

Opportunities for Vanadium Microalloying in AHSS for the Automotive Sector

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Abstract: In this article we review some of the advances made in Vanadium microalloying technology for flat products published over the past 10 years and discuss their application to Advanced High Strength Steels (AHSS) for the automotive sector. The potential benefits to a range of steel grades including Dual Phase (DP), fully bainitic, TRansformation Induced Plasticity (TRIP) and TWinning Induced Plasticity (TWIP) are discussed and examples are given. Areas of ongoing research which merit support from AHSS producers are identified.

Key words: microalloying, AHSS, Vanadium, DP, Bainite, TRIP, TWIP

1 Introduction

The proportion of Advanced High Strength Steel (AHSS) components in vehicle body-in-white (BIW) assemblies has significantly increased over the past decade. The two main driving forces behind this change are weight reduction and improved impact/crash resistance. At this time, a wide range of AHSS materials have been industrialised; these include Dual Phase (DP), TRansformation Induced Plasticity (TRIP), fully bainitic and Complex Phase (CP), TWinning Induced Plasticity (TWIP) and full martensitic (hot press forming) sheets. In this paper we provide a brief review of recent advances made in vanadium microalloying technology over the past 10 years, and discuss some of the advantages of applying vanadium microalloying techniques to each class of AHSS. In particular we focus on applications involving TRIP and TWIP metallurgies. Apart from introducing a useful increase in the yield strength (YS) and ultimate tensile strength (UTS), Vanadium microalloying can potentially contribute to the improvement of other critical in-use properties. These include damage resistance/toughness in TRIP steels and sensitivity to delayed fracture/hydrogen

embrittlement.

2 Advances in Vanadium Technology

2.1 Dual phase (DP) steels

Several authors have investigated the effects of V microalloying on DP steels^[1-5]. Son et al.^[1] studied three ultrafine grained DP1000 grades fabricated by Equal Channel Angular Pressing (ECAP). The base composition was Fe-0.15C-1.1Mn-0.25Si with V additions of 0wt, 0.06%wt, and 0.12%wt. After ECAP at 500°C (cumulative strain ~4) TEM observations showed that the ferrite grains of the two V-microalloyed grades were strongly refined and the dislocation densities were much higher than the reference, suggesting that V strongly retards dynamic recovery at 500°C. However, this refinement was not preserved after intercritical annealing at 730°C although the ferrite grain size did remain <1 µm. In fact the presence of V increased the intercritical austenite fraction at 730°C ($V_\alpha = 35\%$) beyond the expected equilibrium value ($V_\alpha = 27\%$). Compared to the reference steel the UTS of the 0.06%wt. V grade increased from 978 MPa to 1044 MPa and a substantial improvement in the uniform elongation

(9.3% → 11.5%) was recorded. The influence of Vanadium additions on tempering in DP steels was investigated by Liu and co-workers^[3]. They studied the effects of overageing (OA) for 600s at temperatures between 200°C and 400°C on the microalloyed DP900 grade; Fe-0.12C-1.4Mn-0.28Si-0.07V. The presence of V was found to increase the strength levels and to improve the tempering stability, shifting the optimum OA temperature from 250°C (reference steel) to 300°C. Further, V microalloying suppressed the yield point elongation which appeared after tempering at 350°C and above. The ability of V additions to reduce softening during ageing treatments has been investigated by Garcia et al.^[5] for DP980/DP1180 GI/GA process optimisation. This subject will be presented in detail elsewhere at this conference.

2.2 Bainitic steels

The effect of Vanadium additions on low carbon fully bainitic strips is a subject of strong technological interest^[6,7,8]. Starting from a base composition of Fe-0.09C-1.9Mn-0.3Si, Iung and Herman^[8] investigated the effect of V and N microalloying on the bainitic transformation between 500°C and 600°C. They found a strengthening effect of up to +105 MPa in the UTS with V additions of 0.18%wt. An interesting observation was that when 0.014%wt. N was added this strength increase became independent of the bainitic transformation temperature in the range 500°C to 550°C. The mechanism behind the strength increase was not clearly identified. Recently, Siwecki and co-workers studied bainitic hot strips with compositions Fe-0.04C-1.4Mn-0.1Si-1Cr-0.25Mo-0.08V-(0.01~0.038)N coiled at 400°C^[6]. They found a yield strength of 740~790 MPa for V microalloyed strips, compared to 680 MPa for a reference composition without V. Although some V(C,N) precipitation was possibly detected in TEM foils after coiling at 450°C, the authors conclude that the main action of V is not to promote precipitation strengthening but rather to retard the recovery of the bainitic ferrite dislocation structure, an observation which is compatible with the results of Son et al.^[11]. Similar behaviour has been observed during low

temperature tempering of fully martensitic steels^[10]. Further evidence that V does not precipitate in the bainite region comes from a recent Vanitec project^[7] where a steel of composition Fe-0.24C-1.5Mn-0.7Si-0.8Cr-0.2V-0.09N was normalised at 1000°C and air cooled. The final structure was bainitic with 15% retained austenite. Selective chemical dissolution was used to measure the precipitated weight fraction of V and a value of 0.011%wt. was found i.e. only 5% of the nominal value. Tomographic atom probe images (Fig. 1) of the bainitic ferrite show some co-segregation of C and V at lath boundaries or dislocations but no evidence of VC precipitation, even though a net strength increase was observed.

