MITCHELL, P. S. The use of vanadium – a brief review. *INFACON 6. Proceedings of the 6th International Ferroalloys Congress, Cape Town.* Volume 1. Johannesburg, SAIMM, 1992. pp. 217–224.

The Use of Vanadium – A Brief Review

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The use of vanadium, primarily in the steel industry, is reviewed. Reasons for using vanadium, including the solubility, precipitation strengthening, grain control, and weldability it provides, are examined, and examples of its use across a range of steels are discussed. The non-ferrous use of vanadium, especially its use in Ti–Al–V alloys, is noted, and some examples of its potential future use are recorded.

Introduction

Vanadium is a member of a group of elements, including niobium and titanium, which, when present in relatively small amounts in alloys, can have a significant effect on their properties. Henry Ford recognized this as far back as 1908, and his Model T incorporated steels containing vanadium for toughness and fatigue resistance of crankshafts, axles, and other components. While this is not the first recorded use of vanadium, its application has certainly grown from that time.

In considering the modern applications of vanadium, we need first to establish where the element is used, bearing in mind that records are able to describe only historical, and not future, use. The most comprehensive data available are those of the US Bureau of Mines, which indicate that, for some time past, 80 per cent of vanadium used has been consumed by the steel industry, 15 per cent by the non-ferrous industry, and the remaining 5 per cent in various miscellaneous applications, including ferrous foundries, as catalysts, etc. It is likely that use in other countries will broadly follow that in the USA.

I shall therefore concentrate on the use of vanadium in steel, and then examine, to a lesser extent, its use in the non-ferrous industry.

Vanadium in Steel

Reasons for Using Vanadium in Steel

By far the major reason for adding vanadium to steel is because it reacts with carbon and nitrogen to form refractory carbides, nitrides, and carbonitrides, which can act as both precipitation strengtheners and grain refiners, depending on the composition of the steel and the temperature regime within which it is processed.

For a precipitation reaction to take place, vanadium, carbon, and nitrogen require to be taken into solution in austenite at high temperature. As the temperature falls, the solution becomes supersaturated, and carbides, nitrides, and carbonitrides can precipitate. Precipitation is enhanced by the phase change from austenite to ferrite, as the solubilities in ferrite are significantly lower than they are in austenite. For grain refining to occur, the precipitates usually require to be out of solution and they act by pinning austenite or ferrite grain boundaries as they try to migrate.

Figure 1 shows the solubility of vanadium, in austenite, in equilibrium with carbon and nitrogen at 900 and 1200 °C. It is clear that the solubility of vanadium carbide at 900 °C is almost one order of magnitude higher than that of vanadium nitride at 1200 °C. Vanadium carbide is, in fact, the most soluble of the commonly used micro-alloying compounds. Therefore, while both vanadium carbide and vanadium nitride are strong precipitation strengtheners over a wide range of composition, only vanadium nitride is likely to be of significant use as a grain refiner, except at medium–high carbon contents.

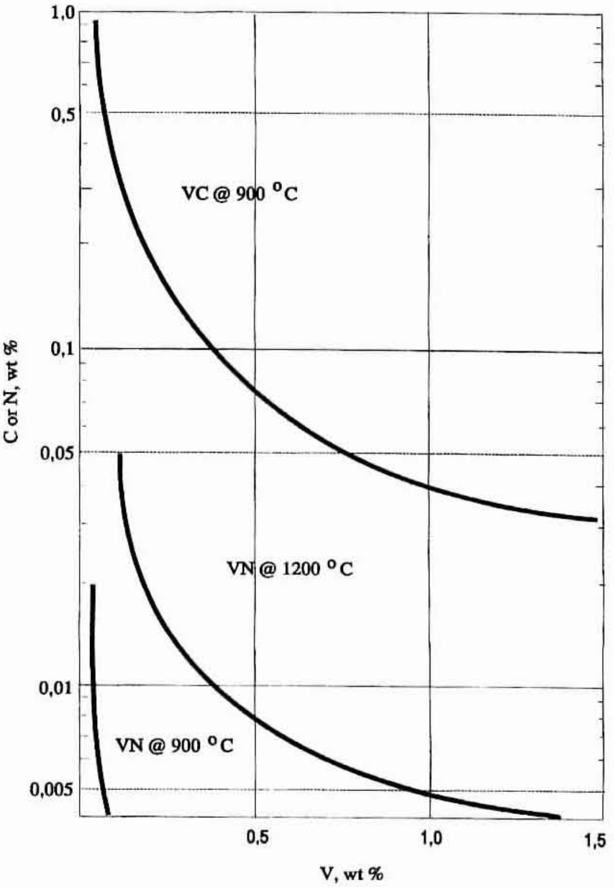


FIGURE 1. Solubility of VC and VN at 900 and 1200 °C (after Narita[1])

