

Recent Developments of Vanadium Microalloyed Strip and Plate

David Neville Crowther¹

¹Vanitec

Hildenbrook House, The Slade, Tonbridge, Kent, UK, TN9 1HR

Phone: +44 (0) 7470 225997

Email: david.crowther@vanitec.org

ABSTRACT

Vanadium microalloying can be applied to a wide range of strip and plate products, and the relatively high solubility of vanadium carbides and nitrides confer numerous benefits. This paper will briefly summarize some of the more recent developments in vanadium containing strip and plate, emphasizing how vanadium precipitates generate microstructures with advantageous properties. In advanced high strength steels for automotive applications such as TRIP steels and dual phase steels, vanadium additions result in a microstructural refinement and an increase in strength. In dual phase steels, differential precipitation of vanadium between ferrite and martensite results in improvements to ductility and hole expansion. In high strength linepipe such as X80, the combination of vanadium and niobium microalloying results in improved toughness and weldability. The reduced mill loads associated with vanadium microalloying allow the production of high strength hot rolled strip with increased width and improved shape. High strength, thick normalized plates with yield strengths up to 460MPa can be produced using vanadium additions, the vanadium precipitates giving both grain refinement and precipitation strengthening.

Keywords: Vanadium, dual phase steels, strip steels, linepipe, plate, normalized

INTRODUCTION

Vanadium microalloy additions have been used for many decades to improve the properties of a wide range of steel types. The beneficial effects of vanadium can be due to precipitation of V(CN), which can result in precipitation strengthening and grain refinement, or due to increased hardenability from vanadium in solution. The relatively high solubility of V(CN) precipitates makes vanadium additions uniquely suited to a wide range of steels, from high carbon eutectoid and hyper-eutectoid rail and rod steels, to low carbon steels for automotive and linepipe applications.

Despite extensive study over many decades, research is still being carried out to develop new and improved vanadium microalloyed steels. In this paper, examples will be given describing recent research studying the role vanadium has in four very different types of flat steel products, namely dual phase (DP) steels, high strength strip steels, X80 linepipe steels, and thick, normalized plate steels.

DUAL PHASE STEELS

Dual Phase (DP) steels remain one of the most commonly used advanced high strength steels (AHSS) for automotive applications, and are used in parts such as bumpers and anti-intrusion components. They are used in the cold rolled and annealed condition (CRA), galvanized (GI) or galvannealed (GA) condition. As with other types of AHSS, there is a trend to producing higher strength DP steels, but also a desire to maintain and improve ductility, and in the case of DP steels, to improve the edge ductility, as measured by tests such as hole expansion. Low edge ductility has been seen as a weak point for DP steels, with the large hardness difference between the ferrite and martensite phases resulting in relatively low edge ductility.

Recent research has shown that vanadium additions to DP steels can result in a significant increase in strength and simultaneous benefits to edge ductility.⁽¹⁾ Vanadium additions to cold rolled and annealed DP steels result in a major refinement of microstructure. Fig. 1 shows the microstructural refinement associated with a vanadium addition of 0.15% to a CRA DP steel.⁽¹⁾ In this particular example, a relatively low coiling temperature of less than 600°C was used to ensure that the majority of

vanadium was in solution prior to annealing. During heating to the inter-critical annealing temperature, vanadium precipitation interacts with recovery, recrystallisation and partial transformation, and following rapid cooling, a fine-grained ferrite-martensite microstructure is formed.