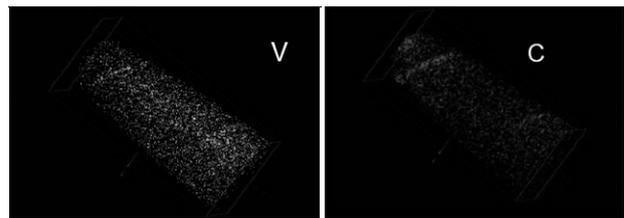


Fig.1 Tomographic atom probe image of C and V in bainitic ferrite (after^[7]). The analysed volume is 34nm×34nm×76nm

A recent Small Angle X-ray Scattering (SAXS) study^[9] of an Fe-0.46C-0.85Mn-0.25Si-0.3V alloy cooled at 20°C/s from 1250°C and held at 600°C for 1800 s confirmed that the mean precipitate diameter was ~0.5 nm i.e. too small to detect in the TEM. These structures were carbon-deficient and did not display the usual NaCl-type crystallography of VC – the authors identified them as clusters or precursors which nevertheless provided a significant strengthening effect.

2.3 TRIP steels

Vanadium microalloying in TRIP steels has been studied by various authors^[11-16] and several beneficial effects have been observed. Increases in UTS of up to +200 MPa with no significant loss in elongation or toughness have been achieved with additions of 0.15%wt. V and 0.09%wt. N (Fig. 2). Obtaining the best performance from this system requires a careful optimisation of composition and process parameters. The principal objective is to strengthen the softer ferrite phase without reducing the carbon

concentration in the residual austenite and hence its stability.

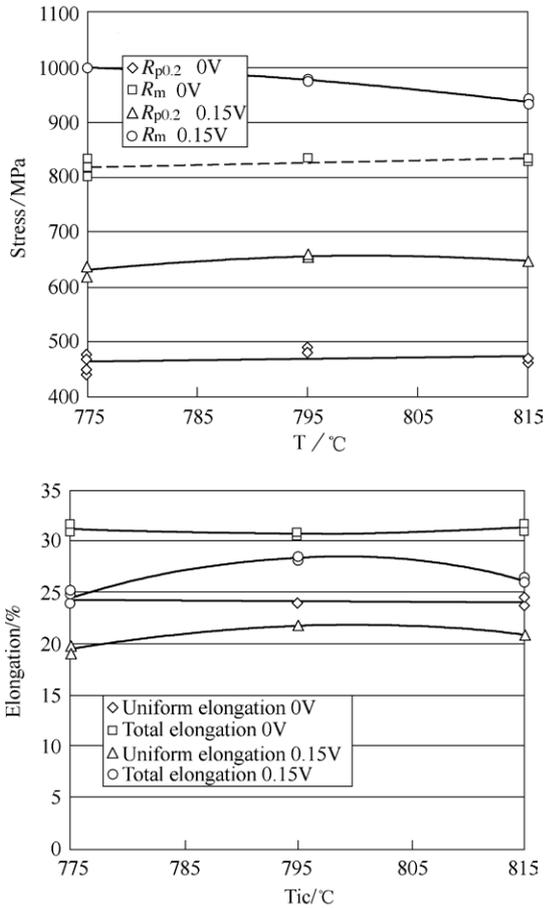


Fig. 2 Mechanical properties of Fe-0.22C-1.6Mn-1.6Si cold rolled TRIP800 microalloyed with 0.15V-0.09N as a function of the intercritical annealing temperature

Vanadium, coupled with the correct amount of nitrogen, is the only microalloying element which can do this^[11,12,14]. The heterogeneous precipitation of V(C,N) in ferrite and austenite is clearly illustrated in the TEM extraction replica images in Fig.3. The explanation for this behaviour can be seen in Fig.4 where the ratio of carbon to nitrogen in V(C,N) precipitates is plotted as a function of precipitate size in ferrite and in austenite quenched from the intercritical domain. Essentially no nucleation of V(C,N) occurs in austenite whereas nucleation and growth is strong in ferrite and depends strongly on the free nitrogen content^[14]. The logic behind this type of alloy design is also applicable to intercritically annealed DP steels and to some proposed process routes for 3rd generation AHSS with high residual austenite fractions^[17,18].

