The Use of Vanadium in High Strength Low Alloy Steels

David N. Crowther, Yu Li

(Vanitec, Kent, UK)

Abstract: The microalloying elements V, Nb and Ti are commonly used to improve the properties of HSLA steels. Of these three microalloying elements, the carbides and nitrides of V have the highest solubility, and this influences the steel types in which V is used, and how they are processed. This paper will review the use of V in HSLA steels and give recent examples of how the high solubility of V carbides and nitrides is utilised in a range of steel types. V additions are well suited to medium and high carbon steels, as the high solubility of V carbo-nitrides, V(C,N), enables the formation of the fine precipitates necessary for precipitation strengthening. In concrete reinforcing bar, V(C,N) precipitation strengthening allows high strengths to be obtained combined with weldability and high ductility for use in seismic zones. In direct forging steels, V additions enable costly quench and temper heat treatments to be eliminated, and in bainitic forgings, increased hardenability allows improved properties to be achieved over a wider section size. V additions to rail steels have been shown to significantly increase rail life, and in wire rod steels, V not only increases strength, but decreases the formation of coarse grain boundary cementite which is detrimental to ductility. In low carbon steels, increased V additions allow significant volume fractions of fine precipitates to be produced, giving exceptionally high precipitation strengthening. This allows high strength single phase ferritic steels to be produced with excellent edge ductility for the automotive sector. At low processing temperatures such as those used for hot forming of structural hollow sections or the annealing of cold rolled dual phase steels, V(C,N) still has sufficient solubility to produce useful precipitation strengthening, and also significant grain refinement. Finally the high solubility of V(C,N) allows reduced reheating and equalisation temperatures to be used prior to rolling, and limits precipitation in austenite. This results in reduced cracking during continuous casting, and gives a minimal increase in rolling loads which allows increased rolling rates and the production of wider material.

Key words: vanadium, precipitation, mechanical properties, processing, products

1 Introduction

The properties of High Strength Low Alloys (HSLA) steels are strongly influenced by the presence of M(C,N) precipitates, where M is a microalloying element such as V, Nb or Ti. These precipitates can act to control grain size and provide precipitation strengthening via the Ashby-Orowan mechanism. Any proportion of the microalloying element which is not contained within M(C,N) precipitates may also influence microstructural development in solid solution.

M(C,N) precipitates can control grain size by several distinct mechanisms. The growth of austenite grains may be restricted, and the resulting finer austenite grains transform to finer ferrite grains. These precipitates can also retard the recrystallisation of austenite during rolling, which results in additional ferrite nucleation sites within the deformed austenite. Finally, some M(C,N) precipitates can act directly as additional nucleation sites for ferrite grains, and hence promote a finer ferrite grain size in the final product.

The influence of M(C,N) precipitates on both grain size control and precipitation strengthening is crucially dependent on the volume fraction of precipitates and their size, with higher volume fractions of finer precipitates being most effective. The volume fraction and size of M(C,N) precipitates is in turn controlled by overall composition and processing conditions. V(C,N) precipitates have a relatively high solubility in austenite and ferrite in comparison with the corresponding precipitates of Nb and Ti. This means that even at relatively high levels of C and N, it is possible to dissolve V(C,N) precipitates during reheating prior to rolling, and this in turn facilitates the formation of fine V(C,N) precipitates during cooling, which are more effective in controlling properties.

This relatively high solubility of V(C,N) means that V is a very versatile alloying element in HSLA steels, suited to a wide range of steel product types. This paper will review some recent developments of V alloying in low, medium and high C steels, and demonstrate the benefits of V alloying for a wide range of processing conditions.

2 The Use of Vanadium in Medium and High Carbon Steels

Reinforcing bar: High C contents are a cost-effective method of increasing strength in rebar, but result in reductions in ductility and weldability, so most standards for weldable rebar limit C content to a maximum of approximately 0.25%. The high solubility of V(C,N) means that for these C levels, V(C,N) can be completely dissolved at normal reheating temperatures, allowing for the formation of fine V(C,N) precipitates after rolling to increase strength. The high solubility of V(C,N) also results in very consistent properties which are not strongly influenced by changes in reheating or rolling temperatures. The limited precipitation of V(C,N) in austenite means that rolling loads are not increased by V additions.

