Influence of Chemical and Processing Variables on Annealing Response of Cold-Rolled Microalloyed Steels

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INTRODUCTION

While effects of aluminum on the properties of vanadium microalloyed steels have been recognized in the past, recent work by Garrison *et al.*[1] reported an interesting competition between vanadium and aluminum for nitrogen in steels. Aluminum variations were found to influence the mechanical properties of vanadium microalloyed sheet steels in both the hot-rolled condition, as well as after subsequent cold-rolling and annealing (including both batch and continuous annealing processing simulations). Because of the "apparent competition" between aluminum and vanadium for the available nitrogen, a reduced level of aluminum was associated with higher strength levels. Recrystallization during annealing after cold rolling was also suppressed in the low-aluminum steel based on the observed microstructure and property responses to continuous annealing over a range of temperatures. These behaviors were believed to be due to aluminum effects on vanadium carbonitride precipitation strengthening. In the high aluminum steel, AlN was the prominent precipitate, while in the low aluminum steel, V(C, N) was prominent. It was concluded that the increase in aluminum content increases the driving force to form aluminum nitrides. AlN formation in turn decreases the amount of nitrogen in solution to combine with vanadium. Vanadium carbonitride is a potent precipitation strengthener in steels, whereas AlN is not a potent strengthener.[1]

Interactions between aluminum and nitrogen in microalloyed steels have been recognized for many years. For example, a reduction in strength due to high aluminum levels was reported in the Proceedings of Microalloying '75: "When vanadium-nitrogen heats are produced with high-aluminum contents, adequate reheating temperatures must be maintained to avoid deterioration in strength properties."[2] However, it should be recognized that this behavior was in reference to as-hot-rolled properties, not cold-rolled properties that are of primary relevance here. Most of the work on microalloying interactions with nitrogen have been similarly applied to hot-rolled products. The importance of nitrogen is commonly reported in vanadium steels, where maximum strength levels are achieved through nitrogen enhancements to optimize the V(C, N) strengthening in ferrite.[3] The strengthening coefficients for nitrogen in vanadium alloyed steels have been reported to be as high as 7 MPa (1 ksi) for every 10 ppm of N, as long as the V: N ratio is greater than 4:1.[3] The literature provides little information on the effects of nitrogen in cold-rolled vanadium steels, although one recent study reports increased strength with increasing nitrogen in both the hot-rolled and cold-rolled/batch annealed conditions.[4]

In niobium microalloyed steels, niobium-aluminum-nitrogen interactions are also not addressed in the literature. However, it might be reasonable to expect that interactions between niobium and aluminum may be less prominent than between vanadium and aluminum, due to greater importance of carbides, rather than nitrides, in niobium steels.

The results reported here are part of an ongoing study to examine the influence of aluminum and nitrogen levels in vanadium and niobium microalloyed cold-rolled sheet steels, extending earlier work to assess a wider range of HSLA steel compositions that will be examined to compare the annealing response through mechanical properties and microstructure. The steels include families of 0.038 wt.% vanadium microalloyed HSLA grades and 0.032 wt.% niobium microalloyed HSLA grades. In the vanadium HSLA steels both the aluminum content and nitrogen content are varied to give high, medium, and low levels, with only one element varied at a time. In the niobium HSLA steel the only element that varies is the aluminum content. Both batch and continuous annealing processes are of interest; the present contribution is focused on batch annealing results.

EXPERIMENTAL PROCEDURE

Material Chemical Composition

The steels selected for evaluation were sampled from the outer wraps of commercially produced hot bands obtained after pickling. Three sets of microalloyed HSLA grades were sampled:

- vanadium microalloyed HSLA steels that vary in aluminum content
- vanadium microalloyed HSLA steels that vary in nitrogen content
- niobium microalloyed HSLA steels that vary in aluminum content

The heats were melted and hot-rolled at Nucor-Decatur holding constant all the aspects of production as closely as possible within each set, except for the aluminum/nitrogen levels. The aluminum and nitrogen variations were made at levels selected to be within typical production constraints. The heat chemical compositions of the three sets of steels are shown in Table I. The manganese variations between the vanadium and niobium microalloyed steels were required to apply existing production grades in this work. Note that the niobium microalloyed steel family contains four aluminum levels and the different levels are label low, lower mid (LMid), upper mid (UMid), and high.

TABLE I - Chemical Compositions of Microalloyed HSLA Steels (wt.%)

Alloy Identification	V	Nb	C	Mn	Al	N
Low-Al V	0.036	0.001	0.045	0.79	0.016	0.0131
Mid-Al V	0.036	0.001	0.052	0.78	0.030	0.0110
High-Al V	0.034	0.001	0.049	0.77	0.038	0.0111
Low-N V	0.038	0.001	0.046	0.79	0.026	0.0118
Mid-N V	0.040	0.001	0.040	0.84	0.028	0.0133
High-N V	0.038	0.001	0.042	0.85	0.028	0.0147
Low-Al Nb	0.001	0.032	0.049	1.20	0.015	0.0091
LMid-Al Nb	0.001	0.035	0.046	1.24	0.024	0.0098
UMid-Al Nb	0.001	0.032	0.051	1.25	0.029	0.0091
High-Al Nb	0.001	0.032	0.053	1.27	0.041	0.0085

Cold Rolling

101.6 mm by 304.8 mm (4 by 12 inch) strips were sheared from the as-received hot strip parallel to the rolling direction. These strips were then laboratory cold rolled using a 2-high mill configuration and 134.4 mm (5.29 inch) diameter work rolls. The strips were reduced 60% over a series of 5 passes.