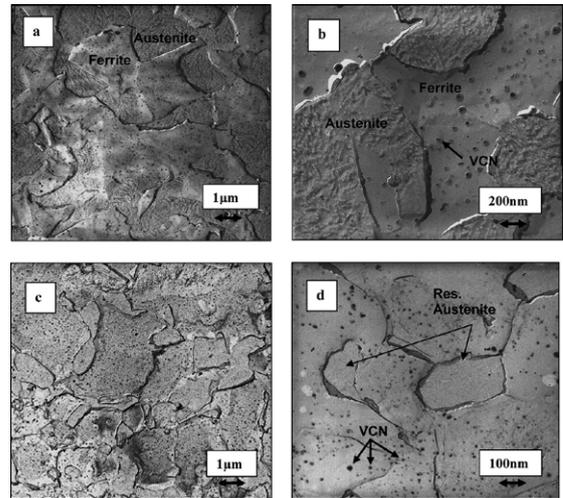


Fig. 3 (a,b) TEM replicas showing heterogeneous V(C, N) precipitate distributions in austenite and ferrite after heating at 5°C/s to 775°C for 180 s and water quenching. (c,d) the final microstructure after cooling and overaging at 400°C for 300 s

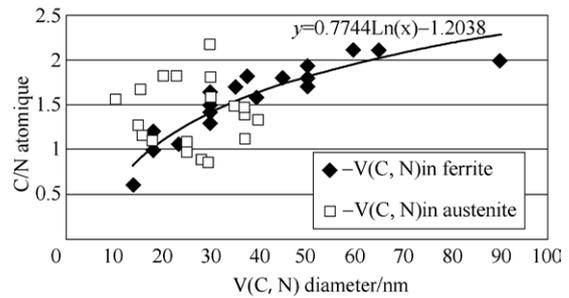


Fig. 4 Comparison of the C/N atomic ratios measured by TEM EELS in V(C, N) precipitates in cold strip ferrite and in cold strip austenite as a function of precipitate size

2.4 TWIP steels

Microalloying in C-Mn austenitic steels has been studied for example to improve shape memory effects^[19]. However, it has recently become a subject of interest in cold rolled and annealed TWIP steels as it is a most effective mechanism to increase the rather low yield strength of this class of steels^[20-23]. As can be seen in Fig. 5, vanadium is the most effective precipitation strengthening agent in these alloys. Indeed, gains of up to +375MPa in the YS have been reported^[21]. Titanium provides very efficient precipitation strengthening at low concentrations (0.1%wt.) but the hardening effect quickly saturates due to the appearance of coarse primary inclusions. The growth kinetics of Nb(C,N) precipitates appears to be too rapid to retain particles that are sufficiently

small for significant Orowan strengthening – some gains in strength due to partial non-recrystallization effects have been observed but at the expense of ductility^[23]. There is currently an open question on the effect of small (< 5nm radius) V(C,N) precipitates on the strain hardening characteristics of TWIP steels^[21,22]. In Fig.6 the flow curves are plotted for three different TWIP base metallurgies microalloyed with Ti, Nb and V. It can be seen that microalloying has little effect on the work hardening rate at small strains but has large effect at larger strains (i.e. $\epsilon > 0.25$, see the arrows in the graph). Note that care was taken to minimize the variation in grain size between the different grades in this Figure^[21]. From this and from synchrotron X-ray diffraction data, a conclusion was drawn that twinning kinetics were not modified by precipitation, at least for strains below ~ 0.25 . However, more detailed TEM studies^[22] suggest that twin/precipitate interactions are actually quite strong, and that this may affect the twinning kinetics at large strains. On the strength of these observations, a physically-based model has been proposed^[28] to describe the effect of nanometer-sized VC on the work hardening rate of TWIP steels. This model suggests that the presence of dispersed nanometer-sized carbides results in a faster initial dislocation accumulation process coupled with a reduction in the rate of twin formation. In comparison to a reference TWIP alloy with no V additions, the work hardening rate is thus higher at the start of plastic deformation and then decreases more rapidly as strain proceeds. This point will be discussed in detail elsewhere in this congress^[28]. From Fig.6 it can be argued that the strain hardening characteristics of micro-alloyed TWIP steels remain extremely good.