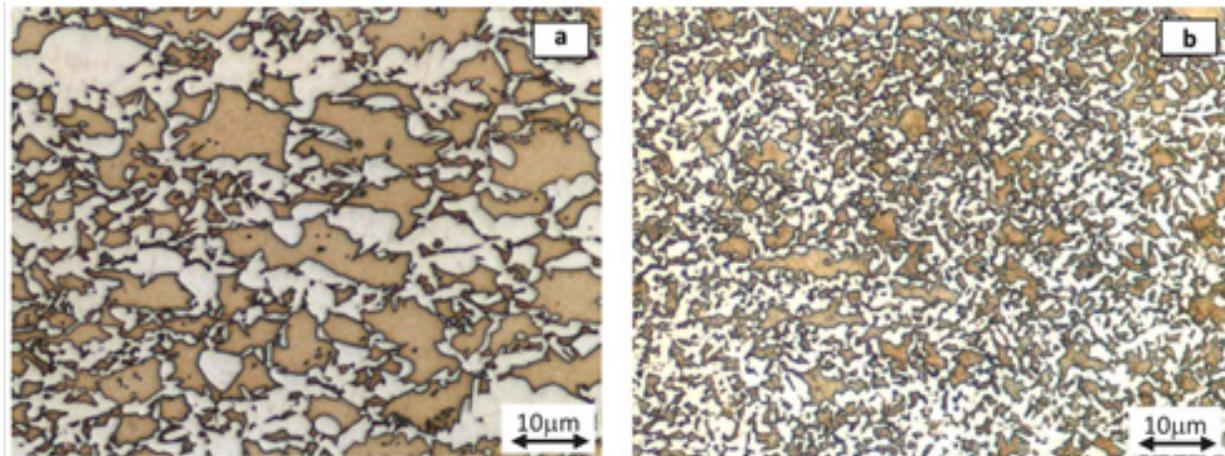


Figure 1. Refinement of microstructure associated with V addition in and cold rolled and annealed DP steel. (a) V free reference steel (b) 0.15%V addition.⁽¹⁾ Etched in Lepera revealing ferrite as tan color and martensite white.

Because of the solubility differences of V(CN) between ferrite and austenite, differences in precipitation are seen between the ferrite and martensite (originally austenite) phases (Fig. 2).⁽¹⁾ The ferrite phase contains extensive fine V(CN) precipitation, whilst the martensite phase shows a relatively small number of coarser V(CN) precipitates. Note that in the final microstructure, some ferrite can form during the rapid cool from the annealing temperature, depending on cooling rates and the hardenability of the steel. This epitaxial ferrite inherits the V(CN) precipitate distribution from the original austenite, and thus contains relatively few V(CN) precipitates.

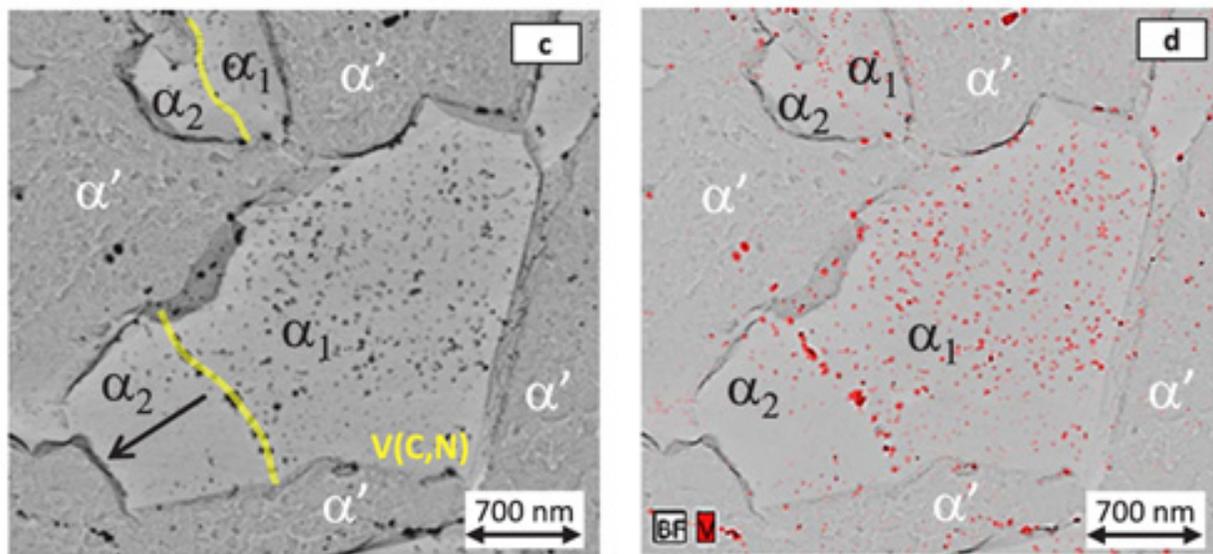


Figure 2. Carbon extraction replicas showing ferrite (α_1) martensite (α') and V(CN) precipitation. α_2 is epitaxial ferrite.⁽¹⁾

The V(CN) precipitation increases the hardness of the ferrite, and it is this increased ferrite hardness combined with the overall microstructural refinement that increases strength. Fig. 3 gives an example of the increase in strength associated with a V addition of 0.15% for various annealing conditions.⁽²⁾ In this example, UTS values in the range 1100-1200MPa have been achieved.