Annealing Simulation

To simulate batch annealing of a coil, two sub-sized tensile samples from each of the cold-rolled alloys were wired together with blanks on either side. These wired samples were placed in stainless steel heat treat bags along with a strip of titanium to getter the oxygen, and the bags were placed in a programmable muffle furnace. To achieve a heating rate similar to commercial batch annealing, the ramp heating rate was set to simulate the slow heating of a large coil, at 0.8°C/min (1.5°F/min). The samples were then held at temperature for 10 hours. The furnaces were reprogrammed to cool to room temperature at a rate to simulate the slow cooling rate of a large coil, at 0.5°C/min (0.9°F/min). Three hold temperatures were used to simulate cold spot 635°C (1175°F), mid-range 663°C (1225°F), and hot spot 690°C (1275°F) temperatures. Continuous annealing simulations are also planned; these results will be reported at a later time.

Tensile Testing

Sub-sized tensile specimens were machined, according to ASTM standard E-8, from the cold rolled strips transverse to the rolling direction. The specimens were 101.6 mm (4 inches) long with a gage width of 6.35 mm (0.25 inches) and a 25.4 mm (1 inch) gage length. Quasi-static tension testing was performed at a crosshead speed of 1.52 mm/min (0.06 in/min) Duplicate tension tests were run for each alloy at each condition.

Metallography

Light optical metallography was performed to understand the differences in properties that were found, and to characterize the recrystallization behavior of the different alloys. The metallographic samples were obtained from the grip section of tensile samples following mechanical testing. Metallographic samples were etched in a 2% Nital solution to reveal grain boundaries. Grain size measurements were made using the Abrams three circle method, described in ASTM standard E 112-96. For each sample condition six micrographs of the longitudinal cross-section were taken at 1000X. The standard three-circle transparency, with perimeters totaling 500 mm, was placed upon each micrograph at random and the total number of intercepts was counted. To calculate the ASTM grain size number Equation 1 was used, where N_L is the number of intercepts per unit length of test line and G is the ASTM grain size number. Equation 2 was then used to calculate the number of grains per mm^2 at 1X, N_A, and N_A was then used to calculate the average grain diameter in mm, d, from Equation 3. This procedure follows ASTM standard E 112-96, “Standard Test Methods for Determining Average Grain Size”.

$$G = 6.644(\log N_L) - 3.29 \tag{1}$$

$$G = 3.322(\log N_A) - 2.95 \tag{2}$$

$$d = \left(\frac{1}{N_A}\right)^{\frac{1}{2}} \tag{3}$$

RESULTS AND DISCUSSION

As-Received Hot-Band Properties

The as-received hot-band mechanical properties are shown in Table II. There were only small differences in the hot-rolled properties within each alloy set, although the niobium microalloyed steel exhibited higher average strength levels than the vanadium microalloyed steels. (It should be noted that the niobium and vanadium steels were produced for different applications, and the hot-band yield strengths were not intended to be identical.) The as-received, hot-band grain sizes exhibited little variation within each alloy set, shown in Table III. However, the niobium steels were somewhat finer than the vanadium steels in the hot-rolled condition, accounting for a substantial portion of the strength differences.

Table II - As Received Hot-Band Material Properties

Alloy Identification	Yield Strength (MPa)	UTS (MPa)	Uniform Elongation (%)	Total Elongation (%)
Low-Al V	345	436	19	39
Mid-Al V	355	460	19	39
High-Al V	350	437	20	41
Low-N V	350	428	19	37
Mid-N V	335	413	20	39
High-N V	350	424	19	39
Low-Al Nb	515	584	16	29
LMid-Al Nb	518	575	16	30
UMid-Al Nb	528	590	15	27
High-Al Nb	528	582	16	29

Table III – Average Grain Diameter for As-Received Hot-Band Microstructures

Alloy Identification	Average Grain Diameter (μm)
Low-Al V	9.5
Mid-Al V	8.6
High-Al V	9.2
Low-N V	7.3
Mid-N V	7.2
High-N V	7.5
Low-Al Nb	3.9
LMid-Al Nb	4.0
UMid-Al Nb	3.4
High-Al Nb	3.5

Vanadium Microalloyed Steel with Aluminum Variation

The vanadium microalloyed steel set with variations in aluminum content exhibited similar results as reported in prior research[1]. The yield and tensile strengths of the Low-Al V steel were greater than those of the Mid-Al V and the High-Al V steels for steels batch annealed at 663 °C and 690 °C, as shown in Figure 1. For clarity, Figure 1 displays one of two stress-strain curves for each steel; properties were generally consistent for a given condition.[*] At the lowest batch annealing temperature, 635 °C, the Mid-Al V steel is stronger than the Low-Al V and High-Al V steels. This difference may reflect some variation in the extent of recrystallization; the microstructure of the Mid-Al V steel batch annealed at 635 °C revealed a more elongated grain structure with fewer equiaxed grains than the Low-Al V and High-Al V microstructures. At the higher batch annealing temperatures of 663 °C and 690 °C, a more equiaxed grain structure was present in each steel, indicating complete recrystallization.