High strength rebar can also be produced using the quench and self-temper (QST) process, which uses water cooling immediately after rolling to produce a layer of martensite in the outer portion of the rebar, which is then tempered by heat from the interior of the rebar. In some regions, concerns have been expressed regarding the use of QST rebar in zones of seismic activity. In China, a recent standard revision has resulted in the QST process being restricted for the production of hot rolled rebar [1]. Rebar for use in seismic zones requires enhanced ductility, specified by uniform elongation and minimum values of the tensile strength to yield strength ratio, and V microalloyed rebar has been shown to easily exceed typical standard requirements in these respects. Rebar failures in seismic zones have been associated with low cycle, high-strain, fatigue, and there are reports of V microalloyed rebar having superior fatigue performance to QST rebar (Fig. 1), possibly as a result of the enhanced strain ageing resistance of V rebar [2]. Concerns have also been raised regarding the high temperature stability of QST rebar in relation to welding and hot straightening, but the use of V containing rebar eliminates these potential problems.

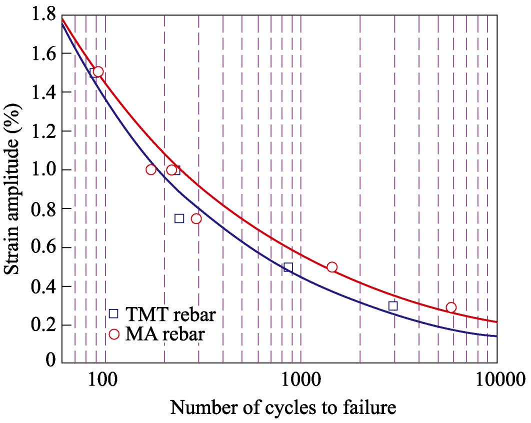


Figure 1 **Comparison between LCF life of TMT and MA rebars**

In China, V microalloyed rebar is widely used for products in the strength range of 400 to 600MPa. Whilst 400MPa is most widely used at present, this is being quickly replaced by 500 grade, with more companies seeking to develop a 600 grade. The V high N route is commonly used, as increased N levels increase strength by promoting the formation of larger volume fractions of finer precipitates. Even at higher N levels, strain ageing does not occur provided an appropriate ratio of V:N in excess of approximately 4 is maintained, due to the rapid formation of N-rich V(C,N).

Forging steels: V containing ferrite-pearlite steels have been successfully used to produce air cooled hot forgings for automotive components for many years, replacing the more expensive quenched and tempered (Q&T) process route. These steels typically contain 0.3-0.5%C and 0.05-0.25%V, and have tensile strengths up to 1000MPa. Demands for higher strength forging steels have continued, together with requirements for improved fatigue and machining performance. For connecting rod applications, it is important that easy fracture splitting is achieved.

The role of V in these steels is to provide increased strength via precipitation and grain refinement, with precipitation strengthening being increased by enhanced N levels. However, V also has an important role in improving the fatigue performance of these steels. The microstructures of these steels are predominantly pearlitic, with typically less than 20% ferrite. Fatigue crack initiation takes place in the ferrite regions adjacent to the ferrite-pearlite boundaries, and fatigue crack propagation then continues in the softer ferrite phase. V(C,N) precipitation in the pro-eutectoid ferrite hardens these regions, and gives a significant improvement in fatigue strength, (Fig. 2) [3].

Precipitation hardened ferrite-pearlite forging steels have been successfully used in many different applications as a replacement for more expensive Q&T steels. However, the toughness of ferrite-pearlite steels is lower than that of some Q&T steels. In an attempt to increase toughness of air-cooled forging steels, bainitic microstructures have been produced by using appropriate hardenability-increasing alloying additions such as Cr, Mo and B. V additions have also successfully been made to these bainitic forging steels, and the increased hardenability associated with V additions means that bainitic microstructures can be generated over larger cross sections [4].