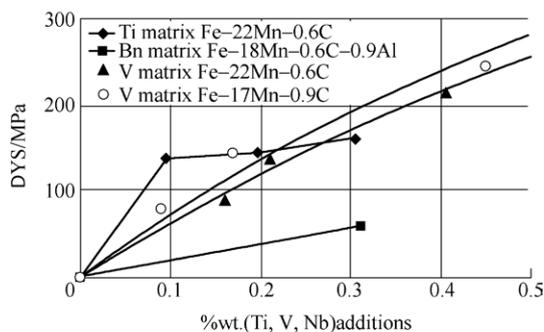


Fig. 5 Yield strength increase in Fe-(17-22)Mn-(0.6C-0.9)C austenitic TWIP cold strips as a function of nominal microalloying additions

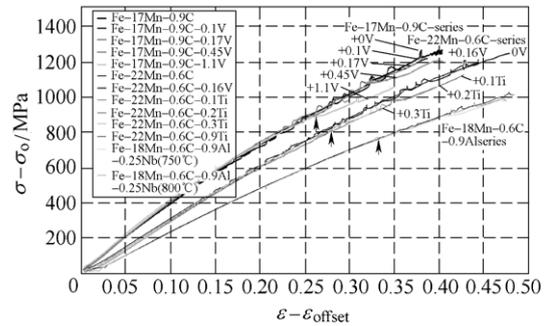


Fig.6 The effect of microalloying with different concentrations of Ti, Nb and V additions on the flow curves of Fe-(17-22)Mn-(0.6C-0.9)C cold strips

2.5 Hydrogen trapping

No discussion of vanadium precipitation in high strength steels can be complete without mentioning hydrogen interactions. It has long been established that vanadium precipitates are useful to prevent delayed fracture (DF) in martensitic steels. Recent studies suggest that the presence of VC appears to reduce the apparent H diffusion coefficient in martensite^[26].

As the UTS of AHSS steels increases to levels around 1 GPa and above, they too become sensitive to DF and especially to stress corrosion cracking (SCC). It has been clearly shown that vanadium precipitates are useful in suppressing DF in TWIP steels and that they have a beneficial effect on SCC^[20]. Contrary to the observations made in martensitic steels, this cannot be attributed to any change in the H diffusion coefficient^[27]. A study by Malard and co-workers^[24] using Small Angle Neutron Scattering (SANS) on deuterium charged Fe-18Mn-0.2Si TWIP samples containing 0.2%wt. V showed that up to 3 ppm wt. of H could be irreversibly trapped inside the precipitates (Fig. 7). This is sufficient to suppress DF, but not SCC where the external source of H is theoretically unlimited.

A very interesting TAP study using deuterium charged Fe-0.087C-0.1Mn-3Al-0.35V ferritic steel was recently carried out by Takahashi and co-workers^[25]. Using a special charging cell they detected strong deuterium trapping on the (001) broad interfaces of large (>8 nm) V₄C₃ platelets. Smaller precipitates did not show any interaction with deuterium atoms – the authors suggest that this was because no misfit dislocations were present, however they did not

discount the possibility the D atoms were trapped on C vacancies in the lattice.

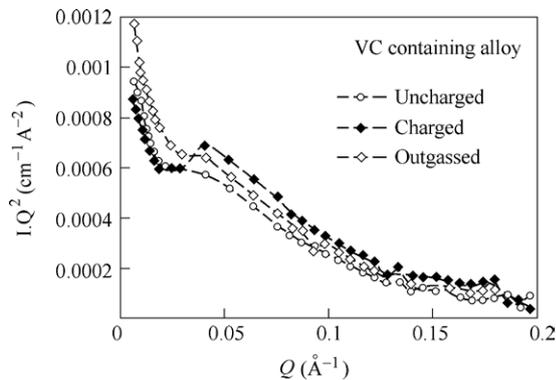


Fig. 7 SANS Kratky plot of IQ^2 versus Q for samples (C) with VC precipitates at different concentrations of H. The shoulder at $Q \sim 0.04$ in the uncharged specimen is due to the presence of 7 nm diameter V(C,N) precipitates. Trapped deuterium changes the apparent size of the particles

3 Conclusions

Applying Vanadium microalloying to AHSS can result in significant improvements in many technologically important areas. DP grades benefit from increased strength and tempering stability. In bainitic steels significant strengthening is observed, most probably due to retarded recovery kinetics rather than precipitation strengthening. More studies are required to clarify the effects of V additions at temperatures below 550 °C in bainite. TRIP steels are excellent candidates for V microalloying as the ferrite phase can be selectively strengthened by V(C,N) nucleated during intercritical annealing. Significant strengthening by fine V(C,N) precipitates of up to +375 MPa on the YS of TWIP steels has been demonstrated. The interaction between these nano-precipitates and twinning is a subject of current scientific debate. As well as providing improved mechanical properties, V precipitates are known to improve DF and SCC resistance in martensitic steels and in austenitic TWIP alloys. The latest analysis techniques are now providing us with some direct evidence of the precipitate-hydrogen interaction mechanisms. This research merits strong support if cold formed AHSS steels with UTS > 1 GPa are to be widely accepted in the automotive sector.

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