Expanded use of vanadium in new generations of high strength steels

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Abstract

The goal of this paper is to present a new role of vanadium on; (i) ferrite grain refinement through nucleation of intragranular ferrite, and (ii) precipitation strengthening of bainitic steels. Microalloying with vanadium is extensively used for strong and easy controllable precipitation strengthening of HSLA with ferrite-pearlite microstructures. The benefits of precipitation strengthening are now being extended on high strength bainitic steels. The experimental results clearly indicate an abundant precipitation of nanoscale nitrides and carbides in the dislocated bainitic ferrite matrix, over a broad temperature range down to 300°C. Vanadium can also by effectively use for ferrite grain refinement. It is shown in this paper that vanadium contributes to the formation of two types of intragranulary nucleated ferrite; polygonal ferrite and acicular ferrite. Intragranular polygonal ferrite nucleates on VN particles in austenite. Acicular ferrite forms during transformation at lower temperatures.

Introduction

Vanadium is best known as an eminent element for strong and easy controllable precipitation strengthening. The principal reason for this is the larger solubility product of its carbo-nitrides resulting in a lower solution temperature and a larger capacity to dissolve them at elevated temperatures. Precipitation strengthening of polygonal ferrite has been studied intensively in recent years and the use of vanadium for precipitation strengthening is a well established technology in HSLA steels with ferrite-pearlite microstructures. The benefits of precipitation strengthening are now being extended on bainitic steels with high and ultra-high strengths. The precipitation reactions in bainitic ferrite are, however, less well exploited for the obvious reasons. On the one hand, bainite is the most complicated microstructure of steel and there are still controversies regarding the formation of bainite and the carbon supersaturation of bainitic ferrite. On the other hand the fine scale of precipitation within bainitic ferrite was very difficult to investigate using conventional experimental techniques. Previously it was believed that the carbon content in steel could not influence homogeneous precipitation in ferrite due to the low equilibrium solubility. However, it was demonstrated that the effective carbon for precipitation in bainitic ferrite is much greater in the times available during transformation [1]. Metastable equilibrium between ferrite and undercooled austenite greatly increases the solubility of carbon in ferrite thereby contributing to profuse nucleation of V-carbides. These findings are of major significance for precipitation strengthening in bainitic ferrite which forms at intermediate transformation temperatures.

Recent experimental data strongly suggest that vanadium can also by effectively use for ferrite grain refinement. There are two conventional approaches to austenite conditioning which provide high density
of planar nucleation sites, i.e. recrystallisation controlled rolling (RCR) and classical controlled rolling (CR) [2-3]. In the new approach to grain refinement vanadium is directly used to increase the number density of nucleation sites for either intragranular polygonal ferrite or acicular ferrite inside the austenitic grains [4-7]. The formation of intragranular polygonal ferrite requires the presence of active VN particles in austenite [6]. For the nucleation of acicular ferrite it appears that the formation of V-clusters in austenite is critical [7].

The main focus of this paper is directed towards to present understanding of precipitation processes of V carbo-nitrides in austenite and ferrite together with microstructure formation, ranging from austenite conditioning to intense dispersion strengthening of bainitic ferrite that underlines these new possibilities of vanadium in hot rolled steels.

Experimental procedure

The investigation was carried out on 0.1%C and 0.2%C, V- and V+Ti-microalloyed steels with various levels of nitrogen. Their chemical compositions are given in Table I. All the steels were prepared as 2 kg laboratory ingots with a cooling rate during solidification designed to simulate commercial continuous casting. A plain C-Mn (V-free) steel was included in this investigation as a reference material.