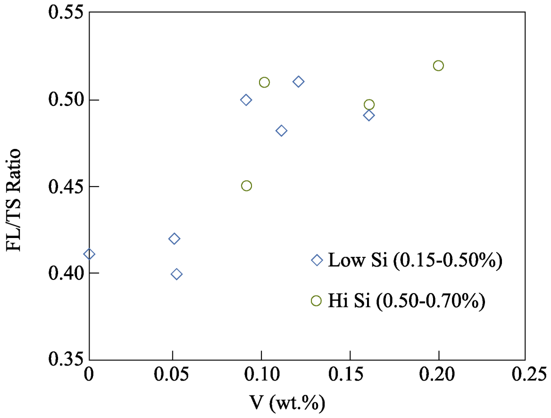


Figure 2 Effect of V and Si content on FL/TS ratio

Rail steels: It is common to use high C, fully pearlitic microstructures in rails as the high hardness of such microstructures results in reduced rail wear, and hence lower rail maintenance costs. In heavy duty areas such as curved track, wear can be more severe, and V containing rails have been developed for use in such environments. V additions can increase rail hardness to greater than 335 HBW, and this increased hardness significantly reduces rail wear. Even at these high C contents, the high solubility of V(C,N) means that sufficient V can remain in solution at the end of hot rolling to significantly modify properties, including the refinement of pearlite interlamellar spacing by V in solution, and increased hardness due to precipitation in pearlitic ferrite. Rolling contact fatigue (RCF) also reduces rail life, and as well as increasing hardness and reducing rail wear, V additions have also been shown to reduce RCF. V additions of 0.09-0.13% have been shown to give reductions in wear and RCF by at least a factor of three, resulting in significant reductions in track maintenance costs.

For rails used in tramways and light rail applications, it is common to use lower C contents in the range 0.4-0.6%C, to facilitate rail repair using welding. V additions of 0.08-0.2% to these grades have been reported to result in a reduction in wear rates by a factor of two in comparison to rails of similar hardness without V additions. It has been suggested that these reduced wear rates are due to V partitioning to pearlitic cementite and modifying its properties. V partitioning to cementite has been reported to improve the fracture toughness and reduce the hardness of cementite [5].

High strength rod: High strength rod for applications such as bridge wire, tyre cord and mooring cables typically use eutectoid or even hyper-eutectoid C contents in the range 0.8-0.9%, and strengths in excess of 2GPa can be achieved in the drawn wire. V additions can increase strength in such wire rod, and the strength increment in the wire rod is maintained in the drawn wire. V additions increase strength via precipitation strengthening and also a reduction in pearlite interlamellar spacing.

In these eutectoid and hyper-eutectoid compositions, V also has an important role to play in modifying the pearlite transformation [6]. Precipitation of fine V(C,N) on the austenite grain boundaries prior to the start of the pearlite transformation alters the subsequent nucleation of cementite. In hyper-eutectoid steels, normally cementite precipitates first on austenite grain boundaries, forming cementite films which have a very detrimental effect on ductility. However, the presence of V(C,N) modifies the cementite formation, resulting in cementite precipitating in a smaller and more fragmented form. Grain boundary ferrite then forms, followed by the conventional pearlite transformation. This process is shown schematically in Fig. 3. The elimination of these networks of grain boundary cementite in hyper-eutectoid steels associated with V additions results in a significant increase in ductility.

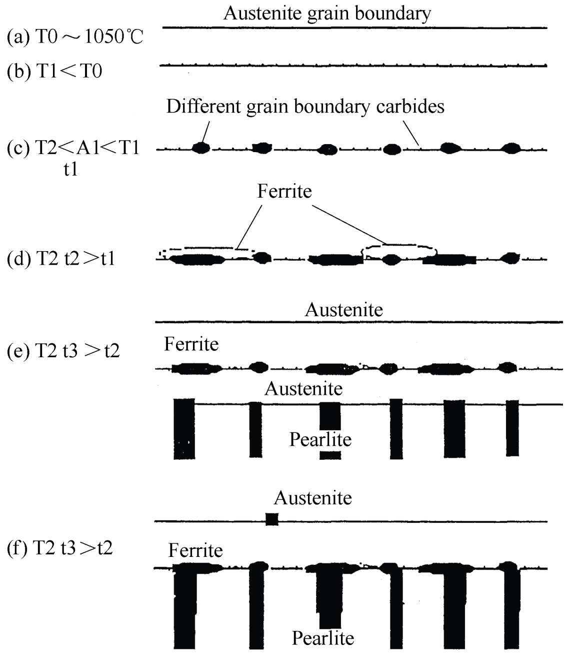


Figure 3 Schematic diagrams of formation of grain boundary phases in steels containing vanadium