The magnitude of any precipitation-strengthening increment depends on, among other things, the transformation temperature and the rate of cooling through the transformation. Figure 2 demonstrates that, for a structural steel containing 0,15 per cent V, as the transformation temperature decreases from 780 to 620 °C, the strength increases by approximately 100 N/mm^2, primarily as a result of precipitation. Additionally, this figure indicates that the optimum cooling rate for peak precipitation strengthening is of the order of 200 °C/min. At slower cooling rates, the strengthening is not as great, because of over-ageing of the precipitates, while, at faster cooling rates, there is insufficient time for development of the optimum precipitate distribution. In this latter case, precipitation strengthening can be recovered by tempering. Figure 3 shows that, in a 0,1 per cent carbon steel that has been quenched and tempered, a clear secondary hardening peak has developed in the temperature range 550 to 650 °C. It should be noted that this temperature range also encompasses the optimum coiling temperature range for the production of hot coils containing vanadium.

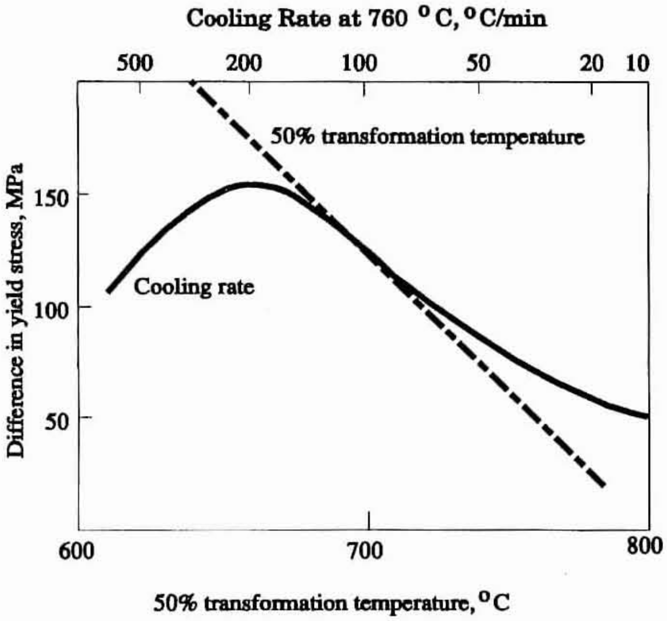


FIGURE 2. The effect of transformation temperature and cooling rate of vanadium steels (after Gladman *et al.*[3])

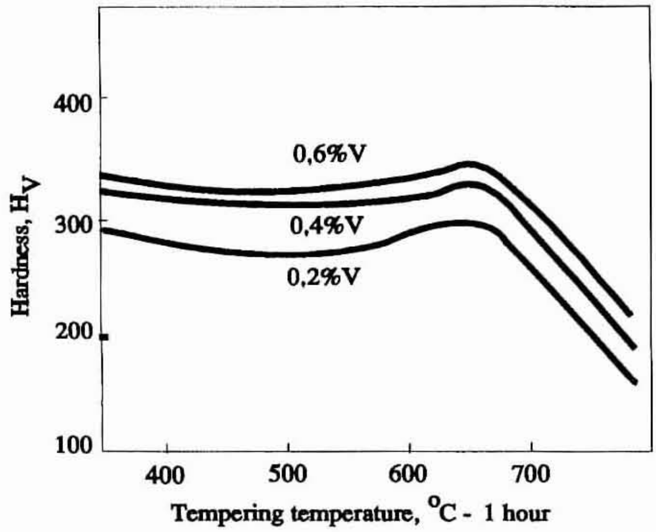


FIGURE 3. The effect of vanadium on the tempering characteristics of 0,1% carbon steels (after Pickering[4])

The precipitates that cause strengthening form in two ways. Interphase precipitates form in sheet-like arrays at the austenite–ferrite interface as transformation occurs. These precipitates usually form at the higher transformation temperatures associated with the formation of polygonal ferrite. General precipitation, usually on dislocations within the matrix, can also occur. This type of precipitation is usually, but not always, found at the lower transformation temperatures associated with acicular ferrite. The amount of precipitation that occurs will obviously depend on the composition of the steel, especially its vanadium, carbon, and nitrogen contents.