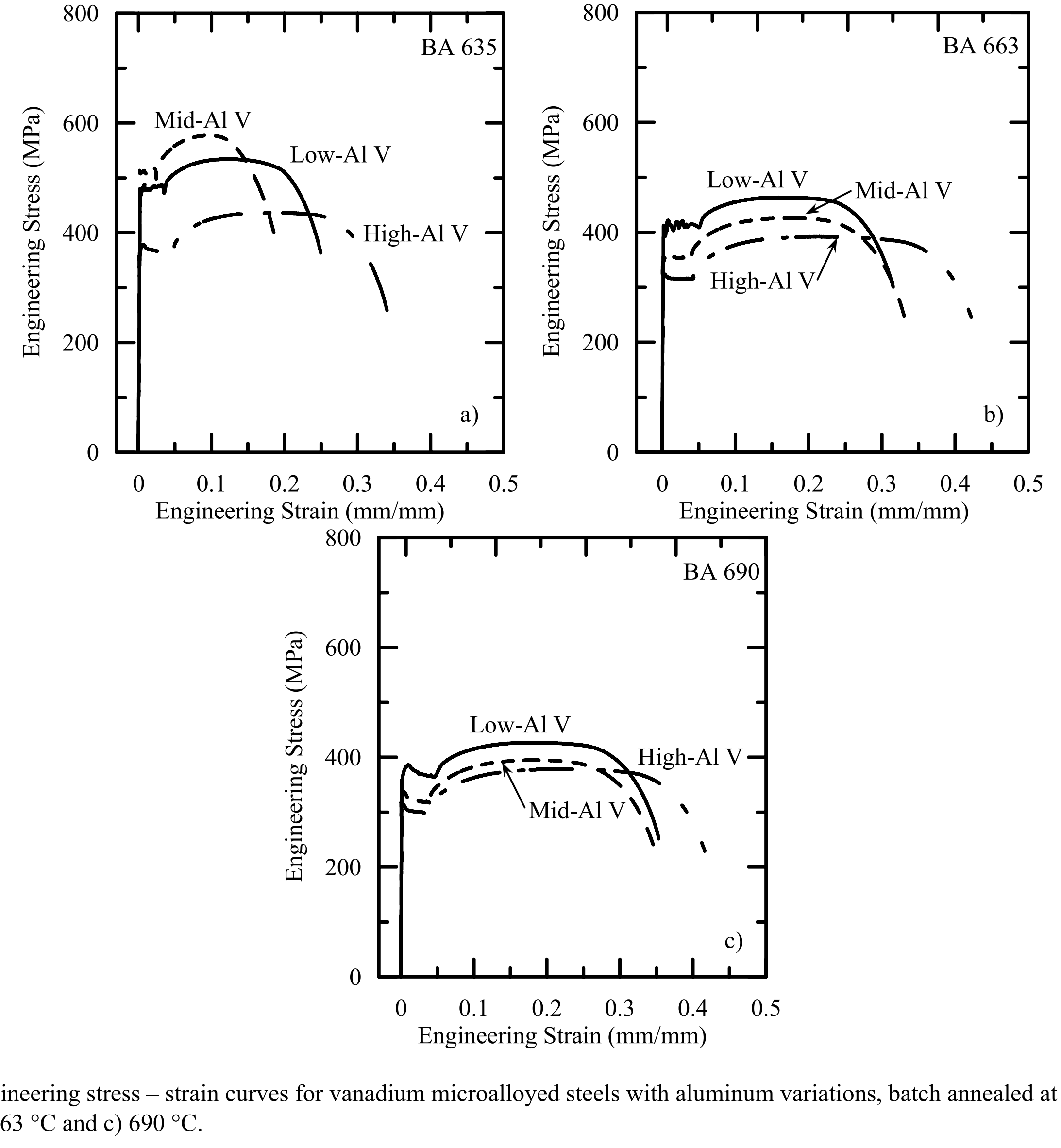

Figure 1 Engineering stress – strain curves for vanadium microalloyed steels with aluminum variations, batch annealed at a) 635 °C, b) 663 °C and c) 690 °C.

Table IV presents a summary of the tensile properties for the vanadium microalloyed steel set with aluminum variations; the data presented are an average of the two tests run for each condition. For conditions where full recrystallization is evident, the yield and tensile strengths are inversely related to aluminum content; with the magnitude of difference diminishing at higher annealing temperatures. Both the uniform and total elongation increased with a decrease in strength, as expected.

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[*] For all conditions examined in this work, duplicate specimens had yield strengths within approximately 5 MPa of one another.