(a) Austenitisation of steels; (b) Precipitation of carbides; (c) Further precipitation of carbides; (d) Formation of grain boundary ferrite on grain boundary; (e) Growth of grain boundary ferrite and another pearlite colony growing towards grain boundary; (f) Impingement of pearlitic cementite and grain boundary cementite

3 The Use of Vanadium in Low Carbon Steels

Precipitation Strengthened Ferritic Steels. In recent years, a range of advanced high strength steels (AHSS) has been developed with increased strength and formability characteristics for automotive applications. This has enabled overall vehicle weight to be controlled, component fabrication costs to be reduced and the requirements of more stringent crash tests to be met. However, some of these so-called first generation AHSS, although having high levels of tensile ductility, edge ductility, as measured by the hole expansion (HE) test, can be limited. The most commonly used first generation AHSS are dual-phase (DP) steels, and these steels have relatively low HE values. This has been associated with the large hardness difference between the ferrite and martensite phases.

To improve particularly the HE performance of AHSS, a new family of single-phase ferritic steels has been developed [7]. The single-phase microstructure has none of the localised strain concentration effects seen in DP steels which contribute to their poor HE performance. To produce high strength in a single-phase steel, which lacks strengthening contributions from pearlite or other hard phases such as bainite or martensite, significant precipitation strengthening is required. The high solubility of V(C,N) means when combined with suitable coiling temperatures, significant volume fractions of nanometer sized V(C,N) precipitates can be produced. By balancing the C content with the V and other alloying additions, a predominantly single-phase ferritic microstructure can be obtained. Mo additions can enhance precipitation strengthening further, and the resulting (V,Mo)(C,N) precipitates can give precipitation strengthening increments approaching 500MPa, with UTS values up to 1000MPa. At UTS values of 800MPa, HE values of 80% are commonly obtained. As well as improved HE values, the single phase microstructure also offers improved fatigue performance.

4 The Use of Vanadium Containing Steels at Low Processing Temperatures

Introduction: During some industrial processes such as annealing or hot forming, the maximum temperatures achieved are low in the austenite range or even in two-phase austenite plus ferrite range. The relatively high solubility of V(C,N) means that even at these low temperatures, a significant amount of V remains in solution, and is available to form fine V(C,N) precipitates which can significantly influence properties at later stages of processing. For suitable V, C and N levels, some V(C,N) may be present in precipitate form at low austenitising temperatures and have a beneficial influence on properties.

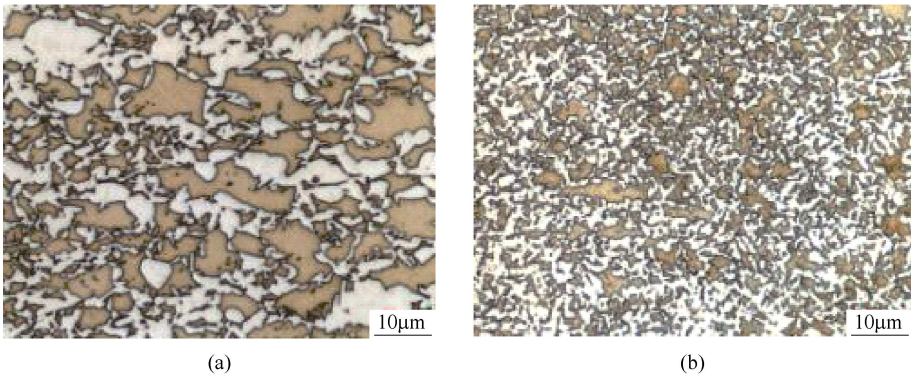
Hot formed structural hollow sections: Structural hollow structural sections (SHS) are used in the construction industry for a variety of applications in welded steel frames which experience loading from multiple directions. They can be produced in different geometries, with circular, square rectangular or elliptical cross sections. One common production route is to cold form hot rolled strip into a circular section, weld the strip edges together, and then form the resulting hollow into the desired final cross section geometry. The forming process can be carried out either at high temperature or room temperature. The high temperature, fully normalized SHS has several technical advantages over the cold formed SHS, including more uniform properties, elimination of weld heat affected zones and much tighter geometrical tolerances. Hot formed SHS with a yield strength of approximately 350MPa can be produced using Nb additions to a low CEV, and hence weldable, C-Mn composition. However, to increase yield strengths to 420 and 460MPa whilst maintaining hot forming temperatures of approximately 900℃ requires a different approach, as the solubility of Nb(C,N) at these temperatures is low, and hence Nb(C,N) dissolution will be minimal, precluding the formation of fine precipitates necessary to increase strength further.