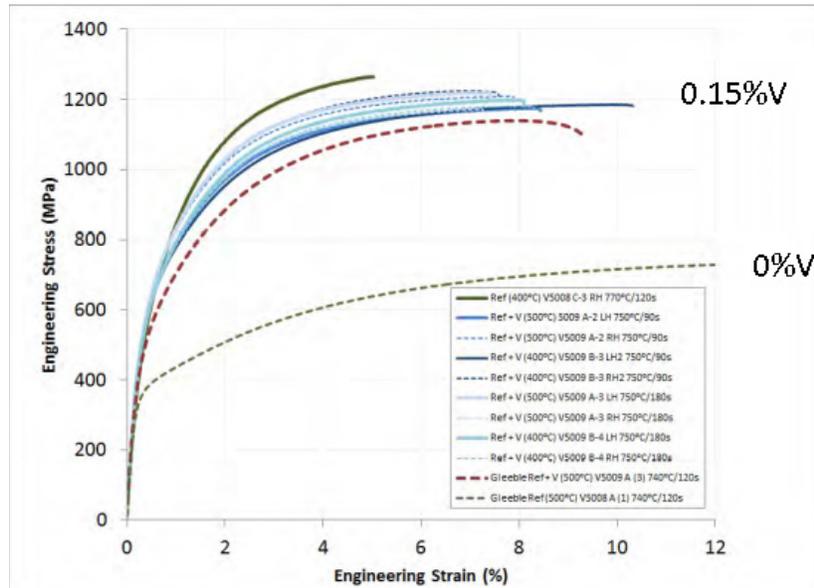


Figure 3. Increase of tensile strength associated with an addition of 0.15% vanadium. Various annealing conditions are shown for the 0.15% vanadium steel ⁽²⁾

In addition to ferrite hardening due to V(CN) precipitation, martensite hardness is reduced by the vanadium additions, as the martensite carbon content is reduced due to V(CN) formation. Fig. 4 shows the nano-hardness distributions for individual ferrite and martensite islands in a vanadium containing DP steel and a vanadium free reference steel. ⁽³⁾ It is clear that the hardness difference between ferrite and martensite has been reduced by the vanadium additions.

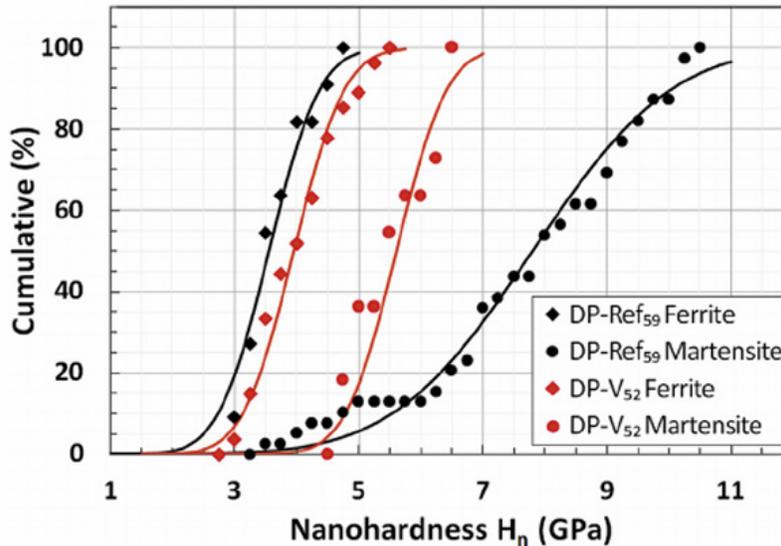


Figure 4. Nano hardness distribution for ferrite and martensite islands in reference steel and vanadium containing steel. Reference steel contains 59% martensite, vanadium steel contains 52% martensite. ⁽³⁾

This in turn leads to reduced strain concentration in the softer ferrite phase during deformation, and an improvement in edge ductility. Fig. 5 shows that for a given tensile strength, vanadium containing DP steels have a higher hole expansion coefficient than a reference steel containing no vanadium. ⁽¹⁾

