associated with the Nb series of steels is somewhat less than associated with the V series of steels, suggesting greater coarsening resistance of Nb-containing precipitates. This effect is slightly magnified by the difference in the scale of the y-axes in the two figures, but this behavior is believed to have limited somewhat the usage of V in cold-rolled HSLA sheet steels.

Note Steeper Slope in Bottom vs. Top Results



These figures are reproduced from R. Pradhan, "Rapid Annealing of Cold-Rolled Rephosphorized Steels Containing Si, Cb, and V", *The Metallurgy of Continuous Annealed Sheet Steel*, TMS, 1982, pp. 203-227. The 0.06%C Al-killed steels contain Mn/Si/P, with the Nb series involving additions of 0.01, 0.035, and 0.065%, and the V-series containing 0.027, 0.048, and 0.078%. Cold reductions are 70%.



Background: non-HSLA Sheet

- **ULTRA-Low Carbon Sheet (<0.005% C)**
 - Stabilization of carbon and ease of recrystallization in IF Steels
(e.g. Mitchell and Gladman, 1997)
 - Partial Stabilization of Carbon in Bake-Hardening Steels
(e.g. Taylor and Speer, 1997)
- **TRIP Sheet Steels**
 - Strengthening of Ferrite Matrix
(Scott, 2004)

Some Other Reported Effects...

- **Reduced deposits of carbon/carbides on annealed surface**
(e.g. Wei, 1988)
- **“Hardenability” in Dual-Phase steel**
(e.g. Repas, 1979)

In addition to strengthening of HSLA products, vanadium has been used in some other cold rolled products. In ultra-low carbon steels, vanadium has been used for “stabilizing” carbon in highly formable “interstitial free” steels. Because vanadium is a weaker carbon stabilizer than Nb or Ti, which are more commonly used in interstitial-free steels, it was considered to have potential for partially stabilized grades offering formability in combination with a bake-hardening response. This development was applied in commercial production. Finally, vanadium has been used to boost the strength in newer high strength products such as transformation induced plasticity (TRIP) steels, and this development may be discussed in another paper given here by Colin Scott. Some references for these developments are as follows:

P. Mitchell, and T. Gladman, “Vanadium in Interstitial Free Steels”, Proceedings of 39th Mechanical Working and Steel Processing Conference, ISS, 1998, pp. 37-48.

Finally, a literature review identified papers suggesting that vanadium may also be useful for reducing carbon deposits or surface carbides on annealed surfaces, and for enhancing hardenability in dual-phase sheet. The speaker does not have direct experience with these developments. Refs. cited by Cambridge Scientific Abstracts include:

F.Y. Wei, “Mechanism and Restraint of Carbon Deposit on the Surface of Cold Rolled Sheet Steel”, Technology and Training (Taiwan), Vol. 13, No. 5, 1988, pp. 1-4. (Also Y. Liu, US Patent 5,795,410, 1998)

P.E. Repas, Metallurgy, “Production Technology and Properties of Dual Phase Sheet Steels”, Proceedings of Conf. Berlin 1978: Dual Phase and Cold Pressing Vanadium Steels in the Automobile Industry, 1979, pp. 13-22.



Part 2:

Some Recent Results

Current Research...

- Jennifer A. Garrison, M.S. 2005
- **Goal:** Consider the influence of nitrogen on behavior of V-containing HSLA sheet steel produced via CSP, in terms of competition between Al and V for the available nitrogen

Premise...

- Nitrogen is well known to enhance the precipitation strengthening behavior of V-containing steels, and V(C,N) precipitates may be more coarsening resistant than VC during annealing

Production Hot-Bands

- Outer wraps from Nucor - Hickman

STEEL	C	Mn	P	S	Si	Cu	V	Al
Low-Al	0.047	0.475	0.015	0.002	0.02	0.114	0.04	0.016
High-Al	0.045	0.461	0.012	0.004	0.02	0.118	0.035	0.047

Having introduced the background related to vanadium in cold-rolled sheet products, it is of interest to show some experimental results from a project at the speaker's laboratories.