Due to the relatively high solubility of V(C,N) additions at 900℃, a significant proportion of V remains in solution at the hot forming temperature, and is available to form fine precipitates during cooling which can result in precipitation strengthening. For the correct combination of V, C and N, some V(C,N) precipitates will remain un-dissolved at the hot forming temperature, and can restrict austenite grain growth, resulting in a fine ferrite grain size following transformation. Increasing N content has been shown to refine both the austenite grain size, and hence the resulting ferrite grain size, by increasing the volume fraction of V(C,N) precipitates present at the hot forming temperature. An additional benefit is achieved by using very low Al contents, which result in further ferrite grain refinement. A low Al content results in the elimination of AlN formation, and its replacement by N-rich V(C,N) precipitates. These N-rich V(C,N) precipitates are significantly smaller than AlN, and as a result are more effective at restricting austenite grain growth during at the hot forming temperature, resulting in a finer transformed ferrite grain size. Thus V additions increase strength both by precipitation hardening and grain refinement, with the grain refinement also helping to maintain high toughness levels.

SHS are now being produced with yield strengths up to 460MPa in a variety of cross sections with a wall thickness up to approximately 16mm using this V-N low Al concept, whilst still maintaining low CEVs to allow ease of welding [8]. Typical V and N contents are 0.15% and 0.015% respectively.

Dual phase steels: Dual phase (DP) steels are the most commonly used Advanced High Strength Steel (AHSS) for automotive applications, and are used for the production of many components, including those used in the safety cage. The predominantly ferrite-martensite structure of these steels can give a wide range of strengths from a UTS of 500MPa to 1300MPa, with excellent forming properties, as measured by total elongation and work-hardening rates. DP steels can be produced in hot rolled or cold rolled condition. In cold rolled and annealed DP steels, the two-phase microstructure is typically formed by annealing the cold rolled strip in the two-phase, austenite plus ferrite temperature range, followed by rapid cooling which results in the austenite (now enriched in carbon) transforming to martensite. As mentioned previously, one relative weakness of DP steels is their poor edge ductility, as measured by the hole expansion (HE) test. One reason for the poor HE results found in DP steels is thought to be the large hardness difference between the relatively soft ferrite and hard martensite. This hardness difference promotes strain concentration and void formation at sites such as the ferrite-martensite interface, resulting in low HE values.

The addition of V to cold rolled DP steels with UTS values in the range 800-1300MPa results in a significant strength increase and an overall microstructure refinement as illustrated in Fig. 4[9]. Fine V(C,N) precipitates are formed in the ferrite phase resulting in a significant increase in ferrite hardness. Due to partial dissolution and rapid growth of the V(C,N) precipitates in the austenite at the annealing temperature, on transformation to martensite the V(C,N) distribution provides little precipitation strengthening in the martensite phase. The overall effect is a reduction in the hardness difference between ferrite and martensite, and an improvement in HE values. V containing DP steels have also been shown to have properties which are less sensitive to martensite volume fraction, giving them more consistent properties when subjected to small variations in annealing conditions.



(a) (b)

Figure 4 Optical micrograph of (a) Ref steel annealed at 750℃/120s, (b) Ref+V steel annealed at 750℃/180s.