Table I  Chemical composition of the experimental steels.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Al</th>
<th>V</th>
<th>N</th>
<th>Ti</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>0.10</td>
<td>0.30</td>
<td>1.50</td>
<td>0.005</td>
<td>0.10-0.12</td>
<td>0.005-0.025</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>0.10</td>
<td>0.30</td>
<td>1.50</td>
<td>0.005</td>
<td>0.05-0.06</td>
<td>0.005-0.025</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>0.04</td>
<td>0.30</td>
<td>1.50</td>
<td>0.005</td>
<td>0.12</td>
<td>0.015</td>
<td>-</td>
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<tr>
<td>D</td>
<td>0.20</td>
<td>0.30</td>
<td>1.50</td>
<td>0.005</td>
<td>0.12</td>
<td>0.005-0.025</td>
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<tr>
<td>E</td>
<td>0.10</td>
<td>0.30</td>
<td>1.50</td>
<td>0.005</td>
<td>0.10-0.2</td>
<td>0.005-0.025</td>
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The effect of V on the intragranular ferrite formation was examined by using a quenching and deformation dilatometer. Two different heat treatment trials were applied to promote formation of VN in austenite; one with isothermal holding at temperatures slightly above Ar3, and the second with deformation. The specimens were then either slow continuously cooled to transformation temperature or quickly quenched for isothermal transformation at temperatures 750-450°C.

The general microstructure was examined using optical microscopy after etching in nital. Precipitate morphology and detailed structural effects were studied on electrolytically polished specimens using FEG-SEM and on thin foils using TEM.

Driving force for precipitation of VN, VC and V(C,N)

The precipitation process proceeds at a perceptible rate only if there is a driving force, that is, a free energy difference between the product and parent phases. The driving force enters the steady state nucleation rate in a central way and must be known with good accuracy if nucleation rates are to be calculated, or even estimated. The steady state nucleation rate J(1/m^3s) of microalloy carbo-nitrides, controlled by diffusion of microalloying elements (MA) can be thus represented as [8],

\[
J \equiv \frac{\rho}{a_f} D_{MA} X_{MA} \exp\left(-\frac{\Delta G^*}{kT}\right)
\]

where \(\rho\) is the dislocation density and \(a\) is the lattice parameter of the matrix, \(D_{MA}\) and \(X_{MA}\) are the diffusivity and concentration of the MA.

The chemical driving force for nucleation can be determined with a high accuracy from the recent evaluation of thermodynamic parameters for microalloy steels, within the well-known thermodynamic
database, Thermocalc [9]. Fig. 1 illustrates the chemical driving force for nucleation of V(C,N) in austenite and ferrite. It can be seen that the chemical driving force for precipitation in austenite is low but increases suddenly and strongly as $\gamma$ is transformed to $\alpha$, reflecting the solubility drop associated with the widely different solubilities in the two phases, Fig. 1(a). The strong increase in the driving force for V(C,N) when the transformation temperature is decreased from that of polygonal ferrite to bainite is also clearly seen from Fig 1(c).

![Fig. 1 The solubility drop of V during $\gamma/\alpha$ transformation (a) and the chemical driving force, $\Delta G_m/RT$, for nucleation of V(C,N) in polygonal ferrite (b) and bainite (c).](image)

**The use of V for ferrite grain refinement**

As the transformation of austenite to ferrite occurs by a thermally activated nucleation and growth process, the formation of fine ferrite grains is favoured by a large number of nucleation sites and by high ratio of N/G, (where N is the nucleation rate per active site and G is the growth rate).

In conventional controlled rolling (CR) the recrystallisation process is suppressed during the pancaking passes and less favourable ferrite nucleation sites on the deformation bands and transgranular twins are activated in addition to nucleation at austenite grain boundaries. The RCR approach is based on maximising the grain boundary area for ferrite nucleation by suppressing grain coarsening after repeated recrystallisation.

Microalloying elements can also be directly used for ferrite grain refinement through nucleation of intragranular ferrite in the centre of austenite grain. This approach is based on conditioning the austenite in such a way as to introduce a large number of nucleating clusters or particles in austenite prior to transformation. This new microstructure refining techniques can be especially useful for heavy gauge plates and sections for which CR and accelerated cooling are not always applicable.

**Nucleation of intragranular polygonal ferrite on VN**

According to the misfit theory, the ferrite nucleation potency of particles is determined by the lattice coherency between particles and ferrite at the interface. The change in the interfacial energy and the driving force for ferrite nucleation on different particles revealed that the phases which should have the highest ferrite nucleation potential are TiN and VN [5]. Recent experimental results clearly demonstrate that intragranular ferrite plates can easy nucleate on VN [6]. This has been related to the atomic matching between (100)$_{VN}$ // (100)$_{\alpha}$ planes which allow the growing ferrite to maintain coherent, low energy interfaces with respect to vanadium nitride. In order to obtain intragranular ferrite the active VN particles must first form in austenite.
Fig. 2 Precipitation-time-temperature diagrams for vanadium carbo-nitrides in undeformed austenite in steel A with 0.12%V-0.0082%N.

