

Use of Vanadium in Long Steel Products

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Vanadium has been widely used in long steel products such as forging grades, reinforcing bars, sections, tubes, rails, springs and wire rods. Vanadium is the preferred addition in long steel products because of the much higher solubility of its carbonitrides in austenite and **lower** sensitivity to carbon level compared to niobium and titanium. Vanadium provides precipitation strengthening and grain refinement, resulting in good combinations of strength and toughness. The precipitation strengthening can be maximized by management of nitrogen level and the preferential precipitation of vanadium with nitrogen also minimizes the risk of nitrogen strain aging. In addition, vanadium enables desired strength levels **to be attained** at lower carbon content, which is beneficial **for** ductility and weldability. Furthermore, vanadium contributes to temper resistance and provides secondary hardening for quenched and tempered steels. Fine vanadium carbides also act as strong trap sites for diffusible hydrogen, leading to good delayed fracture resistance.

The relatively low solution temperature of vanadium carbonitrides permits the use of energy efficient, low reheating temperatures. Conventional hot rolling or forging with high finish working temperatures, which are inevitable for production of long steel products, can be used for vanadium microalloyed steels to achieve **the** required mechanical properties and service performance. In addition, the properties of vanadium microalloyed steels are relatively insensitive to changes in processing conditions.

Keywords: Vanadium microalloyed steel, precipitation strengthening, grain refinement, hydrogen trapping, long steel product

1. Microalloying Choice for Long Products

Microalloying has been increasingly used in long steel products to increase strength and eliminate expensive heat treatment steps while maintaining adequate performance. Microaddition of vanadium is predominant in long steel products because of the significantly greater solubility of V(C,N) in austenite compared to niobium and titanium. The high solubility of V(C,N) in austenite minimises the risk of cracking during continuous casting and permits the use of conventional hot rolling or forging practices, which take place in the recrystallized austenitic phase, followed by air cooling, to produce the desired microstructure and properties. Vanadium is fully dissolved in the austenite during normal reheating temperatures (1150°C-1250°C), either for rolling or forging over the entire spectrum of carbon concentrations relevant to long products as shown in figure 1. Vanadium exhibits relatively lower solute drag coefficient in austenite compared to other microalloys, therefore vanadium microalloyed steels recrystallize during hot rolling or forging and austenite grains are refined by repeated recrystallization. The majority of vanadium added to steels remains in solution in austenite up to the start of transformation from austenite to ferrite and precipitates in ferrite as fine V(C,N) particles during/after the austenite to ferrite transformation, providing substantial and predictable precipitation strengthening regardless of carbon content.

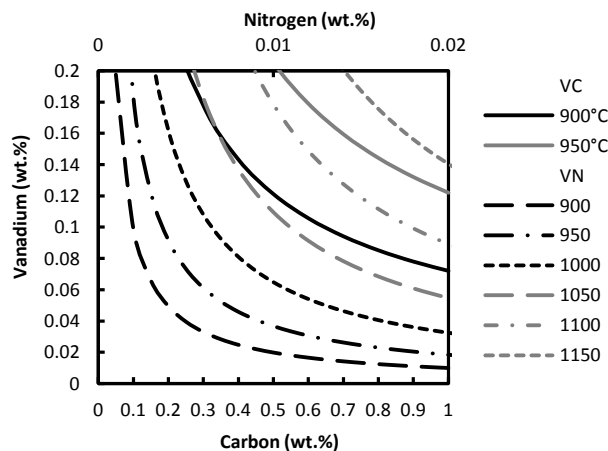


Fig. 1 Solubility isotherms of VN and VC in austenite and the solubility products used to calculate the isotherms are according to Tukdogan^[1]

Niobium carbonitride has lower solubility in austenite than vanadium, therefore niobium is normally used in steel to produce fine grained microstructures by precipitating in austenite to prevent recrystallization during

conventional controlled rolling (CCR), which involves final rolling at temperatures below the recrystallization stop temperature. However, CCR is difficult to apply to long steel products, which are rolled on high speed mills and often finished at 1000°C or higher. In addition, the reduction of the rolling temperature brings an increase of the rolling loads and many mills are not designed to resist the addition stresses. CCR also increases rolling time and adversely reduces productivity, because it is often necessary to incorporate a delay in the rolling schedule to achieve the temperature required to avoid recrystallisation. The low solubility of Nb(C,N), as shown in figure 2, restricts the use of niobium in long steel products, especially with medium and high carbon content, since it significantly reduces the efficiency of precipitation strengthening from niobium microalloying. The precipitation of Nb(C,N) particles on as-cast austenite grain boundaries causes a decrease in hot ductility at a temperature of about 750°C. This low ductility, when combined with the bending stress of the casting machine, results in surface cracking in continuously cast steels. The amount of Nb(C,N) dissolved during conventional reheating is limited and dependent on reheating temperature and the amount of carbon and nitrogen present, therefore the precipitation strengthening effect of niobium is weak and unpredictable. In addition, Nb present in solid solution in coarse grained austenite before the transformation may contribute to bainitic transformation during cooling after rolling or forging, resulting in poor bendability and low toughness.