In the use of vanadium as a grain refiner in normalized and heat-treated steels, care has to be taken to ensure the correct balance between all the elements that may be competing for both nitrogen and carbon. For example, in steels grain-refined with vanadium nitride, the aluminium level requires consideration as this element is also a strong nitride former. Provided the correct balance is achieved, such steels can develop extremely fine grain sizes. Figure 4 shows an example for a steel containing 0,01 to 0,02 per cent Al and 0,015 to 0,020 per cent N, where a ferrite grain

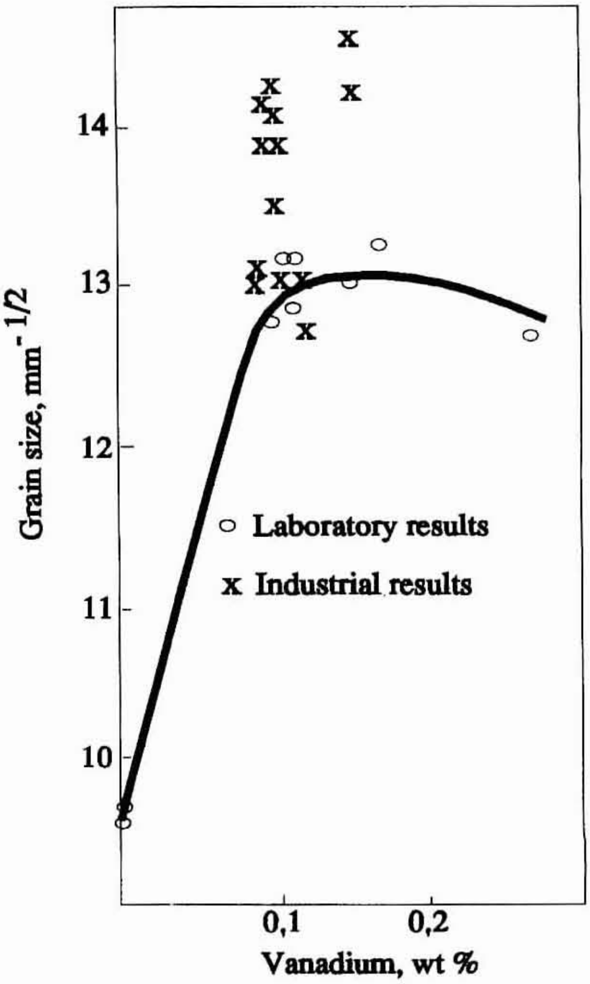


FIGURE 4. The effect of vanadium on the ferrite grain size of normalized C–Mn–Al–V–N steel (after Mitchell *et al.*[5])

size of the order of 13 to 15$d^{-1/2}mm^{-1/2}$ was achieved after normalizing. This is, arguably, one of the finest-grained normalized steels in existence.

Vanadium can also act as a grain refiner in as-rolled steels but, because it does not inhibit austenite recrystallization during rolling, it is not as effective as, for example, niobium or titanium. Nevertheless, when used in conjunction with a balanced addition of titanium and nitrogen, along with the processes of recrystallization rolling and accelerated cooling after rolling, it is possible to achieve fine grain size accompanied by precipitation strengthening. It should be noted that the grain sizes shown in Figure 5 were obtained without resort to the heavy controlled rolling schedules normally associated with niobium-containing steels. Further, because vanadium does not inhibit austenite recrystallization at normal rolling temperatures, the rolling loads associated with the use of vanadium micro-alloyed steels are significantly lower than those associated with niobium steels, especially as the finish rolling temperature falls below about 1000 °C.

Vanadium can also influence the microstructure that forms during cooling; the extent to which this occurs depends on both composition and cooling rate. In low-carbon steels, at cooling rates typical of those found in many metallurgical applications, vanadium has been shown to promote the formation of polygonal ferrite and to reduce