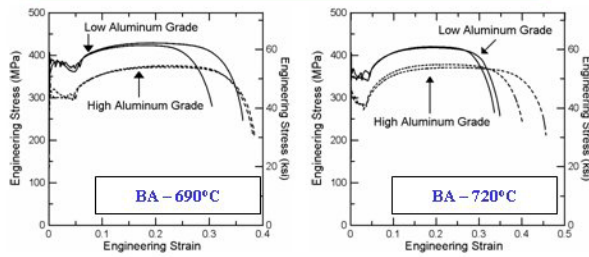
This project is the Master's Degree thesis work of Jennifer Garrison, at the Advanced Steel Processing and Products Research Center of Colorado School of Mines. The work involved direct interactions with our sponsor companies, including Nucor Steel and Stratcor. Jennifer has now completed her work and is employed at Caterpillar, a manufacturer of construction and mining equipment.

The goal of this work was to examine the competition between Al and V for nitrogen in CSP sheet products, since both Al and V are strong nitride formers, and the effects on properties should be very different depending on whether the nitrogen is tied up as a microalloy carbonitride, or as an aluminum nitride.

VN is a more potent strengthener than VC because of its greater driving force for precipitation (directly related to its lower solubility). In addition, VN is known to be much more stable than VC, and hence may be more coarsening resistant during annealing after cold-rolling. Hence, it was considered important to understand nitrogen effects in V-added sheet, in this case via the influence of aluminum concentration.

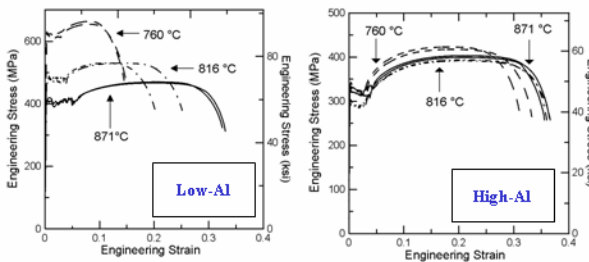
Trials were conducted whereby two V-added low-carbon CSP coils were designed and processed. The coils were nominally identical, except that one was much lower in aluminum than the other.

Batch-Annealed Properties



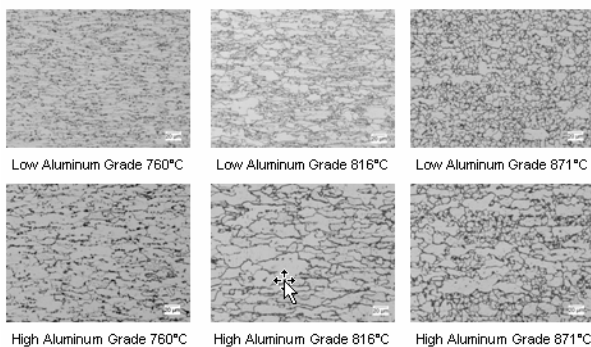
- Al reduces strength (AlN consumes nitrogen)
- No grain size differences

Continuous-Annealed Properties



- Al enhances recrystallization kinetics
- Al reduces strength

Continuous Annealed Microstructures



Stress-strain curves are shown here after batch annealing of the two steels. The results are similar at both annealing temperatures. The low-Al steel again exhibits higher strength than the high-Al steel. The grain sizes of the two steels are not substantially different, indicating that the strength difference is likely related to precipitation effects. Presumably, AlN formation in the high-Al steel consumes nitrogen, which is then unavailable to create an efficient V(C,N) dispersion.

Stress-strain curves are shown here after continuous annealing of the two steels at three different temperatures. The properties in the high-Al steel are not greatly influenced by temperature, and suggest complete recrystallization in each instance. In the low-Al steel, the higher strength and lower ductility at low annealing temperatures is indicative of incomplete recrystallization, presumably due to greater boundary pinning effects of the V(C,N) precipitate dispersion that forms in this steel, in comparison to AlN and VC in the high-Al steel. As in the hot-band and batch annealed conditions, the low-Al steel exhibits higher strength after continuous annealing. The strength difference between the two steels approaches 100MPa when the steels are compared in the fully recrystallized condition.

