THE ROLE OF NITROGEN IN MICROALLOYED STEELS

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ABSTRACT

The key microstructural features of microalloyed steels, i.e. grain refinement and precipitation strengthening, are achieved by the precipitation of microalloy-species in austenite and during or after the transformation to ferrite. The effectiveness of any precipitation reaction depends on the degree of dispersion and particle size. Since nitrides of the microalloying elements are more stable and show less tendency to coalesce than carbides, an enhanced nitrogen content will maximise the ratio between particle volume fraction and particle size and hence maximise grain refinement and precipitation strengthening.

This review considers some of the more important effects of the interaction of nitrogen with microalloying elements in microalloyed steels. The importance of nitrogen for precipitation phenomena, grain size control, transformations, precipitation strengthening and weldability are discussed in relation to various steel chemistry and processing technologies which have been developed within the past twenty years. To provide a basis for improved understanding of the interaction of nitrogen with other alloying elements in HSLA steels a new thermodynamic database for precipitation of carbonitrides in multicomponent systems has recently been developed for use with "Thermo-Calc" software.

The value of nitrogen is particularly recognised in steels microalloyed with vanadium and titanium and it is demonstrated that nitrogen should be considered as an essential and inexpensive alloying element giving several beneficial effects. Nitrogen may be very effectively utilised in microalloyed steels with the aid of knowledge concerning its physical and chemical interactions.

1. INTRODUCTION

Microalloying elements are added to high-strength low-alloy (HSLA) steels for only two purposes-to produce grain refinement and/or precipitation strengthening. In both cases the desired effects are achieved by intelligent use of precipitation reaction of microalloy carbo-nitrides in which nitrogen often plays the dominant role. Thus, an understanding of the effects of nitrogen on the solubility and precipitation reactions of these precipitates is critical to the successful production and application of microalloyed steels, with a minimum of microadditions.

Nitrogen occurs universally in steels, and although its solubility under normal manufacturing conditions is small it can exert large effects. Some of these effects are detrimental, often being associated with various embrittlement phenomena, which has resulted in liquid steel refining processes designed amongst other things to decrease the nitrogen content (Japanese steelmakers have led the way in these developments and have actively published the advantages of such ultra-clean steels in the market place). However, nitrogen has also certain beneficial effects, apart from being abundant and cheap, which in recent years have led to the development of many different steels containing enhanced nitrogen. In almost all cases the beneficial effects of nitrogen are the result of interaction with alloying elements present. To understand the effects of nitrogen in steels, as opposed to the effects of carbon, both of them interstitial solutes, the much increased solubility of nitrogen in the solid state, compared with carbon must be appreciated. In addition the alloy nitrides, such as VN, NbN and TiN are much more stable and thus less soluble than the alloy carbides, and their solubilities are considerably less in ferrite than in austenite. Hence alloy nitrides often form small particles which are slower to grow than are alloy carbides. These differences have a fundamental influence on the effects of nitrogen on the properties of HSLA steels.

The effectiveness of nitride particles in raising the austenite grain coarsening temperature during reheating and welding, inhibition of grain growth during rolling, retardation of recrystallisation, increasing austenite to ferrite transformation ratio and enhancement of precipitation strengthening, was demonstrated many years ago. However, in the last two decades significant metallurgical progress has been made in understanding the technology of microalloyed steels. This progress, initially intended for pipeline steels, has been such that microalloyed steels have now been developed for numerous applications and have become more sophisticated and employed to produce specific and sometimes unique benefits.

It is also worth adding that the beneficial effects of nitrogen are not recognised in steel specifications since although some specifications state a maximum level of nitrogen, there is none which requires a minimum level. There is little justification for reducing nitrogen content in many steel grades to below about 0.005%. Such steel will, however, find ready customers because of widely publicised embrittling effects of nitrogen. However, restricting nitrogen to this low range prevents optimisation of alloy design for many high strength low alloy steels and besides, these degassing and refining practices are extremely costly. Therefore, the main aim of the present paper is to present contrary evidence about the beneficial effect of nitrogen particularly in grain refinement and precipitation strengthening in relation to microalloying with Ti and V.

2. GENERAL EFFECTS OF NITROGEN ON PRECIPITATION AND MICROSTRUCTURE

As was stated above the principle advantages of microadditions are centred around the precipitation of microalloy carbides/nitrides. The precipitates are either completely or partially dissolved during the reheating of slabs prior to rolling, or as part of a heat treatment process, and thus the reprecipitation sequence and kinetics control, to a large extent, the benefits that are achieved. In precipitation reactions there are two parameters which determine the ability of particles for grain refinement and strengthening, namely particle size, d, and their volume fraction, f_v.

The ability of second phase particles to maintain fine grain sizes at high temperatures by pinning migrating boundaries is well established in a wide range of structural materials. The limiting grain size, D_c, in the presence of second phase particles may be expressed by the classical Smith-Zener equation for inhibition of grain growth [1]

$$D_c = \frac{4}{3}\frac{r}{f_v} \qquad \text{or} \qquad \frac{1}{D_c} \approx \frac{f_v}{d} \qquad (1)$$

where r is the particle radius and d the particle diameter.

Despite simplifying assumptions used in the Smith-Zener equation (1) its validity has been confirmed experimentally and it is commonly accepted that for maximum pinning (grain refinement) the ratio between f_v and d should be high [2,3]. Modifications of the Smith-Zener equation pertain mainly to the proportionality factor between the grain dimensions and f_v/d ratio.

Also precipitation strengthening models, based on Ashby-Orowan theory [4], predict that the contribution of the particles to the yield strength of the alloy, $\Delta\sigma_p$, is directly determined by the ratio between f_v and d

$$\Delta\sigma_p \cong \frac{Gb}{L} \qquad \text{or} \qquad \Delta\sigma_p \approx \frac{(f_v)^{1/2}}{d} \qquad (2)$$

where G is the shear modulus, b is the Burgers vector in the slip direction and L is the spacing between the dispersed particles.

Equations (1) and (2) imply that for an effective prevention of grain coarsening as well as for optimum precipitation strengthening the volume fraction of the pinning particles should be high and their size small.

The initial volume fraction of precipitated particles is directly determined by the content of microalloying element and an increase in volume fraction of particles requires simply more microadditions. Microalloying is, however, expensive and should be utilised as effectively as possible for economic production of HSLA steels.

Reduction in the volume fraction, on the other hand requires a corresponding reduction in the size of the particles in order to stabilise a given austenite grain size or maintain certain strengthening effect. The volume fraction will decrease with increasing temperature due to dissolution of the second phase. The volume fraction of a simple precipitate can be derived from the chemical composition of the steel and the solubility product, k_s,

$$\log k_s = \log[M][X] = A - B/T \qquad (3)$$

where [M] is the dissolved microalloy (wt%); [X] is the content (wt%) of nitrogen or carbon, A and B are constants and T is absolute temperature.

From equation (3), it is clear that for good grain refinement the particles should exhibit a limited solubility in austenite over the temperature range of interest. The solubility data for individual microalloy carbides and nitrides are compared in Fig. 1. It should be pointed out that there are significant differences in the published solubility data for a given alloy carbide or nitride (discussed below), and this figure shows only the relative solubilities for various carbides and nitrides. However, it is clear that the solubilities of nitrides are generally much lower than those of the corresponding carbides. This is specially true for titanium and vanadium where the differences are particularly pronounced. Precipitation of nitrides will, as compared to

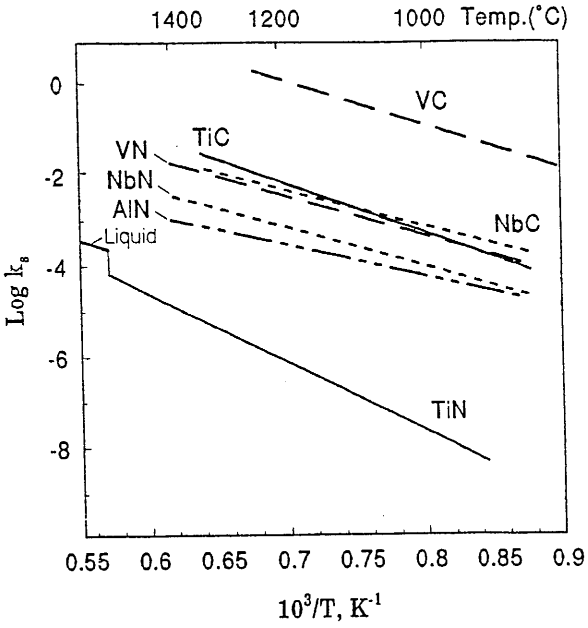

Figure 1. Solubilities of microalloy carbides and nitrides.

carbides, start at a higher temperature and will at any given temperature give higher volume fraction and reduce the dissolved content of microalloy element in the matrix.

A significant feature of fully precipitated particles is their ability to coarsen by coalescence at elevated temperatures. This process is described by the Wagner equation [5].

$$r^3 - r_o^3 = \frac{8}{9}\frac{\gamma D[M]V_m}{RT}t \qquad (4)$$

where r is the mean particle radius at time t, r_o is the initial mean particle radius, γ is the interphase surface energy, D is the diffusivity of the relevant species, [M] is the solubility of the relevant species, V_m is particle molar volume, and R is the gas constant. The much lower value of the product D·[M] makes the substitutional microalloy element the rate controlling species.