Table IV - Batch Annealed Tensile Mechanical Properties for Vanadium Microalloyed Steels with Aluminum Variations

Alloy Identification	Batch Annealing Temperature (°C)	Yield Strength (MPa)	UTS (MPa)	Uniform Elongation (%)	Total Elongation (%)
Low-Al V	635	478	533	12	23
Mid-Al V	635	507	575	10	18
High-Al V	635	370	438	18	32
Low-Al V	663	412	463	17	31
Mid-Al V	663	353	424	18	33
High-Al V	663	323	392	21	40
Low-Al V	690	377	426	19	34
Mid-Al V	690	337	395	19	34
High-Al V	690	312	377	22	42

The average grain diameters for these steels in the 663°C and 690 °C batch annealing conditions are also presented in Table V. For both annealing temperatures the Low-Al V steel has a finer grain size than the Mid-Al V and High-Al V steels. The grain size for Low-Al V is about 2 μm finer for the batch annealed 663 °C condition and about 1 μm finer for the 690 °C condition. The decrease in grain size disparity with increasing temperature is consistent with the reduction in strength differences between the Low-Al V and High-Al V in the batch annealed 690 °C condition compared to the 663°C condition.

Table V – Average Grain Diameter for Vanadium Microalloyed Steels with Aluminum Variations

Alloy Identification	Batch Annealed at 663 °C Avg. Grain Diameter (μm)	Batch Annealed at 690°C Avg. Grain Diameter (μm)
Low-Al V	6.8	7.6
Mid-Al V	9.6	8.1
High-Al V	9.7	8.9

The strength difference between a low-aluminum vanadium and high-aluminum vanadium microalloyed steel has previously been attributed to precipitation differences.[1] In the High-Al V alloy the higher level of aluminum increases the extent of AlN formation, which in turn causes a decrease in V(C, N) precipitation due to less nitrogen being available to form V(C, N). V(C, N) precipitates are potent strengtheners; therefore a decrease in V(C, N) precipitation correlates to a decrease in strength.[1] In the results presented here, there also appears to be a contribution of grain refinement to the strength differences, although Hall-Petch analysis suggests that differences in the precipitation strengthening increments are also needed to account for the observed strength differences.

Vanadium Microalloyed Steel with Nitrogen Variation

The vanadium microalloyed steels with varying nitrogen levels show a significant reduction in overall strength with increasing batch annealing temperature, as illustrated in Figure 2. Again for clarity, Figure 2 displays only one of two stress-strain curves for each steel. The high yield strengths in the 635 °C batch annealed condition corresponded to incompletely recrystallized microstructures, as shown in Figure 3. Metallography indicated complete recrystallization at the two higher batch annealing temperatures. The overall mechanical property results for these steels are summarized in Table VI. The strength levels obtained in this series of steels is somewhat higher than observed in the previous series of vanadium steels with aluminum variations, despite their similar overall compositions. The reason for this behavior is unclear, but the hot-band grain sizes are somewhat different (Table III), suggesting possible differences in hot-rolling and cooling practice, or sampling location.