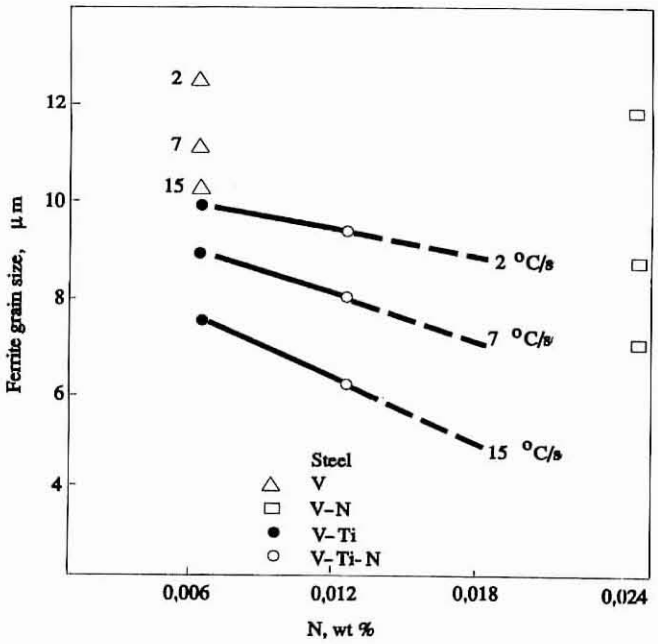


FIGURE 5. The effect of nitrogen content and cooling rate on the ferrite grain size of recrystallized rolled vanadium-containing steels (after Zheng *et al.*[6])

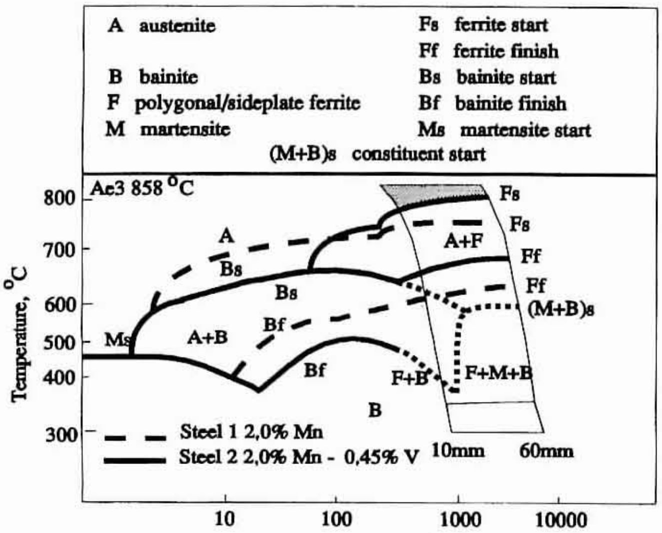
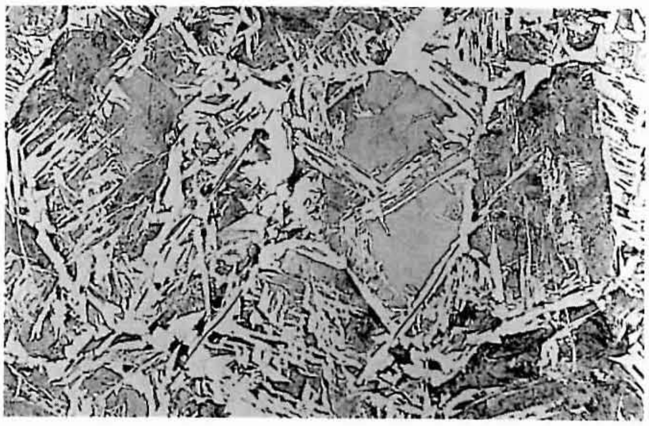
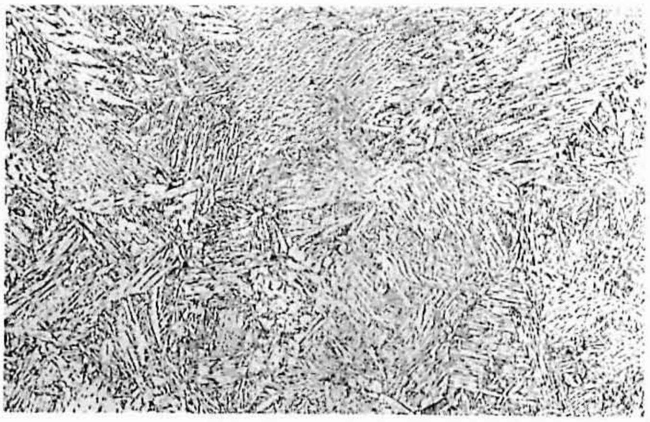


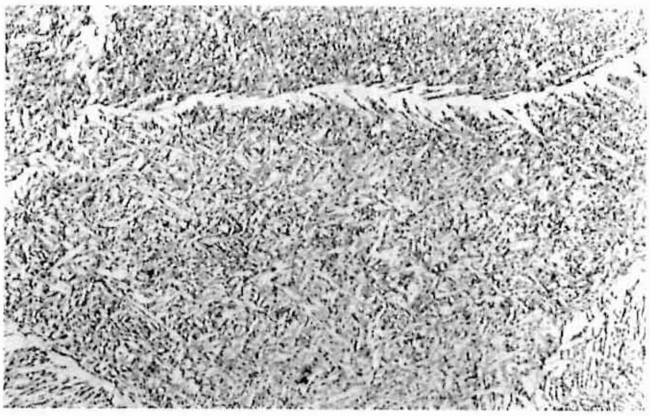
FIGURE 6. CCT diagram showing the effect of 0,45% V on the transformation behaviour of 2,0% Mn steel (after Cochrane and Morrison[2])



a) C–Mn steel (7 kJ/mm)



b) C–Mn–Nb steel (5 kJ/mm)



c) C–Mn–V steel (5 kJ/mm)