Light optical metallography results were obtained to examine recrystallization behavior and measure as-recrystallized grain sizes. The results confirm the microstructural inferences made based on the mechanical properties, wherein the high-Al steel recrystallized at all of the continuous annealing temperatures, while the low-Al steel was fully recrystallized only at the highest temperature of 871°C. The duplex grain sizes present at the highest annealing temperatures may reflect formation of fine ferrite grains from austenite present at the annealing temperature.

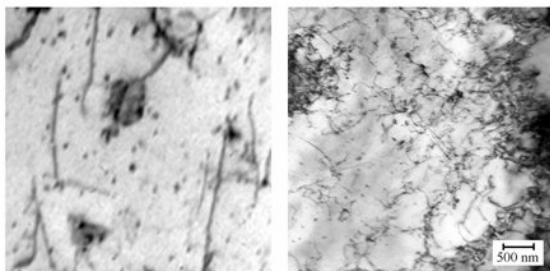
Precipitate Characterization

• Transmission Electron Microscopy

– Continuous annealed at 871°C
(both steels fully recrystallized)

Thin Foils
Carbon Extraction Replicas / EDS

CA 871°C Thin Foil

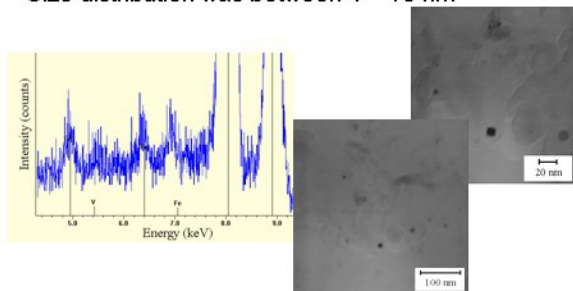


High Aluminum Grade 871°C
Continuous Annealed
Simulation

Low Aluminum Grade 871°C
Continuous Annealed
Simulation

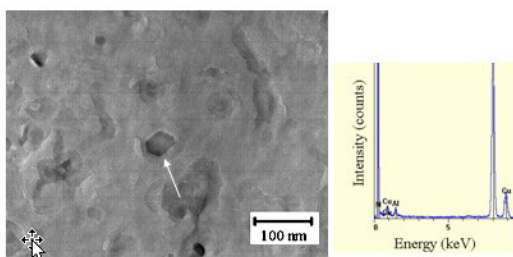
Low-Al: CA 871°C Extraction Replica

- V(C,N) has a cuboidal morphology
- Size distribution was between 4 – 10 nm



High-Al: CA 871°C Extraction Replica

- Precipitates are primarily AlN



The high-Al steel clearly influenced properties and recrystallization behavior, presumably due to AlN formation influencing the V(C,N) precipitation behavior. Electron microscopy was conducted to examine the precipitate distributions directly, and thereby understand more clearly the controlling mechanisms. Both thin foils and carbon extraction replicas were examined, and energy dispersive x-ray microanalysis (EDS) of small particles was conducted to characterize particle compositions. The results presented here will focus on the two steels after continuous annealing at 871°C.

Here are transmission electron micrographs of thin foils produced from the two steels. The images are shown at the same magnification, and clearly illustrate the much finer precipitates in the low-Al steel on the right. The finer precipitate dispersion is consistent with the higher strength and higher recrystallization temperature associated with this steel.

Extraction replicas isolate the precipitates, and are prepared using alcohol-based solutions since AlN is soluble in water. Here, the fine particles in the low-Al steel are shown, along with the EDS spectrum indicating the presence of vanadium. The precipitates are assumed to be nitrogen-rich V(C,N).

In the high-Al steel, the precipitates are mostly coarser AlN, confirmed by EDS. Some smaller vanadium-containing particles were also found; these are assumed to be VC [or carbon-rich V(C,N)].