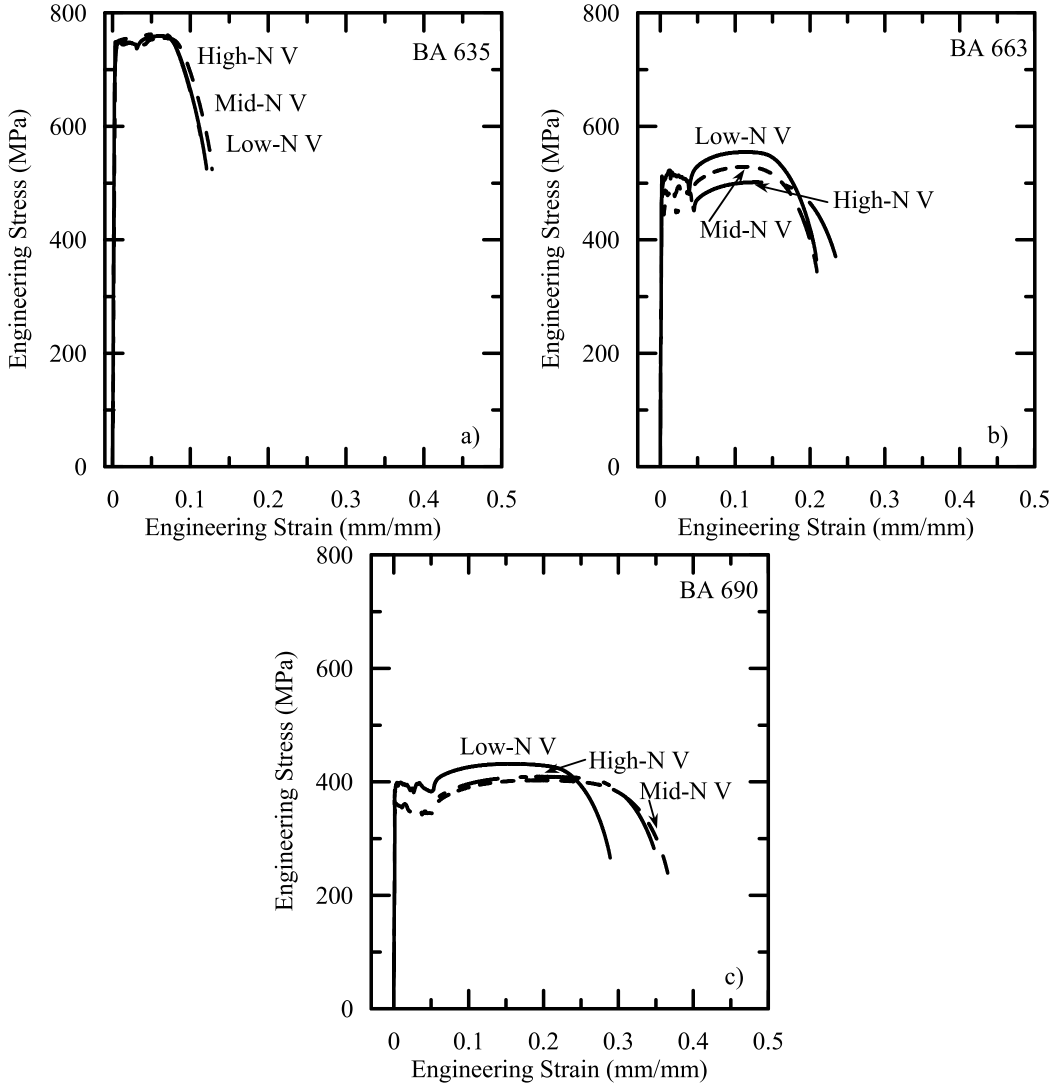
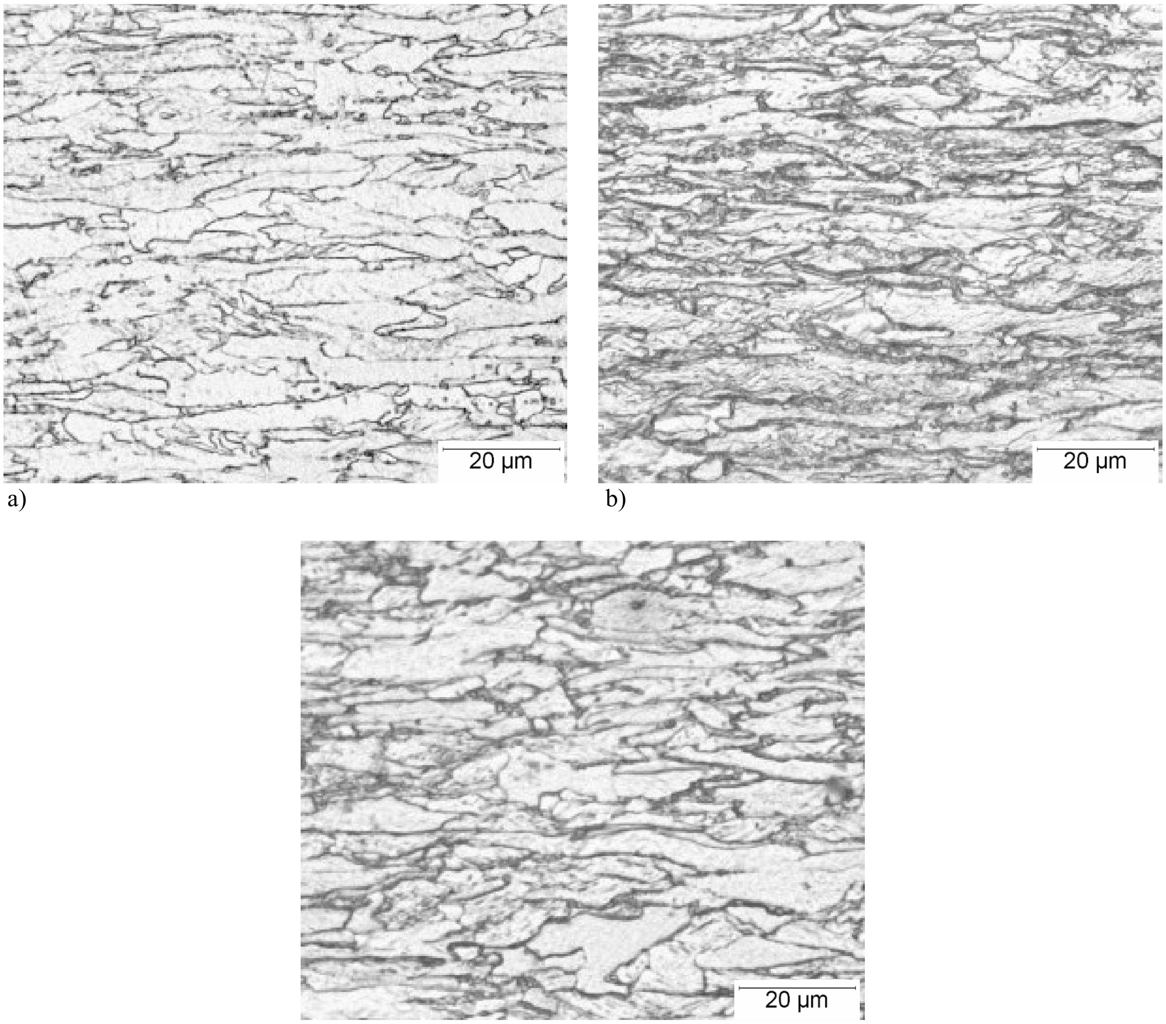