The question of how the nitrogen content should be optimised to the microalloy content may be illustrated by the following case of grain size control by TiN dispersion in a Ti microalloyed steels. Fig. 2 shows the combined effect of precipitate coalescence and precipitate dissolution on the grain coarsening by abnormal growth as the temperature is raised. The dashed lines show the coarsening of the existing nitrides at two levels of nitrogen in the steel. The full lines show the critical precipitate size for inhibition of grain coarsening, at two levels of grain sizes, 25 and 50µm, as the volume fraction of nitrides decreases with increasing temperature. When these two sets of curves intersect the condition for grain coarsening is reached. The slower coalescence rate at the higher nitrogen level is caused by the lower solubility of Ti, as is evident from Fig. 3. This figure also demonstrates that less TiN is dissolved at higher nitrogen level in the steel. This increases the volume fraction of second phase available for particle pinning. The main feature of Fig. 2 is that it demonstrates clearly the strong effect of nitrogen on the grain coarsening temperature; in a 0.01%Ti steel the grain coarsening temperature is shifted from 1190°C at the stoichiometric nitrogen content of 0.003% to above 1320°C at 0.010%N. It is interesting to note that the better resistance to grain coarsening in the

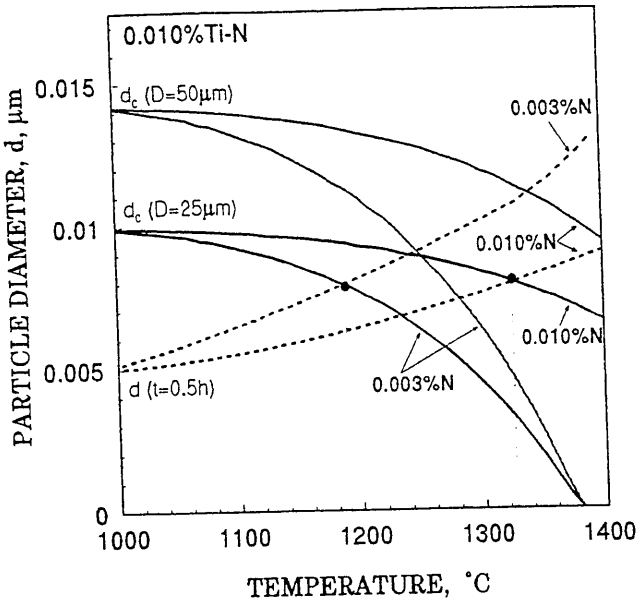

Figure 2. The effects of nitrogen content and temperature on development of the TiN particle size, d resulting from coarsening (dashed line) and on the critical particle size, d_c for maintaining the austenite grain size at 25 or 50μm (full line). The reduction in d_c with temperature arises from a reduction in equilibrium volume fraction of TiN (eq. 3).

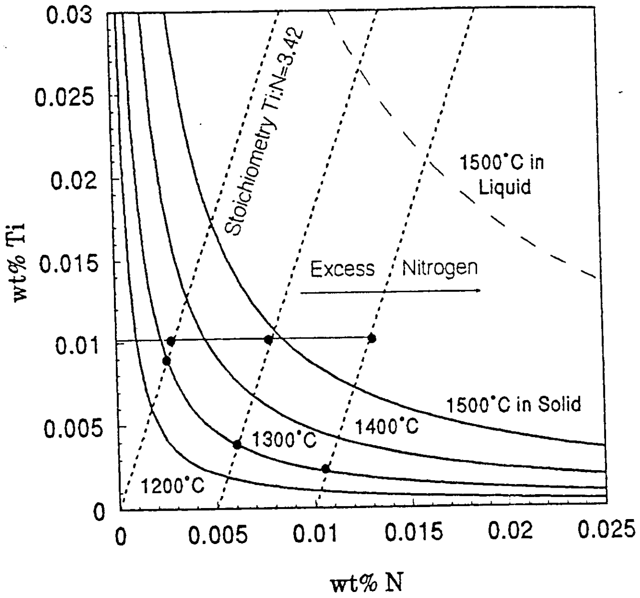

Figure 3. Effect of excess nitrogen on dissolved titanium.

presence of high nitrogen is due partly to the decreased coarsening rate of TiN but more importantly to the lower solubility of TiN.

2.1 Thermodynamical calculations

In order to maximise the effect of microadditions it is necessary to predict the evolution of nitride particles during processing. Up to now the method of analysing the results was rather simple. The volume fraction of alloy nitrides was calculated from individual solubility equations (equation (3)). The result of such calculation depends on the solubility equation taken which has been a source of error. Solubility of nitrides in both austenite and ferrite has been the subject of a number of investigations. The results proposed by various authors as the "best-line" relationships sometimes differ considerably. An analysis of published data concerning the solubility of TiN has shown, for instance, that there exist more than ten different solubility equations for TiN, as shown in Fig. 4, and the spread is greater than 150°C. It should be pointed out that the situation is even more complicated when more than one microalloy element is present and when the ratio of carbon to nitrogen is changed. A probable reason for this is that the interaction of other elements present in steels is not considered in a single solubility equation.

In order to improve the accuracy of calculation a consistent HSLA database for the thermodynamic properties of micro-alloyed steels has been developed at the Swedish Institute for Metals Research in cooperation with the Royal Institute of Technology and Swedish Steel Corporation (SSAB). This database is set up on Thermo-Calc software, based on the regular solution model for multicomponent systems [6] and is designed for HSLA steels containing the following elements:

Fe-C-S-Si-Mn-Cr-Ni-Mo-N-Nb-V-Ti-Al-B-O

An example of Thermo-Calc calculations of nitride precipitation in steels microalloyed with only one element, is shown in Fig. 5. Also shown in this figure is the mole fraction of nitrogen in carbo-nitrides at various temperatures and for various nitrogen contents from hyperstoichiometric levels to zero. This shows that when the solubilities of nitrides and carbides are significantly different, as for Ti and V, the precipitates formed in the austenite are almost pure nitrides, until practically all nitrogen is consumed. Note that in the Ti-steel there is sufficient nitrogen to combine all Ti as TiN except for the lowest level (0.001%N), whereas in the V-steel there is sufficient nitrogen to fully combine V only at the highest

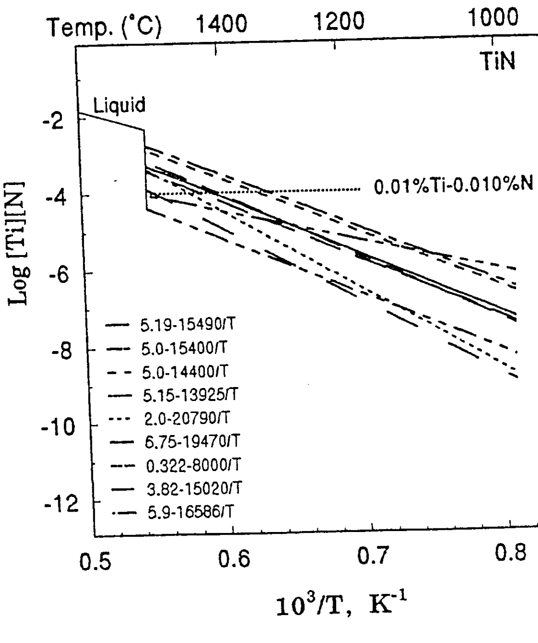

Figure 4. Differences in the published solubility product for TiN.

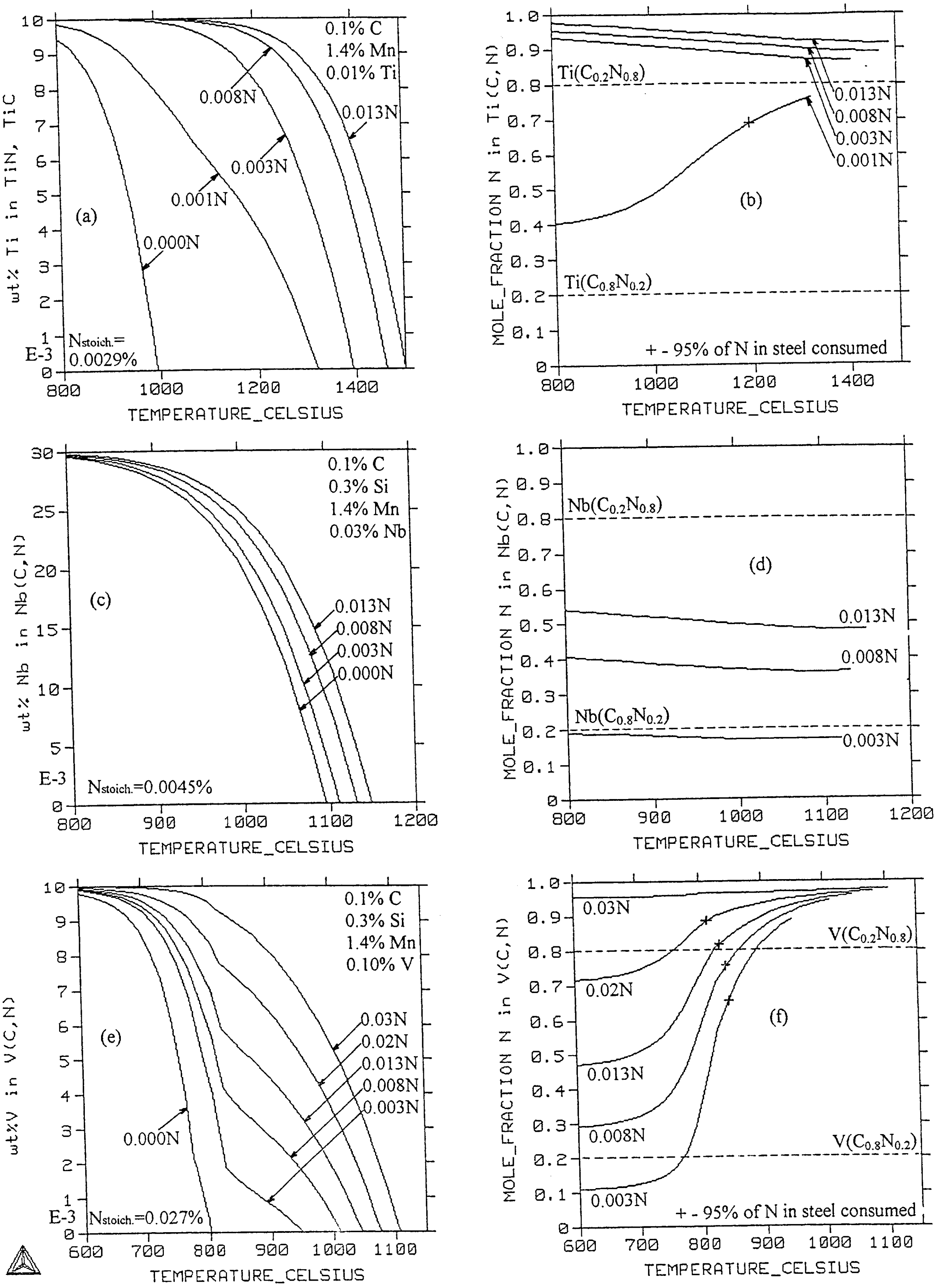

Figure 5. Example showing the precipitation of nitrides, nitrogen-rich carbonitrides and carbides in single-microalloyed steels with 0.1%C and 0.01%Ti (a, b), 0.03%Nb (c, d), and 0.10%V (e, f) at various N content.