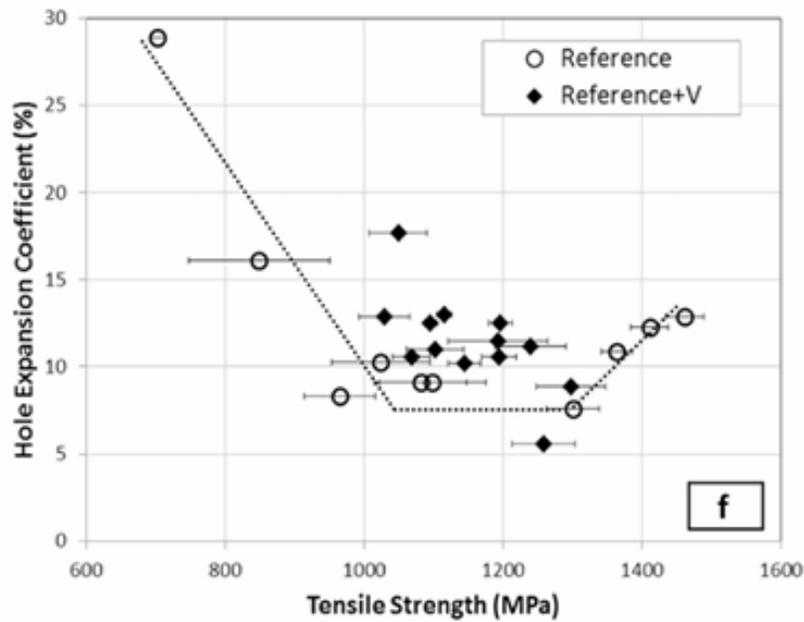


Figure 5. Hole expansion coefficient as a function of tensile strength for reference steel and V steel.⁽¹⁾

THIN HIGH STRENGTH HOT ROLLED STRIP

There is an increasing demand for thin, high strength hot rolled strip to be used for light structural designs and tubing. Yield strengths of approximately 355MPa and above can be readily achieved using vanadium or niobium microalloying with appropriate additions of carbon and manganese and suitable processing parameters on the hot strip mill. However, at thin gauges, 3mm and below, excessive mill loads can lead to poor strip shape, high roll wear, and necessitate the use of reduced coil width. The problems of high mill loads can be more of an issue with niobium steels, as niobium additions delay austenite recrystallisation during rolling, due to a combination of Nb(CN) precipitation and niobium in solution. However, the unrecrystallized austenite is very effective at increasing ferrite nucleation sites, and as a result, very fine ferrite grain sizes are produced after transformation, giving high strength. Vanadium is not as effective at delaying austenite recrystallisation, but fine V(CN) precipitation during and after transformation allows high strengths to be achieved. The limited effect of vanadium on austenite recrystallisation means that rolling loads are reduced.

Production trials were carried out on a hot strip mill to compare the mechanical properties of vanadium and niobium hot rolled strip steels, and assess the rolling performance in terms of strip width, rolling loads and shape.⁽⁴⁾ The compositions assessed are shown in Table 1. The vanadium steel also employed increased nitrogen contents, as there is well known synergy between vanadium and nitrogen in terms of increased strength.

Table 1. Compositions of steels for hot strip mill production trials (wt.%).

Steel	C	Mn	Si	V	Al	Nb	N	P	S	Ti	Cr	Ni
VN	0.075	0.9	0.19	0.054	0.03	0.001	0.010	0.010	0.002	0.002	0.04	0.02
Nb-Ti	0.064	0.8	0.04	0.001	0.02	0.027	0.004	0.009	0.004	0.015	0.04	0.03

A series of strips were hot rolled to a thickness in the range 1.5 to 2.5mm and coil widths in the range 1010mm to 1255mm. Finish rolling temperatures were in the range 840-880°C, and coiling temperatures in the range 575-625°C. For both vanadium and niobium steels, microstructures were fine grained ferrite-pearlite, with the niobium steel having a slightly finer grain size. The variation of yield and tensile strength with strip thickness are shown in Fig. 6.⁽⁴⁾