Figure 2 Engineering stress – strain curves for vanadium microalloyed steels with nitrogen variations, batch annealed at a) 635 °C, b) 663 °C and c) 690 °C.



a) b) c)

Figure 3 Microstructures of a) Low-N V, b) Mid-N V and c) High-N V steels batch annealed at 635 °C displaying substantially incomplete recrystallization in each instance. (2% Nital etch)

Table VI - Batch Annealed Mechanical Properties for Vanadium Microalloyed Steels with Nitrogen Variations

Alloy Identification	Batch Annealing Temperature (°C)	Yield Strength (MPa)	UTS (MPa)	Uniform Elongation (%)	Total Elongation (%)
Low-N V	635	730	756	6	12
Mid-N V	635	743	756	6	12
High-N V	635	745	763	6	12
Low-N V	663	505	551	12	20
Mid-N V	663	481	527	12	20
High-N V	663	458	503	13	23
Low-N V	690	390	432	17	29
Mid-N V	690	375	403	19	35
High-N V	690	370	407	19	33

In the fully recrystallized conditions obtained after batch annealing at 663 °C and 690 °C, the low-nitrogen steel exhibited slightly higher strength than the higher nitrogen steels. This behavior is surprising in light of the well known strengthening effects of nitrogen in vanadium containing steels. Grain size measurements, in Table VII, suggest a slightly finer grain size in the Low-N V steel, which may have contributed to the strengthening effect. Should this effect prove to be reproducible, it could perhaps relate to increased AlN precipitation kinetics resulting from elevated nitrogen levels, thereby increasing the amount of AlN and thus reducing the nitrogen available to form V(C, N) strengthening precipitates. While the observed effect is small, it should be noted that it is observed only after batch annealing and not in the as-rolled condition, suggesting that differences in precipitation during heating to the annealing temperature could warrant further consideration. Lower strength in all three steels at the 690 °C annealing temperature is presumably a consequence of microalloy precipitate coarsening, along with some grain growth.

Table VII – Average Grain Diameter for Vanadium Microalloyed Steels with Nitrogen Variations

Alloy Identification	Batch Annealed at 663 °C Avg. Grain Diameter (μm)	Batch Annealed at 690 °C Avg. Grain Diameter (μm)
Low-N V	5.1	6.8
Mid-N V	5.7	8.6
High-N V	6.2	8.4

Niobium Microalloyed Steel with Aluminum Variation

The niobium microalloyed steels show a small increase in strength with increasing aluminum content, as indicated by the tensile curves in Figure 4. The mechanical properties are summarized in Table VIII. The differences in properties among the niobium steels are somewhat less than observed in the two sets of vanadium steels, and the differences among the steels do not appear to be systematic over the range of annealing temperatures examined. Thus it appears that the cold-rolled niobium containing steels may be less sensitive to aluminum variations than the vanadium containing steels. The strength diminishes with increasing annealing temperature, while grain size correspondingly increases (Table IX). At the highest annealing temperature the strengths and grain sizes are comparable to the vanadium steels, despite much greater differences in the hot-rolled condition.