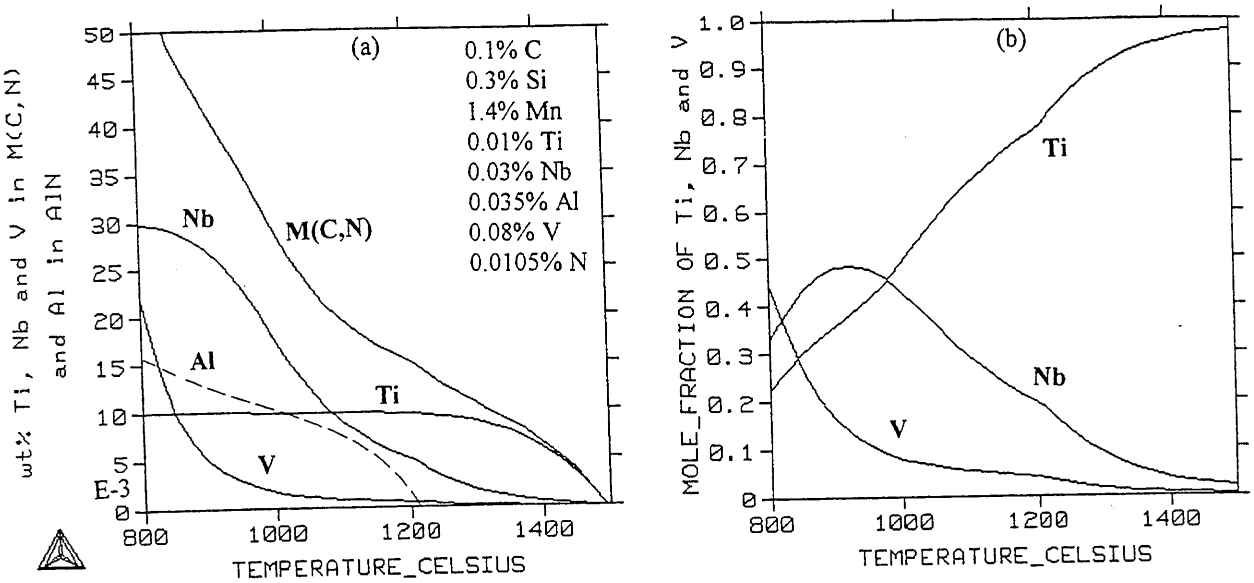

Figure 6. Example showing the precipitation of nitrides and nitrogen-rich carbonitrides in multiple microalloyed steel (a) and the mole fraction of Ti, Nb and V in M(C,N) (b).

level (0.03%N). When the nitrogen is about to be exhausted there is a gradual transition to form mixed carbo-nitrides, Fig. 5b, f. For Nb-steel, Fig. 5c, d, where the difference in solubility between the nitride and the carbide is relatively small, mixed carbo-nitrides form at all nitrogen contents, even at the hyperstoichiometric levels. Hence, for realistic contents of carbon and nitrogen in steel, relatively pure nitrides cannot form at all.

In modern microalloyed steels, the requirements for specific properties may call, however, for the use of more then one microalloying element. Multiple additions can modify the behaviour of the microalloy nitrides by the presence of another element, and the changes are dependent on the particular elements considered. In principle, the behaviour can be divided depending on whether the two nitrides show mutual insolubility or whether they show mutual extended solubility.

An example of Thermo-Calc calculation of nitrides for multiple microalloying of a typical HSLA steel with 0.01%Ti, 0.03%Nb, 0.035%Al, 0.08%V and 0.011%N is shown in Fig. 6, where the soluble components are expressed as a function of temperature. It is clear from this figure that the major part of the precipitate at the highest temperatures is TiN, whilst the further precipitation at lower temperatures is predominantly Nb(C,N). The thermodynamic calculations imply that at 1300°C TiN contains ~20% of Nb and ~5% of V for this particular steel composition. It may be also seen that AlN (with close packed hexagonal structure) has little or no solubility for other microalloying elements and starts to precipitate above 1200°C in the presence of 0.035%Al. It should be mentioned that the uniform composition of second phase particles suggests from the thermodynamic calculations is often incorrect. The particles are frequently cored, reflecting the high temperature stability of a titanium-rich and nitrogen-rich compound in the interior of the particle with relative enrichment of Nb and V towards the surface of the particle.

The nature of the nitride precipitates formed in the austenite of Ti-V HSLA steels have been studied by high resolution analytical transmission electron microscopy [7]. As expected the primary precipitates to be formed in austenite are composite (Ti,V)-nitrides. The Ti and V contents of those depend on steel composition and precipitation temperature. A large V content of the steel raises the fraction of V in the nitride and a lower temperature of formation, corresponding to smaller precipitates, also raises the V-fraction. Another important finding is that these primary composite nitrides can act as nucleation centres for subsequently precipitation at relatively low temperatures, thereby forming a VN-deposit around a core of (Ti,V)N. Similar results have been obtained for Nb-V steels, and niobium-vanadium nitrides have shown Nb and N enrichment in the precipitates, in accord with the higher thermodynamic stability of NbN.

2.2 Prevention of grain growth of austenite

Grain refinement is the key objective of thermo-mechanical treatment (TMT) of steel. The most effective way of controlling the austenite grain size during hot rolling and, at the same time, maintaining a fine initial as-reheated grain size is provided by a dispersion of fine titanium nitrides [8,9]. TiN particle are extremely stable and will, with a favourable dispersion, counteract austenite grain coarsening up to very high temperatures.

The interval of Ti content to create a useful TiN dispersion is relatively limited. This can be appreciated from the solubility curves shown in Fig. 3 where it is clear that for a relatively large Ti addition of 0.04% or more, titanium nitrides may start precipitating in the liquid. Precipitation in the melt will certainly produce coarse, widely dispersed nitrides, but precipitation close to the melting point in the solid state will also tend to create coarse, widely spaced particles due to sparse nucleation under low supersaturation. Also rapid particle coarsening may assist in the same direction. To maintain a fine dispersion of titanium nitrides, the Ti addition is limited to about 0.010 to 0.015%, to lower the precipitation start temperature. Furthermore the rate of solidification and cooling must be fast. This condition exists in continuously cast steels or small ingots.

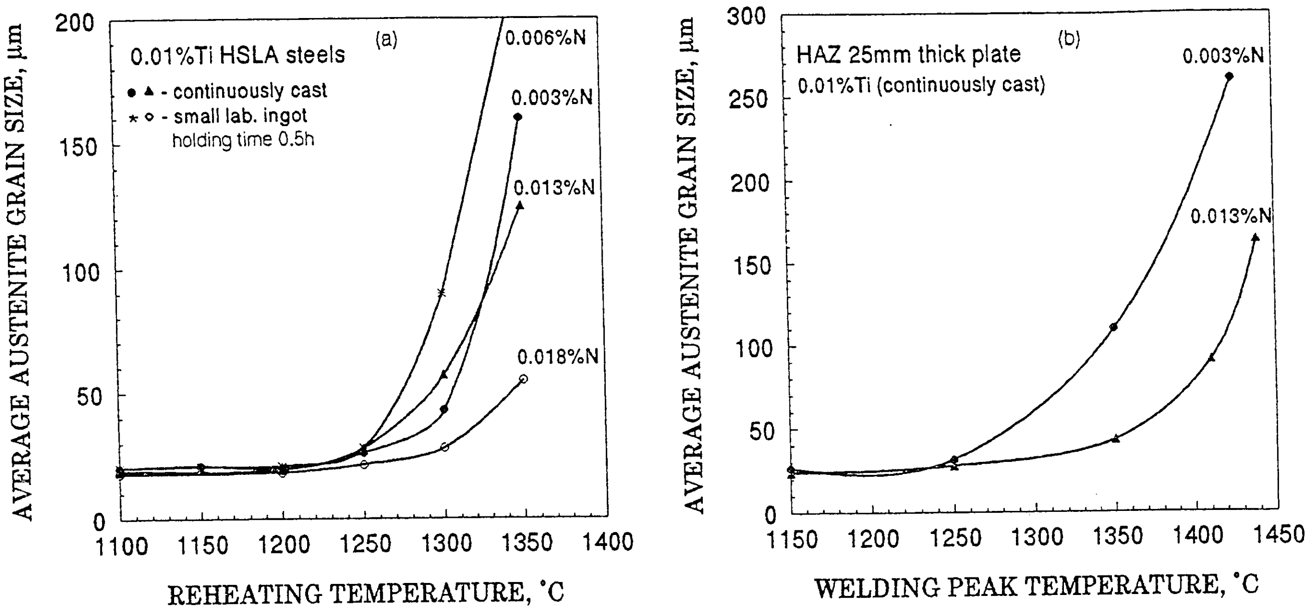

Figure 7. Effect of N on austenite grain growth in 0.01% Ti steels. (a) as cast material, (b) 25mm hot rolled plate [10,12].

Regarding the optimum nitrogen content (Ti:N ratio), two factors should be considered: the volume fraction of fine precipitates and the stability of particles. The optimum ratio of Ti:N for best grain refinement was investigated on a series of low and high nitrogen Ti and Ti-V microalloyed steels, containing ~0.01%Ti [10-13]. A part of the results of detailed investigation of grain size and TiN particles on slowly solidified ingots, continuously cast slabs and small laboratory ingots as well as hot rolled plates are shown in Fig. 7. The initial volume fraction of nitride particles was similar as this is determined by the Ti content. However, the particle size becomes smaller with increasing cooling rate during and after solidification, which leads to an increase in the Zener drag [1-3]. The role of nitrogen is complicated, since higher nitrogen contents are expected, according to solubility arguments, to raise the temperature of precipitation during cooling and, therefore, to give rise to larger, less effective particles. On the other hand, an excess of nitrogen above the stoichiometric level for TiN should suppress the solubility of Ti during heating and so render coarsening of the particles more difficult. Indeed the grain coarsening temperature (GCT) may be decreased by up to 300°C for the same steel composition by unduly large TiN particles, as were identified in slowly solidified ingots [10,11]. Even the cooling conditions during continuous casting are not optimum for precipitation of small TiN at higher nitrogen content.