Strengthening Analysis

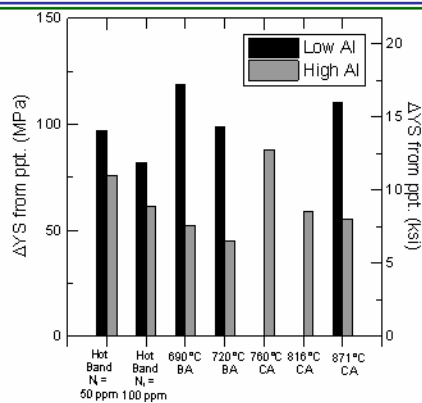
– Dislocation and texture effects assumed negligible

$$\sigma_y = \sigma_o + \sigma_{ss} + \sigma_p + k_y d^{-1/2}$$

- $\sigma_o = 47 \text{ MPa}^*$
 - $\sigma_{ss} = 2918[\text{N}_i] + 678[\text{P}] + 123[\text{Sn}] + 83[\text{Si}] + 59[\text{Al}] + 8[\text{Cu}] + 37[\text{Mn}] + 11[\text{Mo}] + 0[\text{Ni}] - 31[\text{Cr}]^{**}$
– Elements are in wt. %.
 - $k_y = 18.1 \text{ MPa} \times \text{mm}^{1/2}$
- * Cracknell and Petch, 1955.
** Pickering and Gladman, 1963.
Gladman, 1997.
Leslie, 1972.

An analysis was conducted to estimate the level of precipitation strengthening in the two steels in various conditions. Yield strength is a well known function of internal lattice friction, solid solution strengthening, grain size, precipitation strengthening, etc., and these contributions can be estimated based on chemical composition and grain size measurements, allowing the precipitate contribution to then be calculated to make up the difference between the measured and estimated yield strength. Texture effects were ignored here, and work hardening (strength contribution associated with the dislocation content) was assumed negligible for the hot-rolled or fully-recrystallized conditions.

Precipitation Strengthening Contribution



The results of the strengthening analysis are presented here for the two steels. The greater strengthening contribution in the low-Al steel is apparent in all conditions, particularly after annealing, reflecting the enhanced V(C,N) coarsening resistance. The two sets of values shown for the as-rolled hot-band reflect uncertainty in the solute nitrogen level in this condition. Nitrogen is assumed to be fully combined as AlN or V(C,N) after annealing.

Calculated precipitation strengthening increments are not shown for the low-Al steel after continuous annealing at low temperatures, where recrystallization was incomplete.

Summary

- Historical usage of vanadium in cold-rolled sheet is limited.
- New work shows important interactions between V, Al, and N.
 - Low-Al replaces AlN with V(C,N) that is more effective than VC.
 - Some significant influences on recrystallization behavior and properties.
 - Further assessment needed of potential for V(C,N) strengthened cold rolled grades needed.

Interestingly, the precipitation strengthening increment in the cold rolled low-Al steel was greater than in the as-rolled hot-band. This behavior is different than has been reported previously, and may reflect incomplete precipitation in the outer wraps of the hot-rolled coil provided for this study.

In this presentation, the use of vanadium in cold-rolled sheet was reviewed briefly, and it was suggested that precipitate coarsening during annealing has limited the application of vanadium in high strength cold-rolled sheet.

New work was presented that showed important influences of aluminum in V-containing HSLA sheet produced via the CSP (thin slab casting and direct rolling) process. Aluminum competes with vanadium for the available nitrogen, and lower Al levels were



found to result in higher strength in the hot-band, and in the batch and continuous annealed conditions after cold-rolling. The recrystallization temperature in the continuous annealed steels was also shown to increase in the low-Al steel. AlN was prominent in the high-Al steel, while finer V(C,N) was the dominant precipitate in the low-Al steel.

The effectiveness of vanadium as a strengthener in cold-rolled HSLA products should be examined further in steels where sufficient nitrogen is available to enhance the coarsening resistance of the microalloy precipitates.