The precipitation-temperature-time diagram for VN in undeformed austenite is shown in Fig. 2. The experimental results revealed that the precipitation of VN in undeformed austenite is very sluggish and requires long holding time near the temperature of maximum precipitation in order to produce effective VN particles. There are two ways in which the precipitation of VN in austenite can be enhanced. The first alternative is to modify the steel composition to obtain a high density of MnS inclusions or other particles which may act as nucleation sites for VN in austenite, without substantially changing the processing conditions. The second alternative involves a strain-induced precipitation of VN in austenite during hot rolling in the temperature range of VN precipitation.

Nucleation of intragranular ferrite of VN precipitating on the existing MnS inclusions is shown in Fig. 3. Fine V nitrides start to grow on the existing inclusions if the steel containing vanadium is slowly cooled or held at temperatures near the VN precipitation nose. The effect of vanadium in promoting the formation of intragranular polygonal ferrite is more profound in high nitrogen steels. As the nitrogen content is increased the chemical driving force for precipitation is increased and the VN particles become coarser and more numerous, thereby increasing the nucleation rate of intragranular ferrite.

Fig. 3 Intragranular ferrite nucleus in steel A with 0.12%V-0.025%N water quenched from 660°C after ~5% transformation.

An enhancement of VN precipitation in austenite by plastic deformation (strain-induced precipitation) is preferred for HSLA steels, as an increase in sulfur is not advantageous for these steels. Fig. 4 shows the precipitation curves for V-N steels. It was found that the precipitation start time depends on the vanadium and nitrogen contents in steel and on the degree of deformation. For the high nitrogen steels a reduction by ~40% is sufficient for producing a high density of 20-80nm large VN particles.

Fig. 4 Strain induced precipitation of V(C,N) in deformed austenite of V-steel [10].
The strain induced, homogenously nucleated VN particles are predominantly cube-like, Fig. 5. Their faces are active nucleation sites for ferrite. On the planar section they nucleate four-arm ferrite rosettes. Examination of local orientations of intragranular ferrite grains growing from VN particles revealed that the ferrite crystals growing from the opposite VN faces adopt the same orientation. The ferrite crystals growing from the neighbouring edges are misoriented by about 60°. This can be understood on the basis that misorientations are clustered around the unique orientation relationship, according to the analysis shown in Fig. 6(b). Intragranular polygonal ferrite grains grow by migration of the incoherent boundary involving a purely diffusional mechanism which means that any texture arising in polygonal ferrite must be controlled by nucleation alone. The measurement of the misorientations between intragranular ferrite grains in fully transformed specimens revealed that there is no strong texture, however, a local cluster of orientations with the small misorientation within the cluster was observed. It is also possible that the neighboring grains may nucleate at the interphase boundary of a previously formed crystal and austenite.

The microstructures of the specimens isothermally treated at 850°C for 1 hour and partially transformed at the temperatures 700-450°C are shown in Fig. 6. Quenching from 600°C produced a thin band of grain boundary ferrite and higher number of intragranular nucleated polygonal ferrite crystals, Fig. 6(a). Isothermal transformation at 550°C produced a very little grain boundary nucleated allotriomorphs and high density of small ferrite side plates nucleated within the prior austenite grains, Fig. 6(b). When the number density of intragranular ferrite in the isothermally transformed steels are plotted against the transformation temperature as in Fig. 6(d) there is seen to be a narrow temperature range for the formation of intragranular polygonal ferrite. This range is restricted to 650-600°C. At higher temperatures only grain boundary ferrite develops and at lower temperatures ferrite side plates become the dominant phase.
Formation of acicular ferrite structures in V-steels

It has already been demonstrated that the presence of vanadium in austenite can stimulate fine acicular ferrite structures giving considerable improvement in mechanical properties. According to Fig. 6(c) a very fine acicular ferrite structure was formed in V-steels when the isothermal transformation temperature was lowered to 450°C. Similar tendency for the formation of acicular ferrite was observed in the V-microalloyed steel with a very low nitrogen content, Fig. 7. This suggests that vanadium on its own promotes the formation of the acicular ferrite microstructure. If it is assumed that vanadium alone is responsible for the formation of acicular ferrite then the driving force for the nucleation of ferrite which will dictate the profusion of nuclei will be determined by interaction of V with other alloying elements.