FIGURE 7. Comparison of the microstructure of multipass welds of C–Mn, C–Mn–Nb, and C–Mn–V steels (after Hart[7])

the temperature at which brittle bainitic microstructures can form. Figure 6 shows a CCT diagram for a low-carbon linepipe-type steel containing 0,45 per cent V. The temperature at which the polygonal ferrite transformation starts has been raised by about 50 °C, while the bainite starting temperature has been reduced by a similar amount. This may be due to interphase precipitation reducing the carbon content in the austenite/ferrite interface and accelerating the transformation to polygonal ferrite.

Recent work carried out on behalf of VANITEC at The Welding Institute in the UK has demonstrated that vanadium promotes the formation of tough, intragranular ferrite in the grain-coarsened region of the heat-affected zone of multipass welds, carried out at 3 kJ/mm, in structural steels. A comparison of the microstructures developed in C–Mn, C–Mn–Nb, and C–Mn–V steels is shown in Figure 7. It is clear that the vanadium-containing steel has much less of the coarse aligned microstructure present in the other steels. This work holds out the possibility of developing tough, vanadium-containing, weldable structural steels, including those suitable for welding by newer processes such as power-beam welding.

Finally, at higher cooling rates in alloyed medium-carbon steels, vanadium has been shown to increase the martensitic hardenability. Figure 8 indicates that, in this respect, vanadium is more effective than any of the other alloying elements shown.

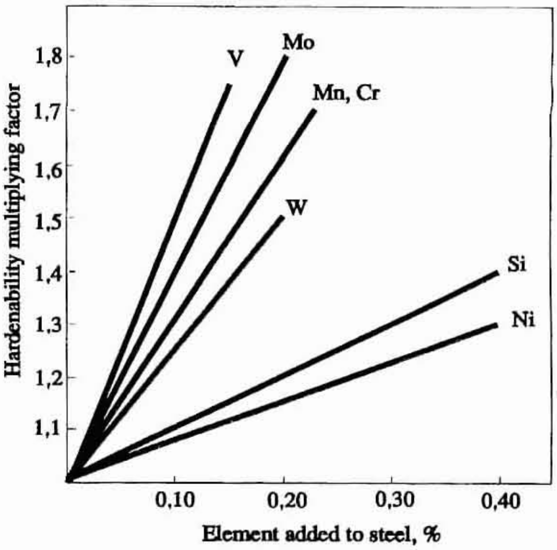


FIGURE 8. Maximum reported hardenability effects for various alloying elements (after Siebert *et al* [8])

Practical Uses of Vanadium in Steel

Structural steels

It is clear that there are many national standard specifications that allow the use of vanadium in structural steels. A summary, by no means complete, of some of these specifications is given in Table I.

Vanadium can be used in structural steels that are hot rolled, controlled rolled, normalized, or quenched and tempered. Products include plates, strip, flats, bars, shapes, and sections. Applications are welded, bolted, and riveted structures, including bridges and buildings, particularly where light weight is desired. Truck and automobile components, where both formability and weight saving are considera-

TABLE I
STRUCTURAL STEELS

Specifications	Product	Application	Steel type	Yield strength N/mm^2	Vanadium level wt %, max	Other alloying elements
EN10 025:1990 Fe510, Fe590, Fe690	HR & N, non-alloy Long products Flat products	Welded, bolted, riveted structures	C–Mn	225–360	*	*
BS4360:1990 Grades 50 & 55	HR, N, and QT plates, strip, flats, bars, sections	Welded, bolted, riveted structures. Some with atmospheric corrosion resistance	C–Mn	305–450	0,1, 0,15, 0,2	Nb
DIN 17100:St52	HR and N plates, strip, flats, rods, bars sections, forgings, semis	General structural purposes	C–Mn	290–360	*	*
ASTM A514	Q and T alloy plates	Welded bridges and other structures	Low Alloy	620–690	0,08	Cu, Cr, Mo, Ni, Si, Ti, Zr, B
A572	HSLA plates, bars, shapes, sheet piling	Welded, bolted, riveted for bridges, buildings, and other structures	C–Mn	290–450	0,15	Nb
A588	HSLA plates, bars, shapes	Welded, bolted, riveted for bridges, buildings, with weight saving, durability, and improved atmospheric corrosion resistance	C-Mn	290–345	0.10	Cu, Cr, Mo, Ni, Nb, Zr
A607	HR and Cr HSLA sheet and strip	Greater strength, weight saving, weather resistance	C–Mn	310–480	*	Nb, Cu
A715	HR and CR HSLA sheet and strip	High strength, weight saving with formability	C–Mn	415–620	*	Nb, Ti, Zr