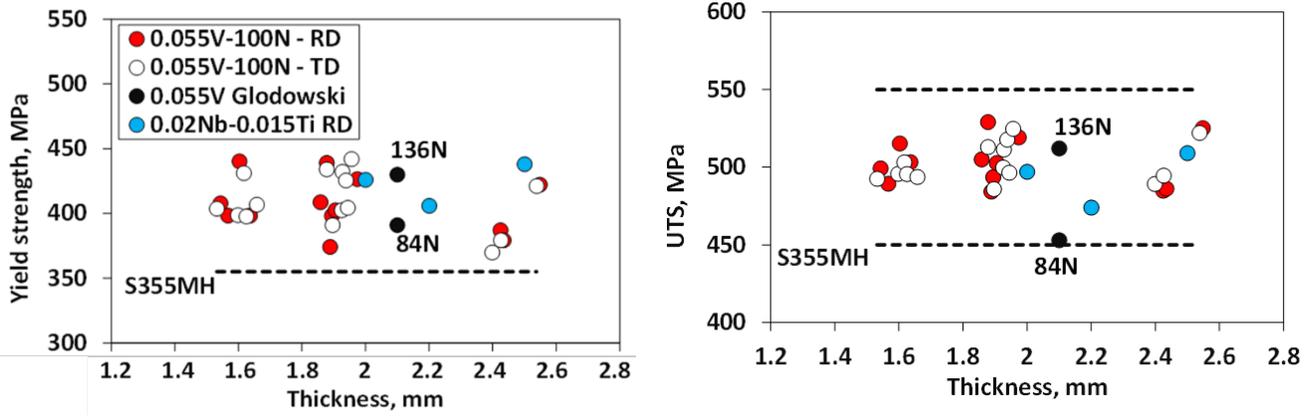


Figure 6. Variation of yield strength and tensile strength with thickness for vanadium steel (red and open symbols) and niobium steel (blue symbol). Black symbols are predicted strengths for different N contents. RD tests parallel to rolling direction, TD transverse to rolling direction

There were no significant differences in strength between the vanadium and niobium steels, and both steel types comfortably achieved a yield strength greater than 355MPa and tensile strengths were within the range required for standards such as EN 10210-3 S355MH.⁽⁵⁾ The vanadium steel also showed very isotropic strengths, with little difference between longitudinal and transverse testing directions. For the vanadium steel, V(CN) precipitation strengthening has compensated for the slightly larger grain size than that of the niobium steel to give a similar strength.

Fig. 7 gives examples of some of the rolling parameters from industrial trials of 2.5mm thick vanadium and niobium steels during finish rolling. The widths of the vanadium and niobium steel stripes were 1255mm and 1205mm respectively.⁽⁴⁾ Fig. 7a shows the variation of strain rate and mean flow stress (MFS) with rolling pass. The niobium steel showed significant variation in MFS, as strain accumulation was eventually relieved by dynamic and/or metadynamic recrystallisation (DRX/MDRX). Rolling temperatures were slightly higher for the niobium steel (Fig. 7b), but despite this the rolling force per unit strip width (Fig. 7c) was generally higher for the niobium steel than the vanadium steel.

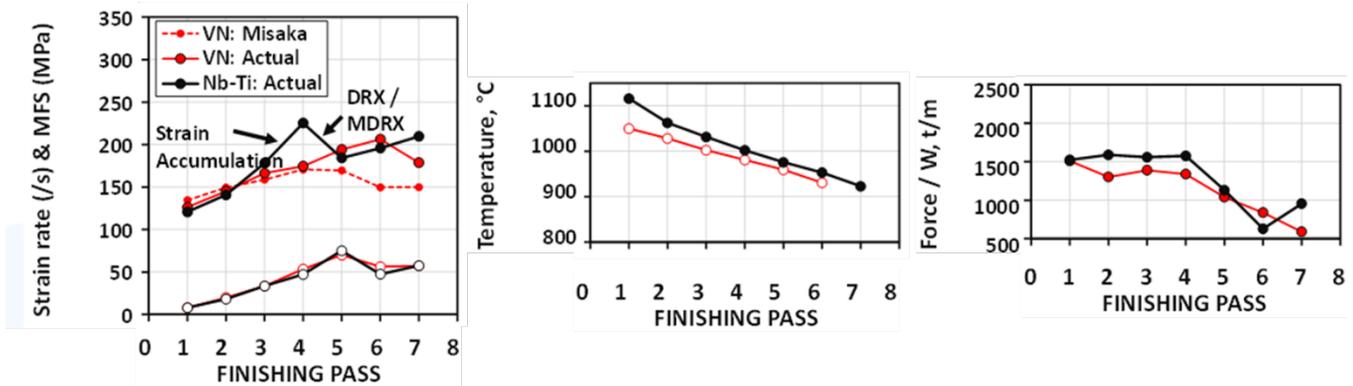


Figure 7. Variation of (a) strain rate and mean flow stress (MFS), (b) rolling temperature and (c) rolling force/width for different rolling passes for vanadium and niobium steels.

It was concluded that similar properties could be achieved in hot rolled vanadium strip steels to those of niobium steels, but the lower rolling loads experienced by the vanadium steels could have benefits in terms of strip shape, and the ability to roll wider strip.