It was suggested that this might be associated with Fe-V clustering in austenite which could stabilise the formation of suitable structural embryos for ferrite nucleation. It may also be speculated that carbon must play an important role in the nucleation of acicular ferrite as carbon has the strongest influence on the transformation kinetics.
Development of precipitation strengthened high and ultra-high strength bainitic steels - a new generation of V-steels.

There is at present enormous interest world-wide for achieving extra high strength steels (Rp>∼700MPa) having bainitic microstructures. These require controlled cooling practice and also hardenability-enhancing alloy elements. Vanadium contributes in this way but also offers the possibility of giving an extra strengthening contribution by precipitation within the dislocation substructure of the bainitic ferrite. This is an almost unexplored subject that offers great potential for future generations of high strength steels.

Precipitation of V(C,N) during γ/α transformation

Precipitation during the γ/α-transformation occurs because the chemical driving force for precipitation of microalloy carbonitrides increases suddenly and strongly as γ is transformed to α reflecting the solubility drop associated with the widely different solubilities in the two phases, as shown in Fig. 1. At low supersaturations corresponding to temperatures between A3 and A1 and slow cooling, nature takes advantage of easier nucleation in interfaces and carbonitrides are formed repeatedly in the moving γ/α-boundary, so called interphase precipitation, Fig. 8(a).

V-microalloyed steels are particularly suited for generating profound interphase precipitation because of their ability to dissolve large quantities of V-carbonitrides at relatively modest temperatures in the γ-range due to the larger solubility as compared to other microalloy carbonitrides. Fig. 8(b) shows the typical morphology of interphase precipitation of V(C,N) in 0.10%C-0.13%V steel. Already from its appearance one can conclude that such a microstructure is formed in sheets parallel to the γ/α-interface by repeated nucleation of particles as the transformation front moves through the austenite. A characteristic feature is also that the rows of particles that are formed in the same region on the same phase boundary all possess the same orientation, a unique variant of the Baker-Nutting (B-N) orientation relationship with the ferrite matrix [11]. The intersheet spacing is affected considerably by the nitrogen content of the steel and the interphase precipitation becomes more refined when the transformation temperature is lowered.

![Fig. 8 Generic CCT diagram for microalloyed steel indicating approximate regions of interphase and random precipitation. Precipitation in bainitic ferrite is also indicated in this figure.](image-url)
Random precipitation in ferrite

On lowering the temperature the interface will gain speed relative to the rate of precipitation, implying that the boundary escapes the precipitates leaving supersaturated ferrite in its wake for subsequent general precipitation to occur behind the migrating γ/α-boundary. In this case the particles are not aligned in rows but are randomly distributed and also are characterised by the occurrence of different variants of the B-N orientation relationship [11]. Experiments show clearly that the V(C,N)-precipitation becomes denser and the particles finer with increasing N-content, Fig. 10(a),(b). This originates from the fact that the chemical driving force for this reaction increases as more N is dissolved in ferrite and therefore increases the nucleation rate. The technically very important effect of N on the strengthening of V-steels is shown in Fig. 10(d).

![Fig. 10 Growth of V(C,N)-precipitates after transformation at 650°C as a function of the N-content and holding time, (a),(b) the effect of N on the density of V(C,N)-precipitates (c), and the effect of N, V and transformation temperature on the precipitation strengthening (d).](image)