* No maximum noted in specification

tions, are also manufactured from vanadium-containing steels. Some of the steels have enhanced corrosion resistance and durability. Simple carbon–manganese steels predominate in this group, although some use is made of additional alloying elements including Cr, Cu, Mo, Ni, Ti, and Zr. Yield strengths are typically in the range 290 to 450 N/mm^2, although some specifications require even higher yield strength, up to 690 N/mm^2. Depending on the specification, up to 0,2 per cent V (maximum) is permitted and, in this type of steel, vanadium competes with niobium for the promotion of the desired properties.

When the steels can be supplied in the as-rolled or fully heat-treated condition (Q and T), as is frequently the case in the USA and some other countries, then precipitation-strengthened vanadium steels are common. Vanadium is also preferred in the manufacture of many as-rolled shapes and sections to promote strength while preventing the formation of bainite, which could have a deleterious effect on ductility and toughness.

Where the highest levels of toughness are required, or where thicker sections are involved, structural steels are usually normalized to achieve fine grain size. In such cases niobium steels have been preferred. However, as noted in Figure 5, it is possible to achieve fine grain size in as-rolled V–Ti steels, especially when used in conjunction with recrystallization rolling and accelerated cooling. This gives an opportunity for vanadium to be used to achieve the highest levels of toughness in structural steels. Provided it can be demonstrated that its use entails both technical advantages and cost benefits, the elimination of normalizing costs and improved weldability would appear to give significant scope to the use of vanadium in this application.

Linepipe steels

The broad requirements for linepipe steels are summarized in Table II. This simple table does not, however, give any indication of the degree of sophistication that is now required for high-test linepipe steels.

Linepipe can be divided into two generic types: steels required for marine environments, which have to resist hydrogen-induced cracking and sulphide stress–corrosion cracking in sour conditions, and steel for overland lines where, although the strength may be higher, the operating conditions that the steel has to withstand are less demanding.

Linepipe for sour service is, undoubtedly, among the most demanding of steels to manufacture. Its use does not extend above the X65, or perhaps X70, level of properties, and steelmakers have invested considerable time and money developing process routes for the manufacture of the steels involved. The routes include desulphurization, dephosphorization, degassing, control of reoxidation during casting, control of segregation during casting, controlled rolling, and accelerated cooling after rolling.

The use of accelerated cooling after rolling has made it possible to mitigate the effects of segregation, which occurs during continuous casting, by reducing carbon and manganese levels in the feedstock to around 0,04 to 0,05 per cent C and 1,0 to 1,3 per cent Mn. When this is adopted, micro-alloying is required to ensure that strength is maintained. In thin X60 plate, niobium alone is probably sufficient. However, as both the thickness and the strength increase, a vanadium addition is made. At the X65 level of properties, the present standard for offshore use in the North Sea, the steels typically contain both 0,04 to 0,06 per cent Nb and 0,04 to 0,06 per cent V additions.

The main difference between sour lines and higher-strength lines for overland use is that the levels of carbon and manganese are higher in the latter—of the order of 0,06 to 0,09 per cent C and 1,5 to 1,8 per cent Mn. Consequently, the need for alloying elements is reduced, especially when accelerated cooling after rolling is used. Nevertheless, at the levels of properties from X65 to X70 and above, steelmakers retain an Nb–V combination at levels similar to those used for sour service, depending on the wall thickness.

Reinforcing steels

Reference to national or international specifications for reinforcing steels for concrete such as BS 4449, BS 4486, ASTM A615, Euronorm 80, etc., yields little information on the use of vanadium in these steels. The specifications deal mainly with strength and ductility requirements, and leave considerable flexibility in the choice of composition. Consequently, because of its high solubility in austenite and the resulting significant precipitation-strengthening increment that accrues, vanadium has found wide use in concrete-reinforcing steels. This use has been particularly evident in steels requiring yield strength above 400 N/mm^2 coupled, perhaps, with an improvement in shop and site weldability. This latter improvement results mainly from a reduction in carbon content made possible by precipitation strengthening. However, it should be noted that the application of rapid cooling after rolling coupled with self-tempering has, in recent years, restricted the use of all alloying elements in concrete-reinforcing steels.