The martensite is white and ferrite is brown (Lepera etchant)

Press hardening steels: High strength press hardening steels (PHS) are being increasingly used in the automotive sector due to their very high strengths, in excess of 1.8GPa, and the ability to produce components for crash resistant structures in a rapid and economical manner. The production route involves austenitisation at temperatures of approximately 900℃, and then quenching between water cooled dies which form the required component shape and also cool the steel rapidly to form a high strength, predominantly martensitic microstructure. At such high strengths, H embrittlement can become a problem. The addition of V to PHS steels such as 30MnB5 and 35MnB5 has been shown to have a number of benefits[10]. At the austenitisation temperature of 900℃, and with a V content of 0.2%, some V(C,N) precipitates remain un-dissolved, and can restrict austenite grain growth resulting in an overall finer microstructure following transformation to martensite. The V(C,N) precipitates themselves can act as trapping sites for H, which can enter the steel during austenitising due to reactions between the furnace atmosphere and the Al-Si coatings commonly used on PHS. The increased interface boundaries due to the overall finer microstructure and H trapping by V(C,N) precipitates result in a reduction in H embrittlement, as measured by the strain to fracture in a tensile test. This process is shown schematically in Fig. 5.

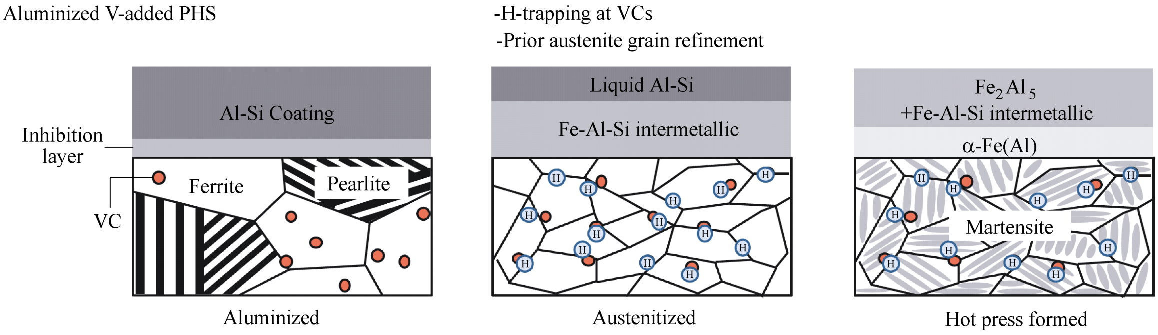


Figure 5 Schematic illustrating the influence of the V addition on the hydrogen absorption in the aluminized PHS. The VC precipitates inhibit grain growth during austenitization and provide an effective trap site for hydrogen

5 Casting and Rolling of Vanadium Containing Steels

The high solubility of V(C,N) means that there is limited precipitation of V(C,N) in austenite during casting, and this results in good levels of hot ductility which in turn means that V containing steels are less likely to form cracks during continuous casting. The high solubility of V(C,N) also means that reduced reheating temperatures and times during reheating can be used in comparison with Nb steels of equivalent strength. This can result in reduced energy use and increased productivity. In industrial trials of hot rolled S355 strip grades, reheating temperatures were reduced by 30℃ and reheating times were reduced by 30 minutes for a V containing grade in comparison to an equivalent Nb grade, leading to significant cost reductions. Good mechanical properties and weldability were achieved [11].

During the thin slab casting and direct rolling of V steels, final mechanical properties were found to be independent of casting conditions such as casting speed. This was attributed to the lack of V precipitation in the tunnel furnace prior to the start of rolling, with furnace equalization temperatures in the range 1150-1170℃[12].

The limited amount of precipitation of V(C,N) in austenite means that V containing steels show similar rolling loads to C-Mn steels, and much lower than Nb containing steels, especially at lower rolling temperatures, Fig. 6. For plate rolling, this means that reduced numbers of rolling passes can be used. For hot strip rolling, the reduced rolling loads for V containing steels allows wider strip to be rolled in comparison to equivalent Nb steels. The V containing steels also resulted in reduced roll wear as a result of the lower rolling loads [12].