X80 LINEPIPE STEELS

The rapidly developing economy in China has resulted in high demand for oil and gas transmission pipelines. China has employed large quantities of high strength X80 linepipe, and by the end of 2020, it has been estimated that approximately 20,000km of X80 linepipe had been installed. The X80 composition used typically has a high niobium content in the range

0.065-0.08%, together with a low carbon content and alloying additions such as molybdenum, chromium and nickel. When combined with appropriate thermo-mechanical processing conditions, this composition is capable of achieving excellent combinations of pipe strength and toughness. However, particularly during the girth welding of linepipe in the field, there have been a number of weld failures. It has been suggested that these failures are associated with poor weld heat affected zone (HAZ) toughness, and that the high niobium content contributes to the formation of low toughness HAZ microstructures containing, for example, martensite-austenite (MA) constituents. In an attempt to improve weld HAZ toughness and hence eliminate weld failures, an alternative X80 linepipe composition has been developed, in which niobium has been partially replaced with vanadium. ⁽⁶⁾

Following a series of laboratory trials, a number of plant trials have been carried out to assess both the parent pipe properties, and weld HAZ properties of the new Nb+V X80 composition, and make comparisons with conventional Nb only X80 composition. Table 2 shows the composition of two Nb+V X80 composition used for pipe production trials, together with an example of the conventional X80.

Table 2. Steel compositions for X80 linepipe plant trials (wt.%).

Steel	C	Si	Mn	Ni	Cr	Mo	Nb	V	Ti	Pcm
Conventional	0.054	0.24	1.70	0.20	0.24	0.21	0.081	residual	0.019	0.18
Nb+V 1	0.051	0.22	1.73	0.17	0.24	0.20	0.062	0.024	0.016	0.18
Nb+V 2	0.060	0.23	1.77	0.16	0.25	0.20	0.062	0.033	0.017	0.19

The steels were hot rolled to strip of thickness 12.5mm, using finish rolling temperatures in the range 800-840°C and low coiling temperatures in the range 400-460°C. The microstructures were similar for all three steels, and consisted of mixtures of acicular and polygonal ferrite, with an average grain size in the range 5-6µm. The dislocation density was slightly higher in the Nb+V steels, and the lath width slightly finer. Fine V(CN) precipitates were also observed in the Nb+V steels. The hot rolled strip properties are summarized in Table 3.

Table 3. Mechanical properties of X80 linepipe steels.

Steel	Rt 0.5	Rm	Rt0.5/ Rm	A	Charpy energy @-20°C, J				DWTT @-20°C, fibrous fracture, %			Hardness
	MPa	MPa		%	1	2	3	Average	1	2	Average	HV10
Conventional	564	699	0.81	29	340	335	374	350	100	90	95	220
Nb+V 1	584	683	0.86	25	362	375	358	365	100	100	100	237
Nb+V 2	595	725	0.82	26	347	361	356	355	100	100	100	244
Requirement	555- 675	625- 765	≤0.91	≥16	Average ≥210				Minimum ≥70%, average ≥85%			≤265

Table 3 shows that all tensile and impact toughness requirements have been met. The Nb+V steels had slightly higher yield strength than the conventional Nb X80 steel, and slightly higher Charpy and drop weight tear test values. Initial weld evaluations have used thermal simulations of submerged arc welding, with different peak temperatures being used to simulate different parts of the weld HAZ. Fig. 8 indicates Charpy toughness and microhardness at different peak temperatures after weld HAZ simulation for a steel containing 0.03% niobium and 0.05% vanadium. Charpy toughness showed minimum values for peak temperatures of 700 and 800°C, which correspond to the sub-critical and inter-critical HAZ. At these peak temperatures, martensite-austenite (MA) islands were observed, which are associated with low toughness. However, even the lowest Charpy values were very good, at approximately 180J at -20°C. There was some evidence of weld HAZ softening, with minimum hardness values corresponding to a peak temperature of 900°C, roughly corresponding to the fine grained HAZ.