The role of carbon

At first sight there is no evident reason why carbon should affect the precipitation of vanadium since the solubility and activity of carbon in ferrite is defined by the iron-carbon equilibrium in the two-phase structure. However, during transformation on cooling the equilibrium phases change from being ferrite + austenite to being ferrite + cementite and there is a substantial change in the carbon solubility in ferrite. Fig. 11(a) shows the two solubility limits for carbon in ferrite. At 600°C, for example, the solubility of carbon in metastable equilibrium with austenite is five times greater than the true solubility in equilibrium with cementite. Thus, during the initial stages of transformation the chemical driving force of carbon in ferrite is very large, Fig. 11(b), and profuse nucleation of V(C,N) will be favoured. The carbon activity will remain unchanged even if V(C,N) is being formed since the diffusion rate is very high and austenite provides an inexhaustible store. The above situation continues until pearlite is nucleated at which point a new equilibrium with a reduced carbon activity is established. The great reduction in carbon activity at this stage is likely to virtually eliminate further nucleation of V(C,N) although some continued growth of existing particles may be expected. The experimental results show that carbon raises ΔRp by ~ 5.5MPa for every 0.01%C in the HSLA steel, Fig. 11(c).

As the total carbon level of the steel increases, the kinetics of the γ → α phase transformation is progressively retarded since more time is required for diffusion of carbon in the shrinking austenite. Not only is the carbon activity in ferrite higher but also the period of time during which the ferrite is supersaturated with carbon is prolonged, so allowing more nucleation of V(C,N) particles and accordingly a more dense precipitation. This is clearly confirmed in Fig. 12.
Fig. 11 Solvus lines for C in ferrite in equilibrium with cementite and austenite (a), chemical driving force, $\Delta G_m/RT$, for precipitation of VC and VN in 0.12% V steels (b) and deduced values of precipitation strengthening for isothermally transformed V-steels as a function of C-content (c).

Fig. 12 Electron micrographs showing V(C,N) precipitation after isothermal transformation at 650°C in 0.12%V-0.013%N steels with different C-contents; (a) 0.04%C, (b) 0.10%C and (c) 0.21%C.

Precipitation in bainitic ferrite

Modern high and ultra-high strength bainitic steels derive their strength from the fine or ultra-fine bainitic ferrite grains in which the contribution from precipitation strengthening is of paramount importance. The precipitation reactions in bainitic ferrite are, however, less well exploited. The main reason for this is that bainite is the most complicated microstructure of steel.

Recent experimental data clearly indicate that there is an abundant precipitation of nanoscale M(C,N) in the dislocated bainitic ferrite matrix, over a broad temperature range down to 300°C, Fig. 13. It was found that there is a sequential precipitation with strong synergy effects between precipitation strengthening and bainite promoting elements. This strong precipitation strengthening effect can be used to increase the yield strength at a given toughness or to improve ductility and toughness. The improvement in ductility and toughness can be achieved by reducing the carbon content and using precipitation strengthening to compensate for the lost of strength due to the lower carbon level.

For precipitation strengthening to be successfully applied in bainitic steels, a number of issues need to be addressed. There is a need to understand better how the bainitic microstructure develops during transformation, in particular, the factors controlling the bainite morphology, the carbon partitioning between austenite and ferrite, carbon supersaturation of ferrite, nucleation conditions and the formation of the second phases. There is also a requirement to understand the solubility of microalloying/alloying elements which control precipitation reactions in bainitic ferrite. Finally, the hot rolling and cooling practices has a big influence on these factors, bainitic transformation from deformed austenite is not well understood.
Summary

Micro-alloying with vanadium provides one of the best ways of transforming standard steel into a high strength product. Small additions of V generate large increases in strength. Much has been achieved in the past for V-steels with ferrite-pearlite microstructures and vanadium is now extensively used for strong and easy controllable precipitation strengthening. The benefits of precipitation strengthening in ferrite-pearlite steels are now being extended on high strength bainitic steels.

Vanadium should also be considered as an important grain refining element. It is shown that vanadium contributes to the formation of two types of intragranular nucleated ferrite; polygonal ferrite and acicular ferrite. Intragranular polygonal ferrite nucleates on VN particles which grow in austenite during isothermal holding or slow cooling. Acicular ferrite microstructure forms in V-microalloyed steels during isothermal transformation at lower temperatures and during continuous cooling at the optimum cooling rate. The acicular ferrite microstructure was obtained in V-microalloyed steels containing either high or very low nitrogen levels. This suggests that vanadium on its own can promote the formation of the acicular ferrite microstructure.

References