There has been much interest in the use of vanadium in higher-carbon control-cooled rod for drawing into wire for use in prestressed concrete reinforcement and tyre cord, springs, etc. In these alloys it is used, sometimes in combination with chromium, to increase strength by precipitation and possibly by reducing the spacing between pearlite lamellae. This enables drawn-wire strength to be achieved at a lower carbon content or with a smaller drawing reduction, both of which increase ductility. Use in this manner is reasonably well established, and continues to excite interest, as demonstrated by a recent publication in Australia[9].

TABLE II
LINEPIPE STEELS

Specification	Product	Application	Steel type	Yield strength N/mm^2	Vanadium level wt %, max	Other alloying elements
API 5L X60	AR, N, Q, and T seamless, ERW, SAW linepipe	High test linepipe	C–Mn	412	*	Nb, Ti
X65				447	*	Nb, Ti
X70				481	*	Nb, Ti
X80				550	*	Nb, Ti

* No maximum noted in specification, but Nb, V, and Ti typically 0,12 percent max.

TABLE III
ENGINEERING STEELS

Specification	Product	Application	Steel type	Yield strength N/mm^2	Vanadium level wt %, max	Other alloying elements
BS 970 280MOI	Micro-alloyed wrought products	Hot-worked and air-cooled engineering products	C–Mn	530–600	0,2	Nb, Ti
897M39	Alloyed wrought and heat-treated products	Engineering products requiring through-hardening and surface nitriding	Low alloy	1160	0,25	Cr Mo
735 A51, H51, A54	Alloyed wrought products	Hot-formed springs	Low alloy		0,25	Cr
DIN 49MnVS3 38MnSiVS5 27MnSiVS6	Micro-alloyed wrought steels	General engineering purposes including forgings	C–Mn	450–550	0,13	–
39CrMoV139	Through-hardening wrought steels	General engineering purposes requiring surface nitriding	Low alloy		0,25	Cr, Mo
508V4	Wrought steel	Hot-formed springs	Low alloy		0,20	Cr
SAE 6118	HR and CR alloy bars and semis	General engineering including case carburizing	Low alloy		0,15	Cr
6150	HR and CR alloy bars and semis	Spring and hand tools	Low alloy		*	Cr

* No maximum noted in specification

General engineering steels

A few of the more important vanadium-containing specifications for steels for general engineering applications are summarized in Table III. Vanadium is used in these steels in all conditions, from as-formed and air-cooled to fully heat-treated and nitrided. The products include wrought blooms, billets, slabs, bars, rods, and forgings, which are converted into an extremely wide range of general engineering products, especially in the truck- and automobile-manufacturing industries. Many of the steels in this group are of the medium- to high-carbon type, and vanadium is incorporated as part of an alloying system that frequently includes both Cr and Cr–Mo additions. There is, at present, no completely satisfactory alternative micro-alloying system available for such steels.

The mechanical properties obtained depend on both the alloys used and the heat treatment employed, and reflect the end use, which includes forgings, case-hardened parts, springs, etc. It is worth noting that the use of vanadium in air-cooled drop forgings for automobile applications has, in both Europe and Japan, eliminated the need for costly heat treatment of parts such as crankshafts, connecting rods, stub axles, and steering knuckles. Cr–V steels are also widely known for their use in spanners and knives.

Tool steels

Some of the main features of BS 4659:1971 are summarized in Table IV. Other major specifications, e.g. AISI and DIN, have similar, or indeed parallel, grades. There are six types of tool steel ranging from the simplest low-temperature, low-speed, water-quenched, BW grades, which are not particularly wear resistant, to the high-temperature, highly wear-resistant oil-, air- or salt-bath hardened high-speed BM and BT grades. Vanadium is added to a significant proportion of the grades manufactured at a level of between 0,25 and 5,25 per cent. Generally, the grades demanding the highest performance at temperatures up to 600 °C contain the highest vanadium levels. With the exception of the simplest water-hardened grades, vanadium is always present in association with Cr, Mo, or W, either singly or, more frequently, in combination.

Tool steels are very hard, being heat-treated to between 600 and 912 H_{V10}, depending on grade. In these steels vanadium forms refractory carbides, which are stable up to relatively high temperatures, thus imparting hardness, strength, and wear resistance. Secondary hardening, which occurs during tempering, enhances these properties. At the higher vanadium levels utilized, particularly in high-speed steels, it also acts as a grain refiner imparting toughness.