The essential effects of nitrogen and cooling rate during and after solidification on GCT are summarised in Fig. 8. Provided that the cooling rate is sufficiently fast, as for the small laboratory ingots, the TiN precipitates will be fine at all nitrogen levels in the 0.01%Ti steels. However, the volume fraction of fine nitrides, remaining at reheating temperature, will rise with enhanced nitrogen in the hyperstoichiometric region, Fig. 3, and as a consequence the pinning of grain growth will increase, giving increasing GCT's. The lower cooling rates in the continuously cast slabs, on the other hand, will cause nitride formation at higher temperatures at the higher nitrogen levels, thus producing coarse, ineffective particles. In this case, therefore, the GCT is lowered with increasing nitrogen. The above results on the effects of nitrogen and casting practice on austenite grain size control implies that we can make more effective use of enhanced nitrogen in processes with fast cooling, such as thin slab casting and strip casting.

The precipitation of TiN was recently investigated also on hot charged and hot direct rolled 0.01-0.03% Ti steels [14-16]. It was suggested that titanium precipitates slowly in undeformed austenite and that, in hot direct rolled samples the higher proportion of titanium remains in solution at the onset of rolling. Most of the titanium precipitates as a fine dispersion when rolling commences.

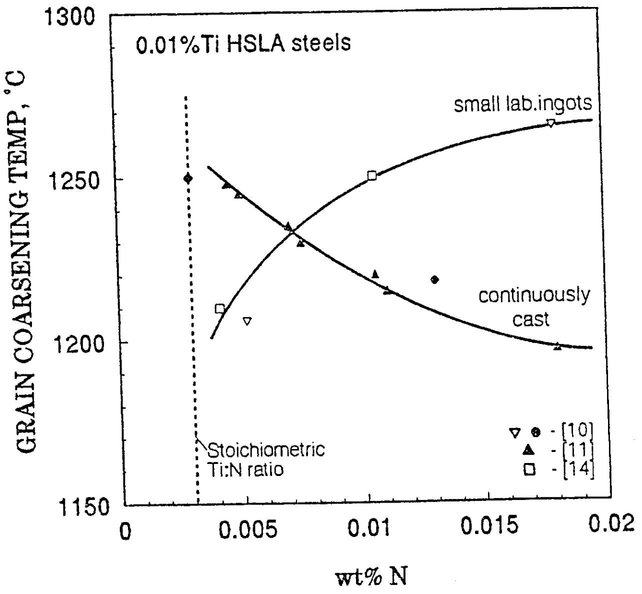

Figure 8. The relationship between austenite grain coarsening temperature (GCT) and nitrogen content for continuously cast slabs (220mm thick) and small laboratory ingots of 0.01%Ti HSLA steels.

These fine TiN precipitates pin grain boundaries more effectively and inhibit recrystallisation of austenite, consequently leading to a finer ferrite grain size on transformation as compared with conventional cold charge rolling. Also other microalloying elements, V, Nb and Al, remain completely dissolved in the austenite of hot direct rolled steels, which allows their better utilization during subsequent thermo-mechanical treatment. It should be pointed out, however, that the suggested sequence of precipitation of TiN in hot direct rolled steels depends in similar manner on nitrogen as described above.

Apart from the effect of TiN in controlling grain size during processing and heat treatment, titanium nitride can also control grain size of the HAZ of welds. The enhanced stability of TiN for the higher nitrogen content Ti-V steels discussed above, are clearly visible in Fig. 7b. As was pointed out in low N steel, where the Ti and N are nearly in stoichiometric balance, the equilibrium composition and volume fraction of the precipitates are more temperature dependent than in the steel with higher nitrogen. Indeed a marked dissolution of TiN occurred, causing significant austenite grain growth during the welding thermal cycle in the low N steel. In the high N steel the TiN particles did not dissolve and only limited particle coarsening was observed; from ~11nm in the as-cast slab to ~24nm in the HAZ [12], which may be associated with particle ripening at high temperature. The higher dissolution temperature of TiN in high N steel effectively reduces grain growth in the HAZ and explains the different responses on welding observed in low and high N steels.

A similar effect of nitrogen is also significant in enabling small particle sizes to be attained in aluminium grain refined steels, Fig. 9 [17]. This effect is not only important in normalised steels but also in thermomechanically processed steels where a fine reheated grain size is advantageous. In steel with the Al:N ratio <2 the AlN ripening is prevented and fine grain structure can be obtained after normalisation. This is due to the greater stability of AlN in the presence of high nitrogen, the effects agreeing well with a model for the grain coarsening temperature. On the other hand, when the Al:N ratio >2 easy growth of AlN particles leads to extensive austenite coarsening [17].

It has also been found that the principal factor influencing the size distribution of VN precipitates is nitrogen content and the ratio between V:N. The effect of nitrogen on the grain coarsening characteristic of V microalloyed steels, Fig. 10, shows that with increasing nitrogen content the austenite grain size decreases and the grain coarsening temperature increases [18]. Being the most stable phase, VN precipitates in preference to VC particularly at the higher temperatures, but in the enhanced nitrogen steels there is still sufficient nitrogen for V(C,N) to cause precipitation strengthening during and after the transformation of the austenite. One feature of microalloying, particularly with Nb, is that strain induced precipitation in the austenite during rolling inhibits recrystallisation and so allows unrecrystallised austenite to be present. This gives a much finer ferrite grain size due to the greater number of nucleation sites for ferrite formation. A similar effect can be obtained with V steels, but the temperature for most rapid VN precipitation is 900°C, and whilst effective controlled rolling can be carried out in this regime with V-N steels [19], it is more usual to employ combination of Nb and V, where Nb facilitates the controlled rolling and V provides precipitation strengthening.

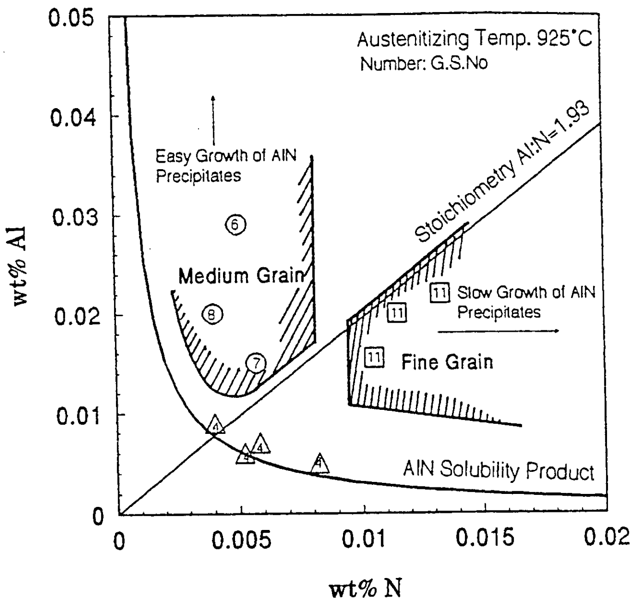

Figure 9. Effect of Al and N on AlN precipitate morphology and austenite grain size [17].

When adding more than one microalloying element, in this case V, Nb and Ti to high nitrogen steel, it is important to determine whether there are some undesirable interactions. Data pertaining to Ti-V steels suggest that titanium is very effective in spite of the presence up to 0.14%V [10,20]. On the other hand, the behaviour of titanium nitrides in a steel containing Nb appears to be different. Fig. 11 shows the amount of Ti, V and Nb, as calculated by Thermo-Calc, precipitated in microalloy nitrides in a Ti, a Ti-V, and a Ti-Nb steel. In the graph we have also inserted the experimental GCT's for the three steels, showing approximately the same GCT for the Ti and Ti-V steels and a GCT for the Ti-Nb steel approximately

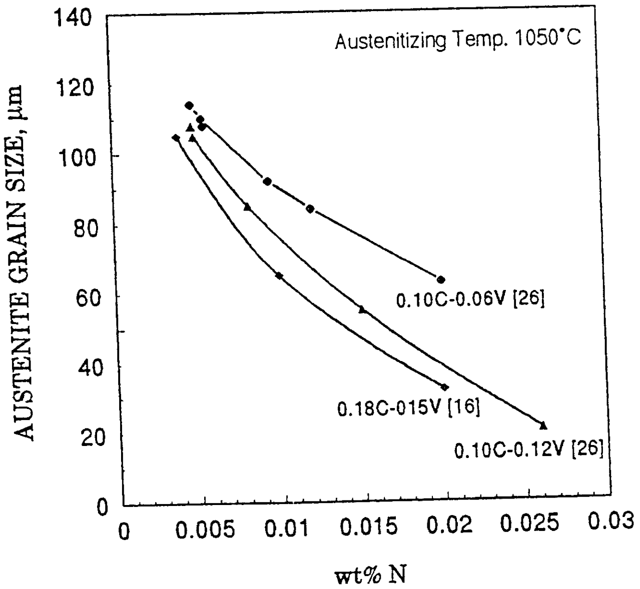

Figure 10. Effect of N on austenite grain coarsening characteristics of V-microalloyed steels [18,26].

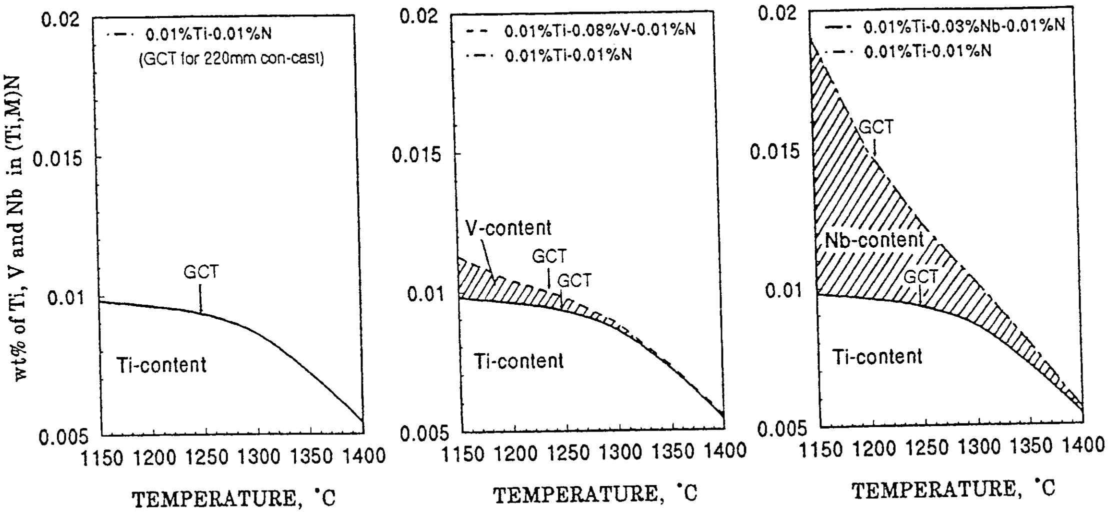

Figure 11. Calculated amount of Ti, V and Nb precipitated as (Ti,M)N in a Ti (a), Ti-V (b) and Ti-Nb (c) steel. GCT-grain coarsening temperature of continuously cast 220mm slabs.