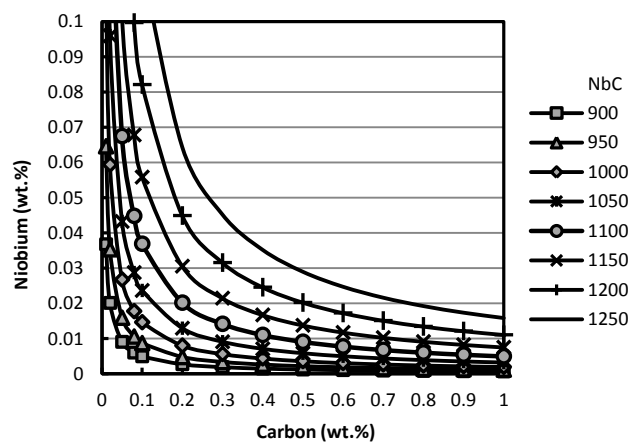


Fig. 2 Solubility isotherms of NbC in austenite and the solubility products used to calculate the isotherms are according to Tuskdogan [1]

Titanium (<0.02wt.%), which forms stable TiN in austenite, is added in steel to control austenite grain size during reheating and after hot rolling or forging. To achieve effective titanium nitride dispersion, the Ti/N ratio should be lower than the stoichiometric ratio of 3.42. Titanium is a very strong nitride former and with higher titanium contents, large TiN particles (1-5µm) can form in liquid steel. These large TiN particles are not useful for grain refinement, but detrimental to toughness, acting as cleavage fracture nucleation sites. In addition, fast solidification (continuous casting) is necessary to produce a fine distribution of TiN particles.

2. Contribution of Vanadium to Mechanical Properties and Performance of Long Steel products

Strength

Vanadium addition to long steel products increases strength mainly through precipitation strengthening. Because of the high solubility of V(C,N) in austenite, most of the vanadium in steel is available to precipitate in ferrite during/after the austenite to ferrite transformation as finely dispersed VN or V(C,N) and provides significant contribution to strength. Vanadium addition up to 0.20% can be used to provide near linear increase in yield strength and the increment has been reported to be 10-20 MPa per 0.01% vanadium addition. The precipitation strengthening can be enhanced by optimizing the vanadium to nitrogen ratio in the steels to approach the stoichiometric ratio of 4:1. It is well established [1] that VN has a considerably lower solubility than VC, both in ferrite and in austenite. The chemical driving force for nucleation of VN is much larger than for VC and the larger chemical driving force makes VN or N-rich V(C,N) the preferred precipitation as long as there is sufficient nitrogen in the matrix. Nitrogen has a strong effect in increasing the driving force for nucleation of VN or N-rich V(C,N), which results in a finer particle size, higher density of the particles and decreased particle coarsening tendency in steels with higher nitrogen content [2]. An increase of yield strength of 7 MPa for every 10 ppm nitrogen added (when N is less than stoichiometric V:N) has been extremely consistent as reported by multiple

investigators [3]. As a consequence, the required strength level can be achieved with less vanadium content. An example is given in figure 3 showing the effects of vanadium and nitrogen additions to medium carbon forging steels [4]. However, any nitride former, such as titanium or aluminium, that has a thermodynamic preference for nitrogen is capable of reducing the amount of nitrogen which is available for precipitation strengthening. There are several reports of reduction in strength of V-Ti steels when compared with a corresponding V steels [5], and the formation of large TiN particles at high temperatures was considered to be responsible for the reduction in yield strength, by removing nitrogen in the formation of TiN particles and therefore decreasing the driving forcing for the development of a high density of fine dispersion strengthening VN precipitates. AlN has lower solubility than VN, making it a competitor to V for the available N. Precipitation of AlN during cooling is very sluggish, however, AlN does form quickly during a reheat cycle. Therefore, reheating temperature should be high enough to dissolve all AlN particles, since any undissolved AlN prior to the transformation will reduce the effective N available for strengthening [3].