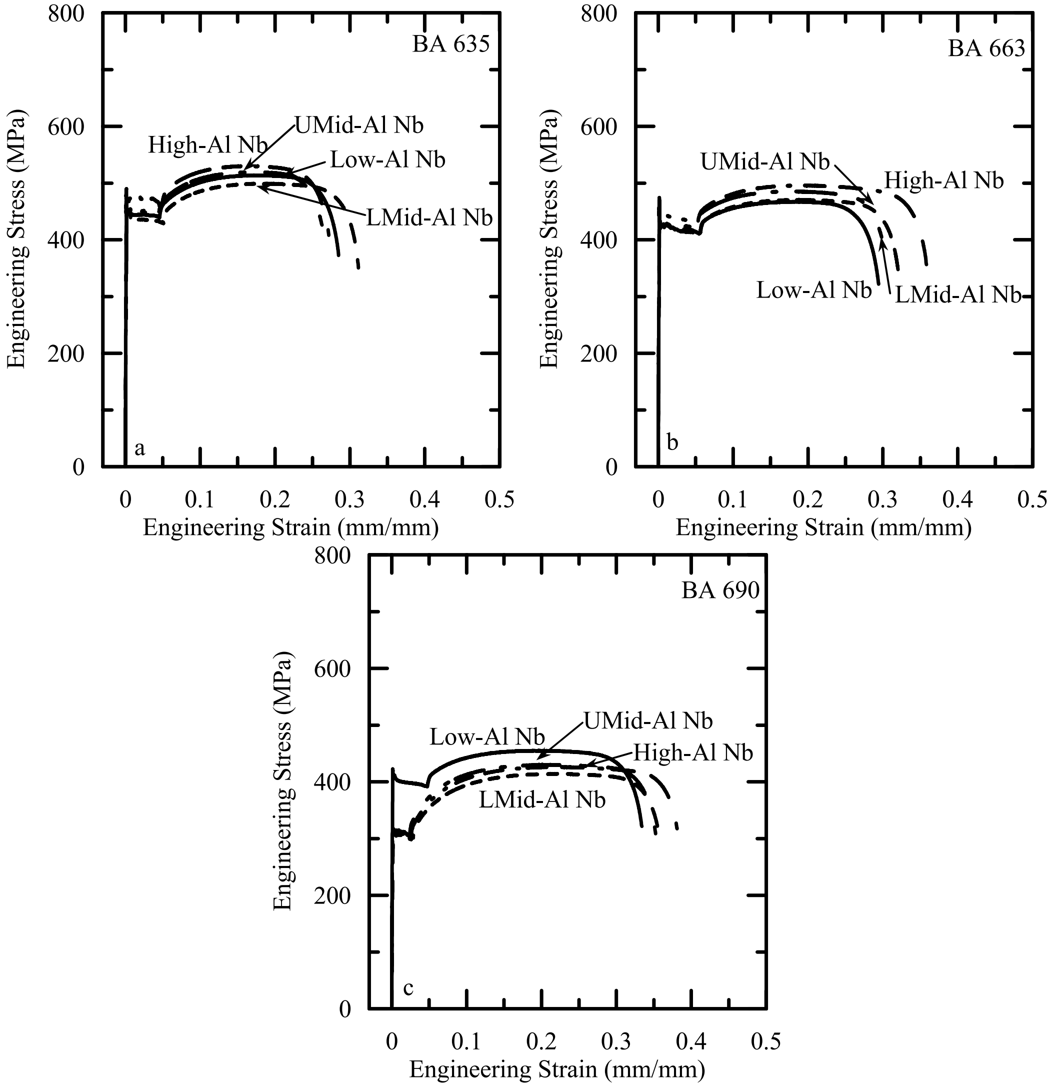


Figure 4 Engineering stress – strain curves for niobium microalloyed steels with aluminum variations, batch annealed at a) 635 °C, b) 663 °C and c) 690 °C.

Table VIII - Batch Annealed Tensile Mechanical Properties for Niobium Microalloyed Steels with Aluminum Variations

Alloy Identification	Batch Annealing Temperature (°C)	Yield Strength (MPa)	UTS (MPa)	% Uniform Elongation	% Total Elongation
Low-Al Nb	635	466	515	18	28
LMid-Al Nb	635	456	500	18	30
UMid-Al Nb	635	465	517	18	26
High-Al V	635	480	530	17	26
Low-Al Nb	663	467	469	19	28
LMid-Al Nb	663	465	471	19	31
UMid-Al Nb	663	448	483	19	30
High-Al Nb	663	457	494	20	35
Low-Al Nb	690	427	453	20	32
LMid-Al Nb	690	313	416	22	35
UMid-Al Nb	690	302	430	21	35
High-Al Nb	690	321	423	21	38

Table IX – Average Grain Diameter for Niobium Microalloyed Steels with Aluminum Variations

Alloy Identification	Batch Annealed at 663 °C Avg. Grain Diameter (μm)	Batch Annealed at 690 °C Avg. Grain Diameter (μm)
Low-Al Nb	6.3	7.3
LMid-Al Nb	5.8	8.1
UMid-Al Nb	6.0	7.1
High-Al Nb	5.3	7.8

The mechanical properties are suggestive of complete recrystallization even at the lowest batch annealing temperature of 635 °C, while the microstructures exhibited elongated ferrite, especially for the two higher aluminum steels, seen in Figure 5. Electron backscattered diffraction (EBSD) could be helpful to confirm morphology differences between the recrystallized ferrite in different steels, as well as to confirm the presence or absence of unrecrystallized ferrite.