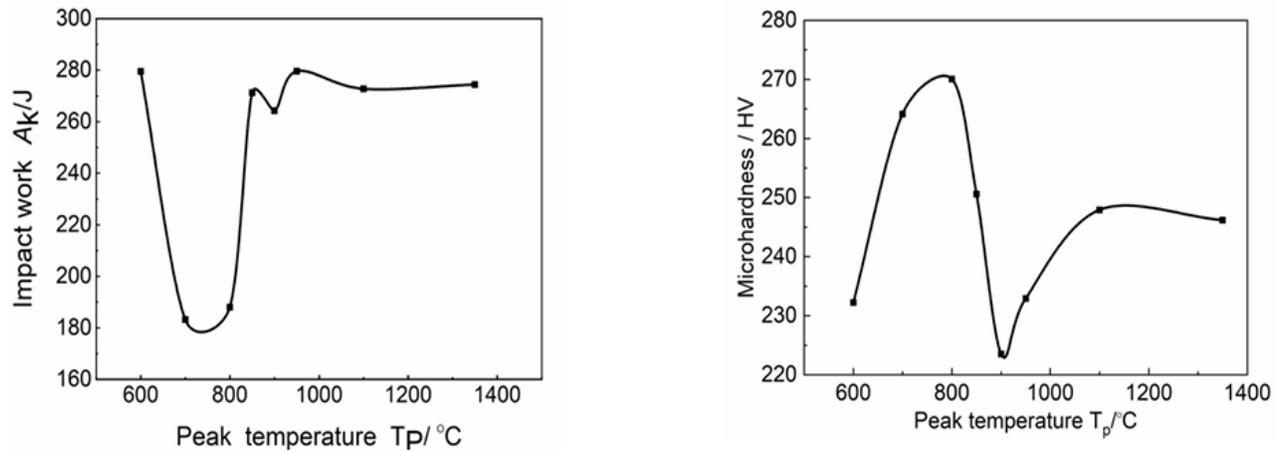


Figure 8. Variation of Charpy impact toughness (-20°C) and microhardness with peak temperature after weld HAZ thermal simulation for 0.03%Nb + 0.05%V steel.

Further work is underway to characterize pipe properties, and to evaluate properties after girth welding, and it is planned to use spiral welded pipe using the Nb+0.03%V composition for a major gas transmission project in China.

HIGH STRENGTH NORMALIZED STEELS

There is an increasing demand for high strength normalized steels for the production of pressure vessels in the rapidly growing Indian economy. The normalizing process, whilst adding extra cost, results in a fine grained uniform microstructure with high toughness and microstructural stability which allows high elevated temperature strengths to be achieved, an important requirement for some pressure vessel grades. Pressure vessel standards such as EN 10028 also put limits on carbon equivalent values (CEV) to ensure good weldability.⁽⁷⁾ Whilst yield strengths of approximately 355MPa can be achieved using microalloying with niobium alone, for higher yield strengths such as 420 and 460MPa, an alternative microalloying strategy is required. This is particularly so for thicker plates, for which slower cooling rates from the normalizing temperature make achieving a fine grain size more difficult. To address the problem of achieving high yield strengths (420 and 40MPa) in thick, normalized plate, a research project was carried out in conjunction with Indian steel companies and academic institutes using microalloying with both niobium and vanadium.⁽⁸⁾

To achieve the required yield strengths in the normalized condition whilst maintaining a low CEV requires a fine-grained ferrite pearlite microstructure in combination with some precipitation strengthening. At typical normalizing temperatures of approximately 900°C , Nb(CN) precipitates are mostly not in solution. The size of these Nb(CN) precipitates is adequate to give austenite grain boundary pinning at the normalizing temperature, resulting in fine ferrite grains after cooling, but these Nb(CN) precipitates are too large to give sufficient precipitation strengthening. The solubility of V(CN) is much higher than that of Nb(CN), so that provided appropriate combinations of vanadium, carbon and nitrogen are selected, at the normalizing temperature, V(CN) will be partly in solution. Thus in this case the role of vanadium is twofold: firstly some V(CN) will be present as precipitates at the normalizing temperature, and together with Nb(CN) will result in austenite grain boundary pinning; and secondly the vanadium in solution at the normalizing temperature is available to precipitate in a fine form during cooling from the normalizing temperature, giving precipitation strengthening. To optimize the composition further, it is important to select the appropriate nitrogen and aluminum contents. An elevated nitrogen content has been found to be beneficial, as this results in a higher volume fraction of VN precipitates at the normalizing temperature, which promote a fine austenite grain size, and hence fine ferrite grain size. Reduced aluminum contents can also be beneficial, as this reduces the amount of AlN formed at the normalizing temperature. AlN precipitates have been found to be coarser than VN, and hence less effective at pinning austenite grain boundaries.

To determine optimum compositions, a number of laboratory melts were produced and rolled to 20mm thickness. The composition of three of these laboratory steels is given in Table 4.

Table 4. Lab. melt compositions (wt.%).