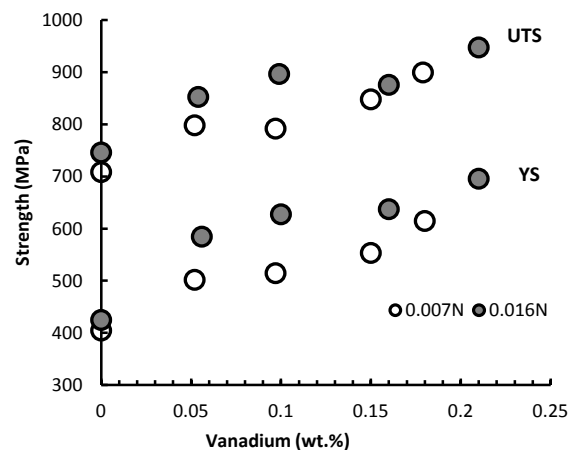


Fig. 3 Effects of vanadium and nitrogen on the strength of steels containing 0.41%C and 1.50%Mn [15]

In addition, there is evidence that the vanadium, which is in solution just before the austenite to ferrite transformation starts, produces a further contribution to the strength of pearlitic steel by decreasing the interlamellar spacing for a given cooling rate [6,7].

Furthermore, for quenched and tempered steels, vanadium dissolved in the austenite during austenitization is in a solid solution state supersaturated in a martensite structure after quenching. When tempering at low temperatures, vanadium increases softening resistance by retarding recovery and recrystallization and slowing down the formation and growth of Fe₃C [8]. When tempering is carried out at a temperature of 450°C or above, vanadium precipitates as a fine dispersion of vanadium carbides, which produce secondary hardening.

Ductility and Toughness

Vanadium in long steel products plays a very important role in the refinement of ferrite, which is beneficial to both of strength and toughness. This beneficial effect of vanadium has been related to: (1) VN precipitated directly in austenite or on MnS inclusions promotes nucleation of ferrite both inside the austenite grains [9] and at the grain boundaries [10]. (2) Vanadium enhances ferrite nucleation by slowing down the austenite to ferrite transformation and therefore giving more time for ferrite nucleation as a consequence of a particle pinning effect associated to interphase precipitation of V(C,N) [11].

Vanadium has a relatively low solute drag coefficient relative to other microalloys, therefore, it is easier to get complete recrystallization of the austenite during rolling. Therefore, vanadium microalloyed steels exhibit a uniform grain size and consistent mechanical properties over a wide range of part sizes and shapes. Tanniru, et. al. [12] used stereological analysis to quantify the microstructure and relate it to the strength-toughness combination of two industrially processed V-Nb-Ti and V microalloyed steel beams with a ferrite-pearlite microstructure. The results showed that the core and flange sections of the V steel are characterised by a marginally finer ferrite grain size and narrower grain size distribution, finer pearlite interlamellar spacing and its distribution, and more uniform distribution of pearlite colony size, in comparison with respective core and flange sections of the V-Nb-Ti steel. The steels have similar average yield strength, which is ~375 for the V-Nb-Ti steel and ~363 MPa for the V steel

and an elongation of ~20%. However, the microstructural features of the V steel result in ~15% ~and 40% higher impact energy, respectively, than the corresponding flange and core sections of the V–Nb–Ti steel, as shown in figure 4. The flange section of the V–Nb–Ti steel exhibits the highest grain boundary surface area compared with its core section and core and flange sections of the V steel, but it has lower impact energy than that of the corresponding V steel, because of a non-uniform grain size distribution.

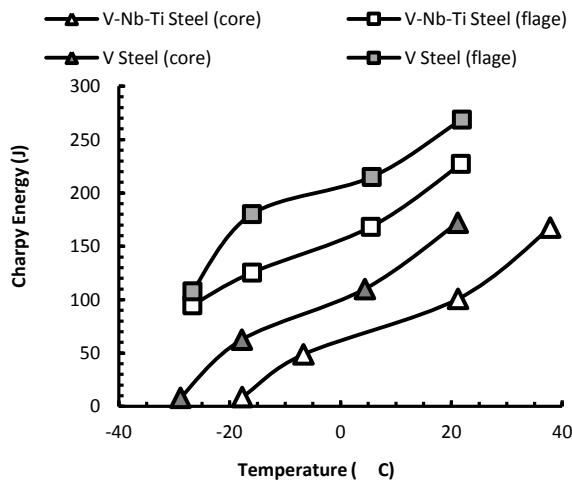


Fig. 4 Charpy impact energy versus temperature plots for core and flange sections of the V-Nb-Ti steel and the V steel