The importance of such steels to manufacturing industry, in general, cannot be under-estimated. Without them we would be unable to manufacture many of the goods on which our civilization depends. Vanadium steels are utilized in the manufacture of, among other things, chisels, punches, blanking tools, shears, dies, taps, mandrels, and rolls.

Vanadium in Cast Irons

Before leaving ferrous materials, the use of vanadium in cast irons should be considered, although this use comprises only a small proportion of the total usage. Over the past few years VANITEC, in conjunction with BCIRA, has been carrying out a research programme into the use of high-duty grey cast irons for brake drums. This work[10] has shown that, provided reasonable care is taken to ensure control of chill and that the carbon level does not exceed approximately 3,7 per cent, significant improvement in strength coupled with a high level of thermal-fatigue resistance can be obtained in irons alloyed with 0,5 per cent V and 0,4 per cent Mo. This exciting development has the potential to

TABLE IV
TOOL STEELS

Specification*	Type	Application	Hardness, min Hv	Vanadium level wt %, max	Other alloying elements
BS 4659 BW2	Water hardening	Low temperature, low speed drills, taps, etc.	790	0,35	–
BA, BD, BO	Cold work, air or oil hardening	Up to 200 °C, blanking, cold forming, punching, etc.	735–763	0,25–1,0	Cr, Mo, W
BS	Shock resisting, oil or water hardening	Impact loading chisels, shear blades, hammers, etc.	600	0,30	Cr, Mo, W
BH	Hot work, air or oil hardening	Forming and shaping hot metals	763 (BH26)	0–2,4	Cr, Mo, W
BM, BT	High-speed oil, air, salt bath hardening	High temperature high speed, wear resistance	823–912	0,6–5,25	Cr, Mo, W

* AISI and DIN have similar grades

extend the use of vanadium in the automobile industry and other industries where high braking loads or weight savings are critical features.

Non-ferrous Uses of Vanadium

Vanadium and vanadium compounds have been applied in a wide range of uses outside the steel industry, including catalysts in the chemical, petrochemical, and power-generation industries, as ceramic pigments, as a component in the red phosphor of TV screens, as part of the alloying system in permanent magnets, to control gas content and microstructure in copper alloys, and to strengthen aluminium alloys used in pistons for internal combustion engines. Their use is also being considered in the development of fusion reactors, in magnetic polymers, in redox batteries, and in the investigation of superconducting materials. However, by far the greatest demand for vanadium in the non-ferrous field is in the manufacture of Ti–6%Al–4%V alloy. This alloy is used in high-performance aircraft, where its strength-to-weight ratio is a primary consideration.

In this alloy, which undergoes an *a/ß* transformation, vanadium is added to stabilize the ß phase, making it possible to strengthen the alloy by heat treatment. This heat treatment includes solution treatment in the range 900 to 950 °C, and annealing at a temperature up to about 800 °C. It enables yield strengths in excess of 450 N/mm^2 and a U.T.S. in excess of 650 N/mm^2 to be achieved at temperatures of 450 °C or greater. This combination of good strength at moderately high temperatures in a low-density material has enabled the alloy to be used in a range of aerospace applications, including jet engines, airframes, and rocket-motor units. As new alloys, that can be utilized at higher loads or higher temperatures are developed or brought into use, it is expected that the application of vanadium will be expanded in this field.

Conclusions

Vanadium has found a wide range of uses in the steel industry and also in the non-ferrous industries. In steel, its main advantage results from the relatively high solubility of vanadium, carbon, and nitrogen in austenite, which enables a significant degree of precipitation strengthening to occur on subsequent transformation to ferrite. This strengthening can be accompanied by microstructural modification, by grain refinement, and by good weldability. These attributes have led to the use of vanadium in a wide range of steels, including structural steels, linepipe steels, reinforcing steels, engineering steels, and tool steels.

In the non-ferrous industries, vanadium's main use is in high-strength, lightweight titanium-based alloys used in the aerospace industry.

In future vanadium will perhaps find use in superconducting materials, in magnetic polymers, in redox batteries, and in fusion reactors. More probably it will continue to be used in the steel and aerospace industries, and as an alloying element in high-duty grey cast irons.

Acknowledgments

The author thanks Highveld Steel & Vanadium Corporation for permission to publish this paper, and Mr P.H.M. Hart, Dr W.B. Morrison, and Dr A.M. Sage for helpful discussions during its preparation.

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