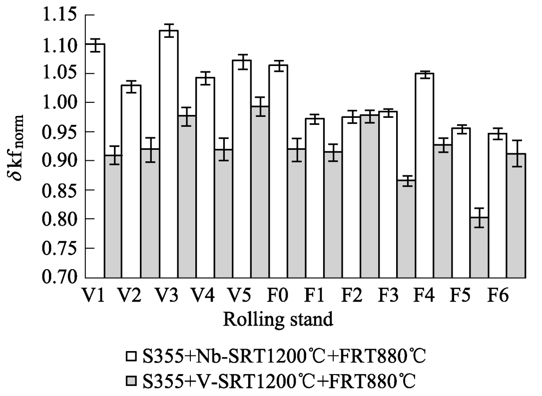


Figure 6 Development of the normalised flow stress for Steel S355+V compared with the values for Steel S355+Nb during hot strip rolling (V = roughing and F = finishing) using similar rolling schedule

6 Conclusions

In this paper, recent developments in V containing HSLA steels have been reviewed, and the versatility of V as an alloying element has been demonstrated.

In medium and high C steels, the relatively high solubility of V(C,N) allows the formation of fine V(C,N) precipitates, which improve properties such as strength, wear resistance and fatigue performance.

In low C steels, V additions can produce precipitation strengthened single phase ferritic steels with improved edge ductility.

At relatively low processing temperatures, such as those experienced during hot forming and annealing, V(C,N) precipitates can increase strength, refine grain size and reduce H embrittlement phenomena.

The high solubility of V(C,N) results in limited V(C,N) precipitation in austenite, which leads to low rolling loads and improved ductility during casting. Reduced reheating temperatures and increased rolling rates may be used to reduce production costs, and make V containing steels particularly suited to direct rolling applications.

References

[1] China National Standard GB/T 1499.2-2018. Steel for the reinforcement of concrete - Part 2: Hot Rolled Ribbed Bars.

[2] S. K. Paul, P. K. Rana, D. Das, et al. High and Low Cycle Fatigue Performance Comparison Between Microalloyed and TMT Rebar, Construction and Building Materials, 2014, 54: 170-179.

[3] P. Clarke, M. Green, R. Dolman, Development of High Strength Microalloyed Steel for Powertrain Applications, 4th International Conference on Steels for Cars and Trucks (SCT2014), 2014: 15-19.

[4] L. Garcia-Mateo, C., Morales-Rivas, F. G. Caballero, et al. Vanadium Effect on a Medium Carbon Forging Steel, Metals, 2016, 6(6): 130.

[5] W. Solano-Alvarez, L. F. Gonzalez and H. K. D. H. Bhadeshia, The Effect of Vanadium Alloying on the Wear Resistance of Pearlitic Rails, Wear, 2019, 436: 203004.

[6] K. Han, T. D. Mottishaw, G. D. W. Smith, et al. Effects of Vanadium Addition on Nucleation and Growth of Pearlite in High Carbon Steel, Materials Science and Technology, 1994, 10(11): 955-963.

[7] R. A. Rijkenberg, A High Strength Hot-rolled Steel Strip or Sheet with Excellent Formability and Fatigue Performance and A Method of Manufacturing Said Steel Strip or Sheet, European Patent: EP2954074B1.

[8] D. Crowther, et al., High Strength Hot-Finished Steel Structural Hollow Sections with Low Carbon Equivalent for Improved Welding, European Patent: EP3084030B1.

[9] C. P. Scott, F. Fazeli, B. S. Amirkhiz, et al. Structure-properties Relationship of Ultra-fine Grained V-Microalloyed Dual Phase Steels, Materials Science and Engineering: A, 2017: 703, 293-303.

[10] L. Cho, E. J. Seo, D. H. Sulistiyo, et al. Influence of Vanadium on the Hydrogen Embrittlement of Aluminized Ultra-high Strength Press Hardening Steel, Materials Science and Engineering: A, 2018, 735: 448-455.

[11] David J Milbourn and Yu Li, Development of Vanadium Microalloyed High Strength Hot Strip for Production with Reduced Rolling Forces, Steel Processing, Product and Applications Symposium, 2009: 1521-1531.

[12] D. Bhattacharya and S. Misra, Development of Microalloyed Steels Through Thin Slab Casting and Rolling (TSCR) Route, Transactions of the Indian Institute of Metals, 2017, 70(6): 1647-1659.