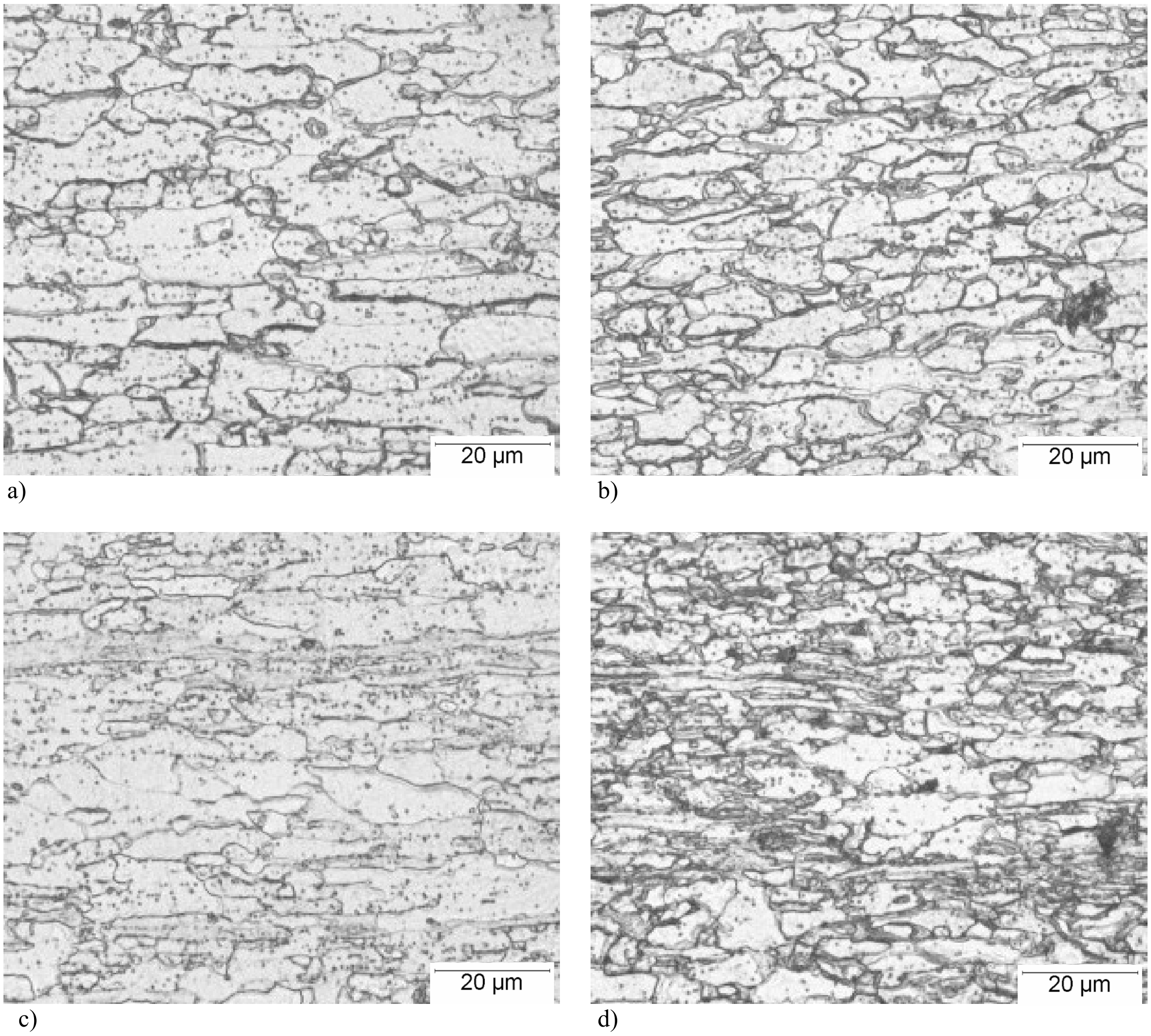


Figure 5 Microstructures of a) Low-Al Nb, b) LMid-Al Nb, c) UMid-Al Nb and d) High-Al Nb steels batch annealed at 635 °C displaying an elongated ferrite morphology, particularly in the UMid-Al Nb and High-Al Nb samples. (2% Nital etch)

While published literature does not provide clear guidance related to niobium-aluminum-nitrogen interactions, it is perhaps not surprising that the niobium steels are less sensitive to aluminum variations in comparison to vanadium steels. NbN and NbC in niobium steels have solubilities in iron that are very similar, in comparison to vanadium steels where VN is much less soluble than VC (and thus more effective as a strengthener due to the greater driving force for precipitation). In niobium steels, small variations in nitrogen are less important since ample carbon is usually available to develop NbC strengthening precipitates.[5] [Note to reviewers: We are currently repeating the 690 °C batch anneal for the niobium steels, to examine repeatability of the higher yield strength observed in this condition. The new results will be available prior to final publication.]

SUMMARY

The mechanical behavior and batch annealing responses were evaluated for three families of HSLA sheet steels: 1) 0.036 wt.% vanadium with varying aluminum levels, 2) 0.038 wt.% vanadium with varying nitrogen levels and 3) 0.032 wt.% niobium with varying aluminum levels. Batch annealing soak temperatures ranged from 635 °C to 690 °C, simulating typical cold-spot and hot-spot temperatures for one grade. The steels were commercially melted, cast and hot-rolled, prior to laboratory processing.

The results confirmed earlier work showing reduced strength resulting from high aluminum levels in vanadium containing steels. This effect is presumed to be related to increased AlN precipitation in high aluminum steels, reducing the amount of nitrogen available to form V(C, N) strengthening precipitates. The vanadium steels with nitrogen variations exhibited incomplete recrystallization at the lowest annealing temperature, along with higher strength and finer grain size in the as-rolled condition when compared to the vanadium steels with aluminum variations. Since the two families had very similar nominal composition ranges, the differences may reflect unanticipated differences in processing or sampling procedures. The lower nitrogen steel exhibited a slightly higher strength and finer microstructure; this behavior was unexpected and is not fully understood, but may be a consequence of increased AlN precipitation resulting from the higher nitrogen level. It should be noted that the recrystallization and associated property variations between the simulated cold-spot and hot-spot conditions in the vanadium steels with nitrogen variations would be unacceptable for industrial cold-rolled products, and additional processing is underway to examine the behavior for a higher hot (and cold) spot temperature.

The family of niobium containing steels was less sensitive to variations in aluminum content, presumably due to the greater importance of carbide (rather than nitride) precipitation in niobium microalloyed steels when compared to vanadium microalloyed steels. The strengths were higher and the microstructures were finer in the as hot-rolled condition when compared to the vanadium steels, and the recrystallized grains at low annealing temperatures exhibited a more elongated morphology. The differences in strength and grain size between the vanadium and niobium families were less pronounced after recrystallization annealing. Further studies are needed to assess the continuous annealing response of these steels, and understand the precipitation sequences and mechanisms.

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