50°C lower. The results in Fig. 11 show that the volume fraction of microalloy nitrides will be considerably larger in the Ti-Nb steel than in the other two steels. In addition, the average precipitate size of the Ti-Nb steel is likely to be smaller since the precipitation will continue at lower temperatures and therefore under larger supersaturations. On heating the cast steel the finer dispersion of nitrides in the Ti-Nb steel will initially restrict grain growth to a lower grain size. But as the temperature is rased a larger portion of the nitrides in this steel will be dissolved as compared to the Ti and Ti-V steels where there only be a limited nitride dissolution. This creates a situation in the Ti-Nb steel which favours grain coarsening by abnormal growth, and we suggest this to be the explanation of the lower GCT for Ti-Nb steel.

Another important aspect of multiple microalloying is that the vanadium or niobium tied up as (Ti,Nb,V)N particles is not available for subsequent thermo-mechanical treatment. Fig. 11 shows that significant fraction of added niobium may remain undissolved even at high reheating temperature of 1250°C and is lost for retardation of recrystallisation and/or precipitation strengthening. Vanadium, on the other hand, exhibits higher solubility which not only produces a satisfactory degree of resistance to abnormal grain growth, derived from TiN but also precipitation strengthening in ferrite.

2.3 Effect of nitrogen on γ/α transformation

As is well known, nitrogen stabilizes austenite, lowers the Ar_3 temperature, and therefore retards decomposition of austenite. However, the experimental results on V microalloyed steels indicate that an increase in nitrogen raises the austenite to ferrite transformation temperature and accelerates the transformation reaction as compared with low nitrogen alloys, at a fixed content of V and C [21-26]. It was suggested that the Ar_3 temperature may be raised relative to a plain carbon steel by the replacement of some carbon by nitrogen, since the $\gamma/\gamma+\alpha$ phase line in the Fe-C constitution diagram is "steeper" (about 600°C/wt.%C) than that in the Fe-N diagram (about 200°C/wt.%N) [21]. This higher Ar_3 temperature will give rise to a higher driving force for the reaction at a given temperature in alloys with high nitrogen than in alloys with low nitrogen, and will therefore result in more rapid transformation in the former [22].

A more important aspect of nitrogen in combination with V in HSLA-steels is an augmented ratio between austenite grain size and ferrite grain size (γ/α-transformation ratio) as compared with C-Mn and V-low N grades, Fig. 12 [23,24]. Material with 0.1%V and 0.02%N is found to be more effectively grain refined after a given processing route than either C-Mn steel or V microalloyed steel with low nitrogen. The same applies for Ti-V-N steels processed via high temperature rolling, Fig. 13 [10]. An increase in nitrogen leads to significant augmentation in transformation ratio which can be further increased when accelerated cooling is applied.

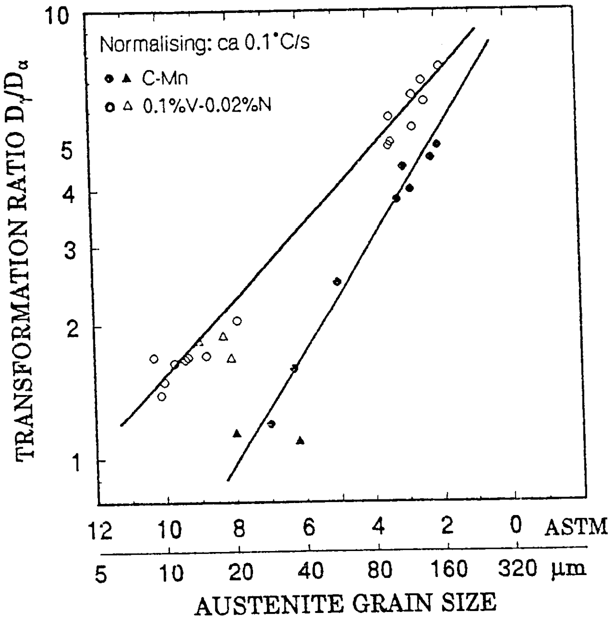

Figure 12. Illustrating the effect of V and high N in refining the polygonal ferrite grain size produced during γ-α [23,24].

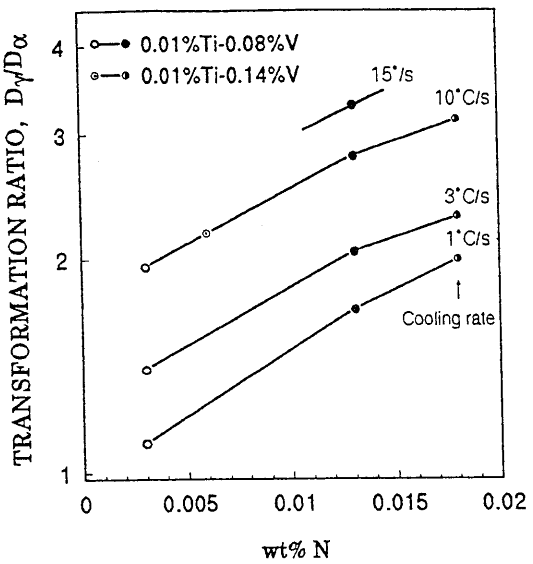

Figure 13. Effect of N on the refinement of ferrite microstructure during γ-α transformation in Ti-V-N steels [10].

Much work has identified the ferrite nucleation sites and the factors controlling the ferrite grain size. According to most of them [10,23], the increased γ/α-transformation ratio in V-N steels arises as a result of interphase precipitation of VN slowing down the rate of migration of α/γ interphases during transformation. However, it has also been demonstrated that the specific nucleation frequency of α is augmented in high nitrogen austenite in comparison to that in C-Mn steels [24]. These observations were made after normalising and led to propose the explanation that ferrite nucleation is promoted by scalloped" austenite grain boundaries resulting from "bowing-out" between pinning VN particles. Both of the above mechanisms are plausible and probably make individual contributions to the overall grain refinement in V-N steels.

2.4 Strengthening effects of nitrogen

One of the most effective mechanisms for increasing the strength of steels is through fine nitride precipitates which form in ferrite during or after transformation. It is now generally accepted that the precipitation-hardening response engendered in V-microalloyed steels as a result of cooling through the γ-polygonal ferrite transformation, increases with nitrogen level up to the stoichiometric limit. An increase in nitrogen results in finer and larger amounts of V(C,N) interphase precipitation, together with a smaller inter-sheet spacing and a suppression of the less strengthening fibrous interphase morphology [25,26]. Moreover, nitrogen extends the temperature range over which interphase precipitation occurs due to it depressing the Widmanstatten ferrite temperature range and the B_S [22].

Precipitate composition

The larger stability of VN over VC means that vanadium, which is in solution after hot rolling or normalizing, will tend to first react with nitrogen and then carbon only when all of the former has been consumed. In fact, at all but the slowest cooling rates, it would appear that the relative kinetics for precipitation of VN and VC are such that the former is usually the dominating phase even when the nitrogen level of the steel is low and vanadium is available to form VC [25].

A thermodynamic analysis of dilute Fe-V-C-N alloys and an evaluation thereby of the expected composition of VC_xN_y precipitates under various conditions, has recently been performed for 0.12%V steels [25,26]. Some typical predictions are given in Fig. 14 for decomposition of austenite at 800°C and for precipitation in ferrite at 600 and 700°C; the austenite data are for different carbon levels whereas for ferrite, the relevant C-content is determined from equilibrium with austenite. The curves in Fig. 14 are drawn for a starting wt% N in the steel of 0.02%; for lower nitrogen contents one simply begins at the appropriate point on the curve. It is quite clear that VC_xN_y is nitrogen rich until the level of nitrogen remaining in solution has fallen to quite low values; this is especially true for precipitation in ferrite. For compositions typical of HSLA steels it is clear that the majority of vanadium precipitates is relatively close to VN in composition. In austenite this is due to the fact that the solubility limit is reached, and thus precipitation ceases, at rather low C-fraction in VC_xN_y ; in ferrite it is only for nitrogen contents below about 0.005% that the majority of the carbonitrides can be carbon rich before the solubility limit is reached and even then it is unlikely to occur because it would require the reaction to proceed to equilibrium at low temperature and low driving force. The predictions of the thermodynamic analysis that the VC_xN_y precipitates in V microalloyed steels are nitrogen rich, have been confirmed experimentally, indirectly via X-ray lattice-parameter determinations [27] and directly by energy-loss electron spectrometry [28].

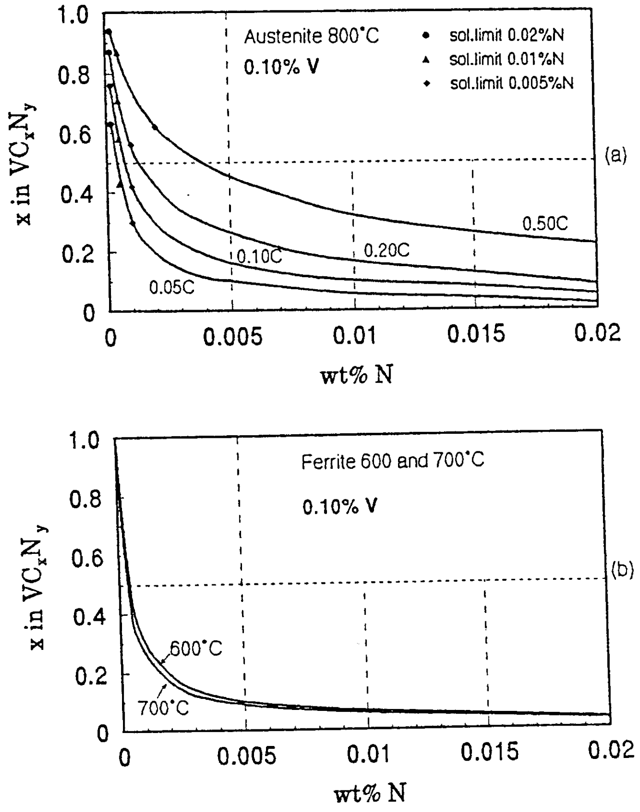

Figure 14. Example showing the variation in the composition of VC_xN_y with content of nitrogen remaining in solution during precipitation in (a) austenite or (b) ferrite with various initial carbon levels [25].