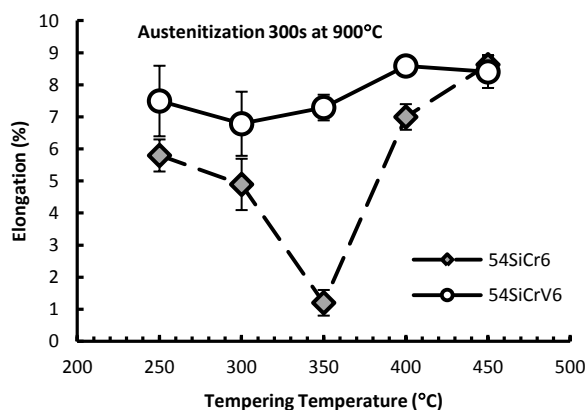


Fig. 5 Elongation to fracture of 54SiCr6 and 54SiCrV6 for different tempering temperatures^[13]

Addition of vanadium can also be used to refine the austenite grain size during austenitization. Austenite grain size before quenching plays an important role in controlling the toughness and ductility of martensitic steels, since the austenite grain size determines the martensitic packet size, which controls the propagation of cleavage fracture. Undissolved V(C,N) precipitates during austenitization prevent austenite grain coarsening and refine austenite grain size. Ardehali Barani, et. al.^[13] showed that addition of 0.163% vanadium to a conventional heat treated spring steel (55SiCr6) results in a superior combination of strength and ductility. The austenite grain size is much smaller in the vanadium containing steel (54SiCrV6) than that in Steel 54SiCr6 after austenitization at 850-900°C. As a consequence, the average effective grain size, which is defined as the area enclosed by high angle grain boundaries (grain boundaries with a misorientation larger than 15°), is refined in Steel 54SiCrV6 compared to that in Steel 55SiCr6. For example, the average effective grain size is 7.5 μm in Steel 54SiCrV6 and 30.5 μm in Steel 55SiCr6 after austenitizing at 900°C for 300s, quenched and tempered at 350°C for 1 h. The grain refinement in Steel 54SiCrV6 leads to significantly higher ductility compared to Steel 55SiCr6 after the quenching and tempering, as shown in figure 5. Moreover, Steel 55SiCr6 has minimum ductility value at tempering temperature of 350°C, but Steel 54SiCrV6 shows no minimum. The loss of ductility observed in the vanadium free steel after tempering at 350°C is suggested to be related to the formation of cementite films at prior austenite grain boundaries, which act as slip barriers and are sources for crack initiation. Such cementite films are absent in the vanadium containing steel.

Hydrogen trapping

Vanadium is widely used in ultra high strength steel products such as bolts and springs to provide good resistance to delayed fracture^[14,15]. Delayed fracture results from a very small amount of diffusible hydrogen that come into steel during steel production processes welding, surface or heat treatments, corrosion etc. Delayed fracture is one of the key factors that obstruct the strengthening of steels, because delayed fracture susceptibility increases as the strength of steel increases. However, it is found that delayed fracture can be avoided by using vanadium in steels since fine vanadium carbides formed during proper tempering are able to trap most of the hydrogen in steel and retard hydrogen diffusion to prior austenite grain boundaries, therefore, reducing hydrogen concentration at the tip of cracks^[16]. Vanadium carbide has a f.c.c NaCl-type structure and ideally vanadium carbide should be represented as VC. However, it has lattice defects in which some of the sites for carbon are unfilled, therefore, V₄C₃ predominates in steel^[17]. It is suggested that those empty carbon sites of the V₄C₃ may be the physical trap sites for diffusing hydrogen. Asahi et al.^[18] showed the de-trapping of hydrogen is very slow while the trapping presumably proceeds rapidly in a V-added steel with tempered martensite structure and the density of hydrogen trapping sites decides the maximum trapped-hydrogen content. For 1% V steel tempered at peak secondary hardening temperature, the maximum trapped-hydrogen content is 9 ppm. A recent study carried out by University of Cambridge^[19] using thermal desorption analysis to investigate the type of hydrogen traps present in the microstructure of two bearing steels also demonstrated that the 100Cr6+V (0.5% V) steel displayed a very high trapping capacity compared to the baseline steel, 100Cr6. The 100Cr6 steel displayed a peak at 188°C, believed to appear due to dislocation trapping, whereas a peak at 219°C in the 100Cr6+V steel is ascribed to hydrogen trapped by V₄C₃.

Conclusions

Vanadium is an essential element in a wide variety of long steel products, providing good combinations of mechanical properties and enabling easy processing to be achieved across the full range of carbon contents and in a multitude of section sizes and formats.

The ease of use and consistent performance of vanadium clearly differentiates it from other microalloying elements and makes it the preferred addition in long steel products to be used in the air cooled condition after rolling or forging.

Nitrogen is an important addition to vanadium microalloyed steels in order to maximise mechanical properties and utilise vanadium in the most efficient and cost effective manner.

In high strength quenched and tempered steels vanadium precipitation is exploited to retard softening and maintain ductility, and can also play a vital role in mitigating the harmful effects of hydrogen in specific applications.

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