Steel Type	C	Mn	Si	V	P	S	Al	N	Nb
0.15V-90N	0.20	1.42	0.12	0.15	0.015	0.006	0.015	0.009	-
0.15V-150N	0.20	1.41	0.11	0.15	0.012	0.006	0.008	0.015	-
0.03Nb-0.1V 100N	0.19	1.53	0.25	0.10	0.016	0.006	0.02	0.010	0.03

The 20mm plates were normalized at 900°C, and then slow cooled at a rate of 10°C/min, which approximates the cooling rate of a 65mm air-cooled plate. To determine the austenite grain size at the normalizing temperature, separate samples were quenched from 900°C to produce a martensitic microstructure, and then etched in picric acid to reveal the prior austenite grain structure. Fig. 9a shows the austenite grain size at the normalizing temperature, and the ferrite grain size in the normalized condition for all three steels. The finest austenite and ferrite grain sizes were observed in the 0.1V-0.03Nb steel, believed to be due to an optimum distribution of VN and Nb(CN) to restrict austenite grain growth. Tensile properties of the three steels in the normalized condition are shown in Fig. 9b. Tensile strengths were similar for all three steels, in the range 575-595MPa, but the 0.1V-0.03Nb steel had the highest yield strength of 475MPa.

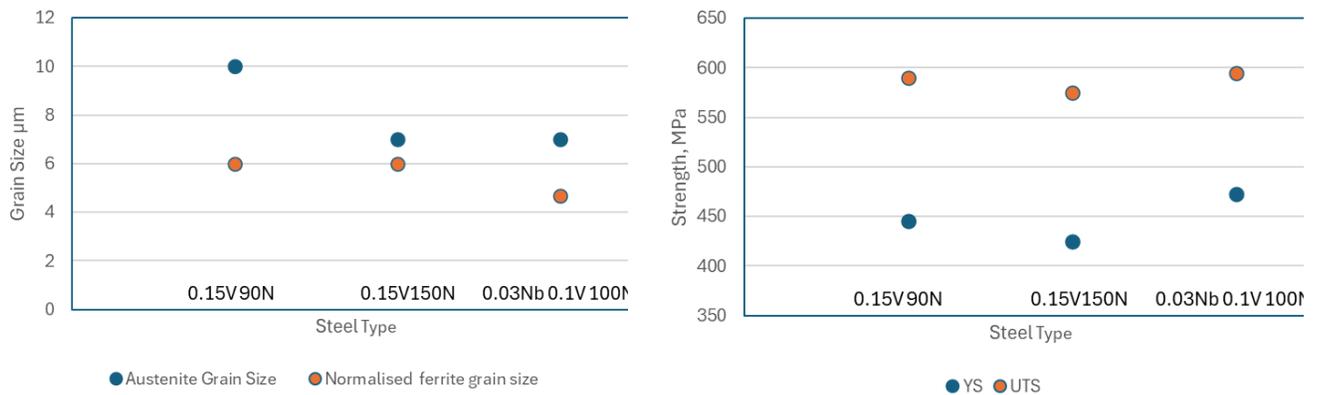


Figure 9. Variation of austenite and normalized ferrite grain size for different steel types (a) and variation of normalized yield and tensile strength for different steel types (b)

Based on the results of the laboratory studies, a Nb-V-N composition was selected for full scaled industrial trials. A small addition of nickel was also included to improve strength and toughness. The composition chosen is shown in Table 5.

Table 5. Composition of industrial trial (wt. %).

C	Mn	Si	V	P	S	Al	N	Nb	Ni
0.18	1.55	0.46	0.13	0.015	0.003	0.015	0.009	0.02	0.2

Plates were rolled to 90mm thickness and normalized at 890°C. A fine grained ferrite-pearlite microstructure was obtained with a ferrite grain size of 5-6µm. Tensile and Charpy properties are summarized in Table 6. The combination of tensile and Charpy properties meet the requirements for 90mm thick plate for grades such as P460N in standard EN 10028.

Table 6. Properties of 90mm thick normalized plate, industrial trial.

YS, MPa	UTS, MPa	A, %	Average Charpy energy at -50°C, J
455	620	26	110

SUMMARY AND CONCLUSIONS

Four examples have been given of recent developments in the use of vanadium microalloying in flat products. The relatively high solubility of V(CN), and the limited hardenability effects of vanadium in solution confer advantages in certain situations, and enable unique properties to be obtained. In dual phase steels, the difference in solubility of V(CN) in ferrite and austenite, and the relatively high solubility of V(CN), enables high strength steels with enhanced edge ductility to be produced. In thin hot rolled strip, the limited influence of vanadium on austenite recrystallisation during hot rolling reduces mill rolling loads compared with niobium steels, with potential benefits to strip shape and the ability to roll wider strip. In X80 linepipe steels, the combination of vanadium and niobium microalloying allows high strength, high toughness linepipe to be produced with enhanced weldability. Finally thick, normalized high strength plates can be produced with vanadium and niobium microalloying, the combined microalloy additions producing a fine grain size, and the high solubility of V(CN) at the normalizing temperature resulting in precipitation strengthening in the final normalized plate.

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