Precipitate morphology

During the controlled processing of microalloyed steels the austenite can decompose to a fine dispersion of alloy nitrides and carbo-nitrides arranged in a ferrite matrix. The results for the isothermally and continuously transformed samples of V-N steels revealed the following correlation between precipitate form, transformation temperature and ferrite morphology [26].

Interphase VN precipitation forms at the γ/α interphase boundary by repeated nucleation of nitride particles as the transformation front moves through the austenite, at temperatures 800-700°C [29,30]. From Fig. 15 it is clear that the inter-sheet spacing of the interphase precipitates is controlled by the nitrogen content in steel and the transformation temperature. As one would expect the precipitate size decreases with decreasing spacing. The reduction of inter-sheet spacing and precipitate size with decreasing γ/α transformation temperature is clearly associated with the fact that the supersaturation driving the precipitation increases. Raising the nitrogen content up to the stoichiometric level, corresponding to 0.032% in the steels of Fig. 15b, will similarly increase the supersaturation and therefore refine the precipitation. As we go from VN to VC precipitation by reducing the nitrogen content from 0.026% to practically zero the precipitates become somewhat coarser, Fig. 15a. Again, we believe this is caused by a decrease of the supersaturation due to larger solubility of VC than of VN.

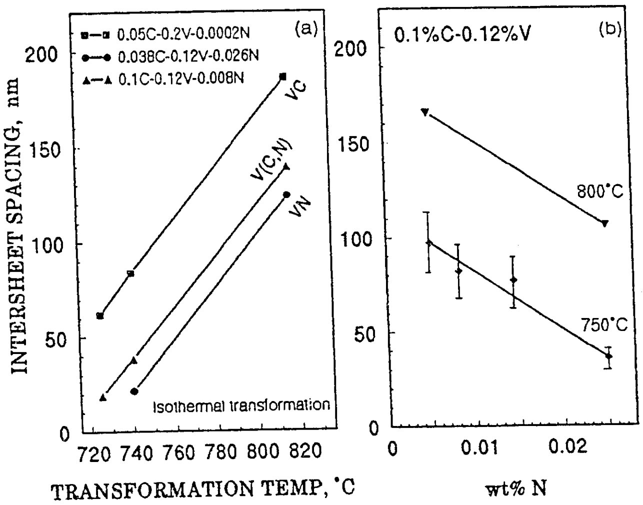

Figure 15. Effect of transformation temperature (a) and nitrogen content (b) on inter-sheet spacing of interphase precipitation in V steels [22,26].

Randomly distributed VN particles are most common in samples transformed at 600-650°C and it is evident that particle size decreases, the number of particles increases and their coarsening tendency decreases with increasing nitrogen level, Fig. 16. It was shown that the VN particles are coherent with the ferrite and would also be expected to maintain coherency with prolonged holding at transformation temperature, especially in higher nitrogen steels, as the coarsening rate of VN is about fifty times slower than VC [26,30]. Moreover, theoretical calculations indicate that VN can maintain coherency up to larger precipitate size (about 60nm) than VC (about 20nm) [30].

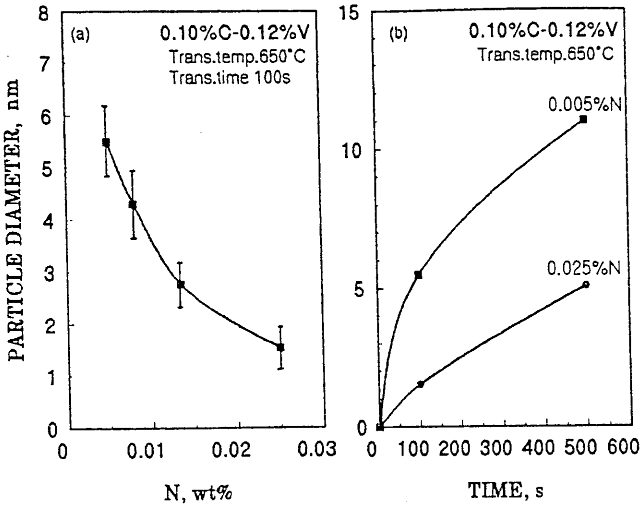

Figure 16. Average size of VN particles after transformation at 650°C/100s (a) and their growth with isothermal holding at this temperature (b) [26].

Precipitation strengthening by VN

The strengthening effect of nitrogen in V-microalloyed steel is shown in Fig 17a, b for isothermal and continuous transformation [25,26]. It is clear from these figures that the dependence of precipitation strengthening, $\Delta\sigma_p$, on nitrogen is very large and virtually linear over the ranges investigated. The nearly linear dependence of $\Delta\sigma_p$ on nitrogen, which was found experimentally, is probably only valid over the limited range of nitrogen contents examinated. At lower nitrogen levels it is thought that the supersaturation of V after the termination of VN precipitation is high enough for VC precipitation but these coarsen more rapidly than VN.

It is also clear that low temperature controlled rolling gives less precipitation strengthening than high temperature rolling due to the strain induced precipitation of VN in the austenite. In the normalised condition strengthening is much lower and levels off with increasing nitrogen content due to large and increasing portion of undissolved V nitrides [25].

The effect of nitrogen on the volume fraction of VN, particle size and the distance between particles is illustrated in Fig. 18. This graph is based on experimental curves for the precipitate size; the volume fraction corresponding to complete precipitation is computed from the V and N contents in steel and the time of complete precipitation is taken from the point where maximum strengthening is reached; furthermore use has been made of measurements of L during the precipitation. By suitable combination of this information the curves of Fig. 18 have been calculated. As indicated in this figure nitrogen increases the volume fraction and at the same time decreases particle size so giving the lowest planar spacing at a given transformation temperature. Thus the enhanced precipitation strengthening contribution to the yield strength obtained in V microalloyed steels at higher nitrogen is the result of two factors;

(i) nitrogen increases the volume fraction of strengthening precipitates. This is the result of faster precipitation kinetics of VN or nitrogen-rich V(C,N) as compared with VC. The highest volume fraction of precipitates is attained in practice for a stoichiometric V:N ratio (3.65:1) and above.

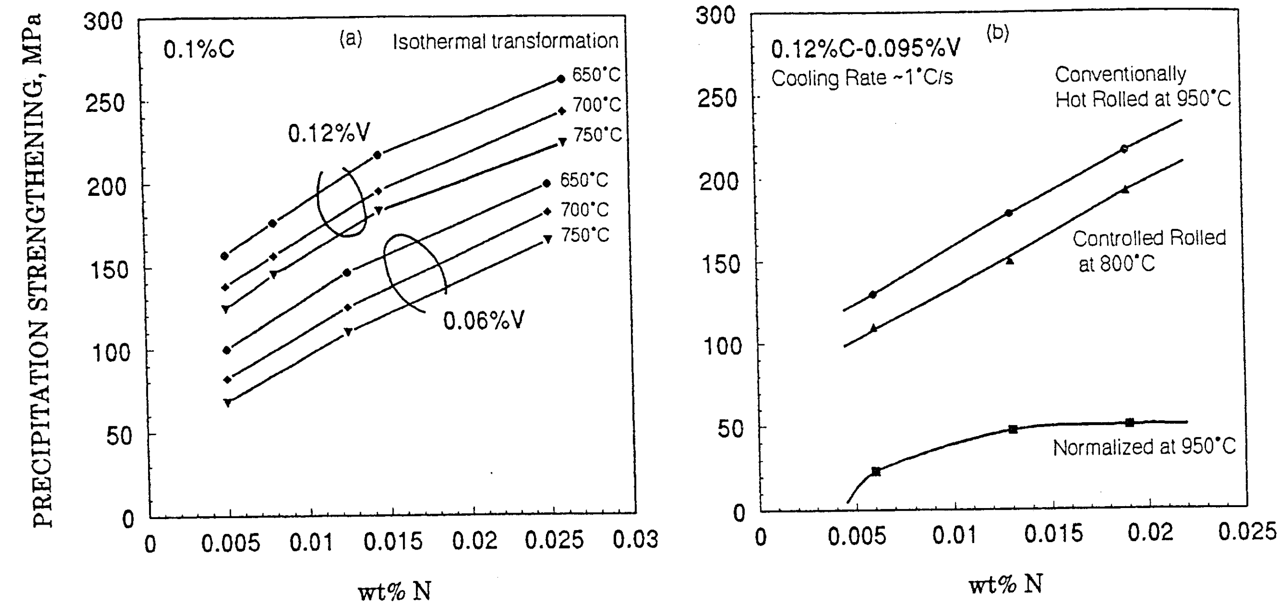

Figure 17. Effect of N, V and transformation temperature on the precipitation strengthening in 0.1%C-V-N steels after (a) isothermal and (b) continuous transformation [25,26].

(ii) nitrogen increases the degree of dispersion of VN. An increase in the N content refines the precipitate dispersions, decreases the inter-sheet spacing or the distance between randomly distributed particles.

Thus according to the above results, nitrogen increases the precipitation strengthening component of the yield strength by maximising the ratio between VN volume fraction and particle size. Maximum strengthening was achieved in V-N steels after isothermal transformation at 650°C with randomly distributed particles precipitated from supersaturated ferrite [26].

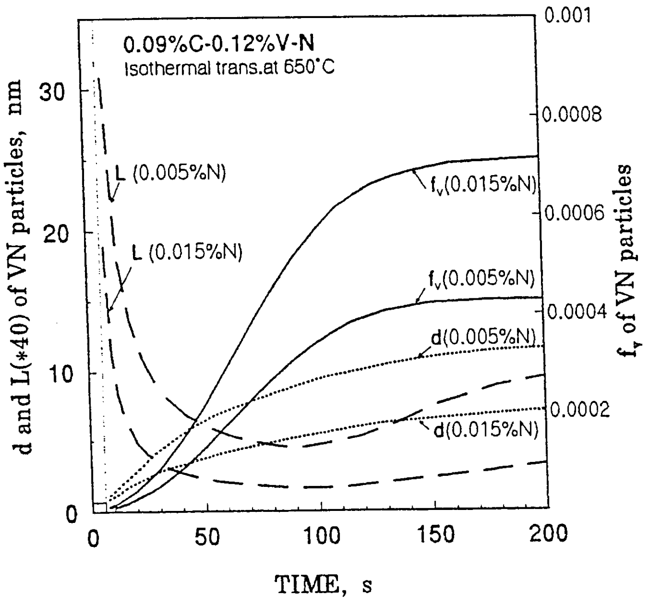

Figure 18. Effect of N on particle size, d, particle volume fraction f_v and planar spacing L. The curves are based on experimental data.

A calculation of $\Delta\sigma_p$, based on recent refinements of the Orowan theory for dispersion strengthening [31,32] combined with the experimentally-established VN particle size distributions, gives values in good agreement with the measured ones for random precipitation. For this calculation, the particle size distribution was determined experimentally and the volume fraction of precipitates was deduced from the nitrogen content of steel, on the assumption that the particles are vanadium nitrides. Good agreement indicates that the evaluation of f_v directly from the nitrogen content is an acceptable approximation, i.e. precipitates which make the overriding contribution to $\Delta\sigma_p$, consist predominantly of VN or low carbon V(C,N).

There are two practical benefits of the increased N content in V-microalloyed steels; nitrogen significantly reduce the amount of vanadium needed to achieve a desired yield strength level by decreasing the particle size/volume fraction ratio. The increased particle stability at high nitrogen makes the strength properties less sensitive to variation in cooling rate. It has also been suggested that high nitrogen VN compounds not only contribute a greater degree to strengthening but also have a less detrimental effect on both impact transition temperature and upper shelf energy than low nitrogen compounds [11,25].

2.5 Strain ageing

Due to higher solubility of nitrogen compared with carbon, nitrogen is predominantly responsible for strain ageing. It has been shown that Mn decreases the strain ageing by interacting with nitrogen atoms to form Mn-N clusters which restrict long range nitrogen diffusion. Other elements, mainly Ti and Al, are such strong nitride formers that they minimise strain ageing by decreasing the dissolved nitrogen. It has also been shown that the precipitation of VN or V(CN) so decreases the nitrogen dissolved in the ferrite, when the ratio exceeds stoichiometry, that the steel shows little or no strain aging [33].

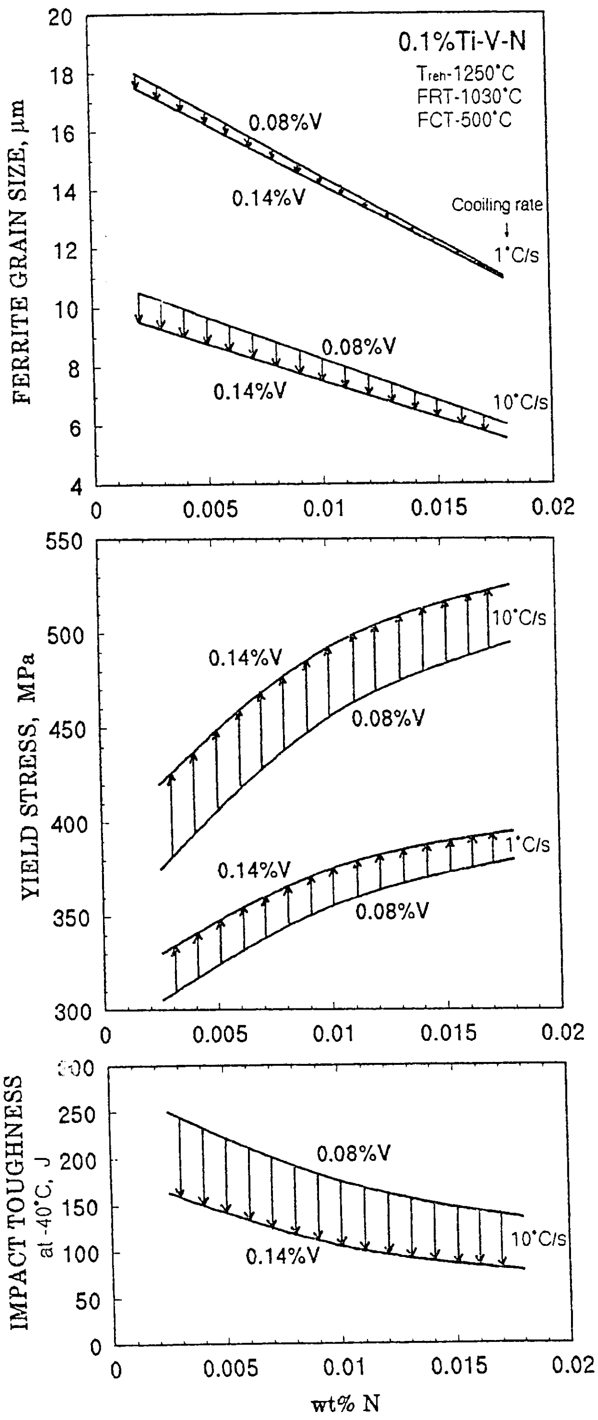

Figure 19. Effect of N, V and cooling rate on the yield stress and impact toughness of Ti-V-N steels in the as-recrystallization controlled rolling condition [10].

3. EFFECT OF NITROGEN IN PROCESSING OF HSLA STEELS

3.1 Recrystallisation Controlled Rolling (RCR)

Most of the positive effects of nitrogen are applied in RCR of Ti-V steels. This concept of TMT is based on high finish temperature recrystallisation controlled rolling of a steel microalloyed with Ti and V, in which nitrogen is used as an essential alloying element addition. Titanium nitride technology is utilised to inhibit grain growth during reheating and refine austenite grains by repeated static recrystallisation after each rolling pass, in the high temperature regime, above the recrystallisation-stop temperature. The excess of nitrogen, that is not combined as TiN, is utilised for precipitation strengthening of ferrite by vanadium nitrides. The properties of high nitrogen Ti-V steels can undergo pronounced improvement via application of interrupted accelerated cooling (ACC).

It was also shown that the presence of vanadium in solid solution has little effect on the kinetics of recrystallization of austenite and that the kinetics of VN formation in non-deformed austenite are sluggish. For RCR with finish rolling temperature above 1000°C, virtually all vanadium in Ti-V-N microalloyed steel is available for precipitation in ferrite. By contrast, nitrogen exerts a detrimental effect in the presence of niobium, since niobium carbonitrides are less soluble and tend to precipitate excessively in austenite [10].

A strong tendency of nitrogen to refine the ferrite grain structure and improve strength in Ti-V microalloyed steel is supported by the results presented in Fig. 19 [10]. It may be seen that the strengthening potential of V can be effectively utilised only at high levels of nitrogen and that increased cooling rate has a profound effect, especially at the higher nitrogen level. An increase in the nitrogen content in the Ti-V steel results, however, in a deterioration of impact properties (Fig. 19) but even at the highest nitrogen content, the impact toughness is above 100 J at -40°C.

These metallurgical considerations led to the development of 0.01Ti-V-N steels which are particularly suitable for RCR plates. Optimum thermo-mechanical controlled processing of Ti-V-N steels (0.01%Ti, 0.08-0.14%V, 0.010-0.018%N) provides a yield stress of 500MPa combined with a Charpy transition temperature bellow -60°C and ferrite grain size ~6μm in the as-hot rolled condition. Mechanical properties of such plates in the RCR+ACC condition were generally superior to those after controlled rolling with finish rolling temperature around 800°C. It was demonstrated that RCR+ACC is a more economical process than low finish temperature controlled rolling, which contributes to loss in productivity and may lead to excessive mill loads.

As for plate rolling the RCR process is very well suited for rolling of sections as controlled rolling cannot by applied in the normal section rolling mill. Sections are mostly used in the as rolled condition and increased strength is achieved with vanadium-nitrogen additions [34]. In the lighter sections the niobium is to be avoided as the combination of the high cooling rate of the thin section and Nb in solution tends to produce bainite which reduces the toughness.

3.2 Interrupted accelerated cooling

The enhanced precipitation hardening from V-N combinations with interrupted accelerated cooling has been utilised for many years in high-strength hot strip [35]. The V-N addition not only gives extensive precipitation strengthening but also refines the ferrite grain size which is advantageous on toughness. In hot strip processing, it is important that the cooling rate on the run-out table and the coiling temperature are suitably adjusted in order to promote maximum precipitation strengthening. In this content nitrogen is a very useful addition as it makes precipitation strengthening less sensitive to cooling conditions, so providing maximum strengthening over a broader coiling temperature range [26]. There is always a danger that too rapid cooling, in addition to suppressing precipitation will cause bainite to be formed rather than polygonal ferrite, and this will be detrimental to toughness in other than very low carbon steels. More recently, Nb-V steels with high nitrogen have been developed for hot-strip processing [35]. Such grades are characterised by yield strengths >690MPa combined with very good formability, achieved via desulphurization and inclusion-shape control.

3.3 Normalisation

In the structural C-Mn steels, nitrogen is used in conjunction with an Al addition in order to achieve a refined ferrite grain size which together with the increased Mn content of 1.5% results in increased yield strength and also improved toughness. These steels were some of the earliest high strength low alloy steels [36] and were quickly adopted for fracture-tough ship plate. The formation of AlN is well known to maintain a fine austenite grain size by increasing the grain coarsening temperature (see Fig. 9), and this results in much reduced ferrite grain size which is further refined by the depression of the transformation temperature by Mn and by an increased rate of cooling.

For any given nitrogen content, it is observed that there is a maximum grain coarsening temperature at an Al content where the Al:N ratio corresponds to the stoichiometry of AlN [37,38]. Hence too great an addition of Al is to be avoided, and it is not surprising that for steels containing about 0.012%N, the normal grain refining Al addition is 0.02-0.03% corresponding to the stoichiometric level. As with plate rolling, the strength achievable from grain refinement is limited and strength is frequently supplemented by precipitation using a vanadium addition.

A notable application of the grain refinement in 0.1%V-0.02%N microalloyed steels following normalising, has been shown for very heavy (69-100mm) plate with relatively low carbon equivalent (0.08%C-1.4%Mn) and high strength (R_m>500MPa) [39]. It is found that the grain-refining effect accruing from normalising is very considerable even for the slow cooling rates in thick plates (~0.05°C/s), e.g. for 950°C-normalising, $D\alpha$=6-8μm is typical. Furthermore, it was reported that the V-N steel exhibits excellent welding characteristics in 75mm-sections, both as regarded weld-metal hardness and toughness in the weld-metal and HAZ [39]. This finding which is in strong contrast with a widely held opinion that vanadium, and especially vanadium combined with nitrogen, is detrimental for toughness in both HAZ and weld-metal, is supported by the results of a recent investigation discussed below.

4. EFFECT OF NITROGEN ON WELDABILITY OF HSLA STEELS

The beneficial role of nitrogen, in association with RCR and ACC, on the base metal properties demonstrated above must be weighed against possible detrimental effect on HAZ toughness. Much controversy exists in the literature concerning the role of nitrogen on the deterioration of HAZ toughness [40]. High nitrogen steel has sometimes been considered as having an unsatisfactory weldability due to "free" nitrogen which impairs toughness in the HAZ. This detrimental effect was primarily attributed to solution hardening but contributions from an increase in hardenability or alternatively from a strain ageing cannot be ruled out. If the nitrides in the heat affected zone are dissolved then the austenite grain growth is unrestricted and rapid. The formation of coarse transformation products on cooling together with free nitrogen in solid solution may lead to relatively poor toughness. This is the situation which occurs in high heat input single pass welds in Ti-free steel, in which case nitrogen may be detrimental to the toughness. It was reported that C-Mn as well as Nb-microalloyed steel welds exhibited an increase in transition temperature of 2-4°C per 10ppm increase in nitrogen [41]. In a few cases authors have assumed that the deviation of Charpy toughness is due to nitrogen "for lack of a better explanation" [42].

However, recent results show that high nitrogen steel can have good weldability, as regards HAZ hardness and toughness, by careful selection of microadditions and the welding parameters [43-46]. Using effective grain growth inhibition a fine austenite grain size can also be maintained in the HAZ of these steels. The most practical way of controlling the austenite grain size, and at the same time lowering the free nitrogen is provided by a dispersion of fine titanium nitrides. The effectiveness of titanium nitride dispersion in austenite grain growth inhibition during welding was shown to depend on nitrogen content. In Fig. 7b it can be seen that extensive grain growth occurs just above 1250°C in commercial Ti-V plates with 0.003%N whereas the 0.013%N plate preserves small grains up to 1350°C [12]. The austenite grain size at 1350°C was about 3 times larger in low N steel plates than in the high N plates having the same levels of Ti and V.

For the nearly stoichiometric steel with 0.01%Ti and 0.003%N, in Fig. 7b, the major proportion of TiN is dissolved at the welding temperature, so that it loses its pinning function, causing extensive grain growth in the HAZ. TiN reprecipitates during the cooling stage and it is believed that all nitrogen is again tied with Ti in a stoichiometric steel. Thus near the transformation temperature, large austenite grains existed with all V in solid solution. These two factors increase significantly the hardenability and as a result transformation take place at lower temperature giving large volume fraction of lathy (bainitic) phases. In the high N steel, Fig. 7b, the TiN particles are more stable and inhibit effectively grain growth of austenite at 1350°C. In this case relatively small austenite grains existed with nitrogen and vanadium in solid solution prior to transformation (assuming that there was no precipitation in austenite). During transformation, which takes place at higher temperature than in the low N steel more primary ferrite is formed. If nitrogen in solid solution alone would affect the microstructure in HAZ a decrease in grain boundary ferrite would be expected, as a higher nitrogen content will stabilise the austenite and thereby result in a lower transformation temperature during cooling.

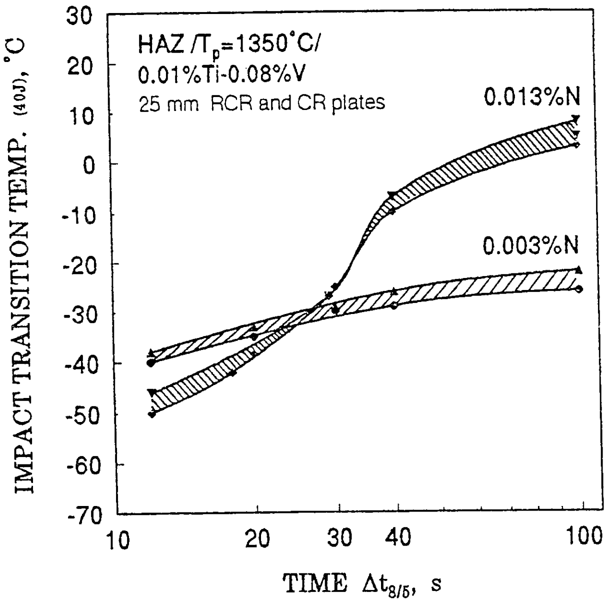

Figure 20. Dependence of 40J impact transition temperature on cooling time between 800-500°C for high and low nitrogen Ti-V plates [12].

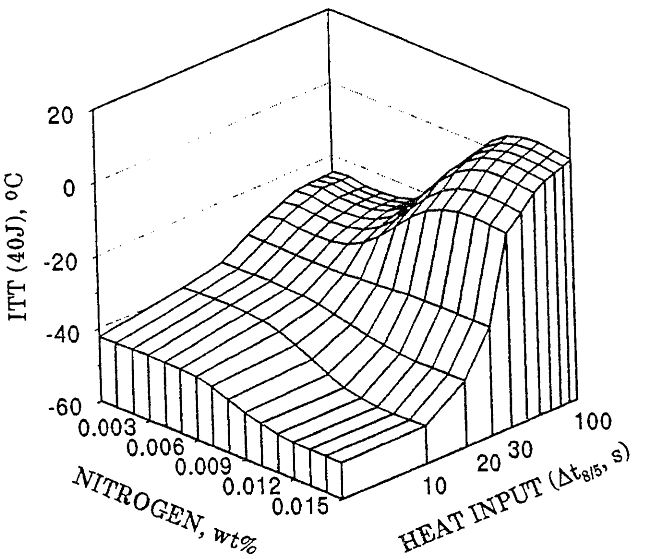

Figure 21. Effect of heat input and nitrogen content on the impact transition temperature of 0.01%Ti-0.8%V plates [12].

The results presented recently [12,44], clearly demonstrate that free nitrogen is not directly responsible for the HAZ properties in Ti-V steels. On the contrary, as shown in Figs 20 and 21, higher N steels exhibit the highest HAZ-toughness for the cooling time below 25s (heat input <2.5kJ/mm). For such fast cooling condition one does not expect precipitation of VN in austenite during cooling to the transformation temperature and the amount of "free" nitrogen in ferrite should be higher than in the slower cooled specimens. This view is also supported by strain ageing results [12]. With decreasing cooling rate, precipitation of V(C,N) should be more abundant reducing the amount of "free" nitrogen in solid solution. However these specimens exhibited low toughness. The drastic increase in ITT for higher energy input $30s<\Delta t_{8/5}<40s$, corresponded to formation of coarse grained proeutectoid ferrite. Toughness improved when the entire HAZ become a ferrite with aligned second phase, FS, according to the IIW classification of the HAZ microstructure constituents [47]. Fractographic analysis confirms that cracks often follow the coarse grain boundary ferrite veins [12]. The balance between the FS phase and the grain boundary ferrite depends on N content and austenite grain size.

On this basis it may be considered that the toughness of HAZ is affected not so much by "free" nitrogen, but rather by the nature of the transformation products. If the HAZ microstructure is fine, good toughness can be expected even with higher nitrogen contents. Such proper microstructure, and hence good toughness, can be obtained for high nitrogen steel, by balancing heat input to provide a cooling time $\Delta t_{8/5} \leq 40s$. For example excellent HAZ impact properties were obtained for 25mm thick plate of high nitrogen Ti-V steel after welding with small or medium energy input <4kJ/mm, which were superior to those for low N steels [12].

It has also been shown that it is possible to successfully weld high nitrogen, V-microalloyed steel (without Ti) by using multi-run technique [45]. Fig. 22 demonstrated that it is possible to reach a Charpy impact transition temperature of -80°C both at low (0.005%) and high (0.013%) nitrogen contents in 0.1%V steel for multi-run welding at the heat input 1.6-3.0 kJ/mm. This is due to the VN precipitates which dissolve during the first pass and reprecipitate in the following pass acting then as inhibitors to austenite grain growth in the subsequent pass. This results in fine grained polygonal ferrite microstructures of high toughness after "weld normalization". Moreover, the nitrogen dissolved in the ferrite is greatly decreased, which may further improve the toughness.

Combining the microstructural information and toughness data, it may be concluded that the effect of nitrogen on weldability of HSLA steels can be understood by considering the general microstructure, and for the high nitrogen steel to exhibit superior properties than the low N steel, the final HAZ microstructure must contain at least 50% of lathy FS phases, balanced with ferritic products.

Investigation of the HAZ hardenability of microalloyed steels having different carbon equivalents and similar nitrogen content (~0.007%N) revealed that Nb microalloying gives rise to an increase in hardenability referred to plain C-Mn steel [43]. Microalloying with V produces a decrease in the amount of martensite compared with C-Mn. Ti-microalloying reduces hardenability as a result of the grain growth inhibiting effect of TiN particles during the welding cycle. This effect was especially evident for a Ti+V steel with an enhanced nitrogen.

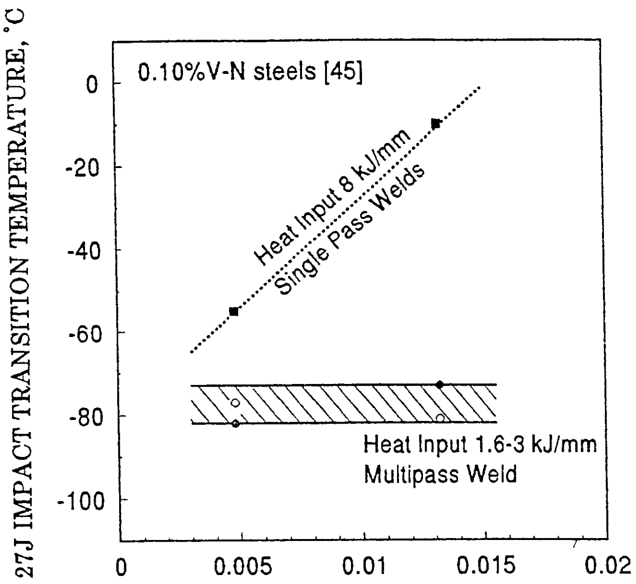

Figure 22. Effect of N on toughness of heat affected zone of welded 0.1%V steels [45].

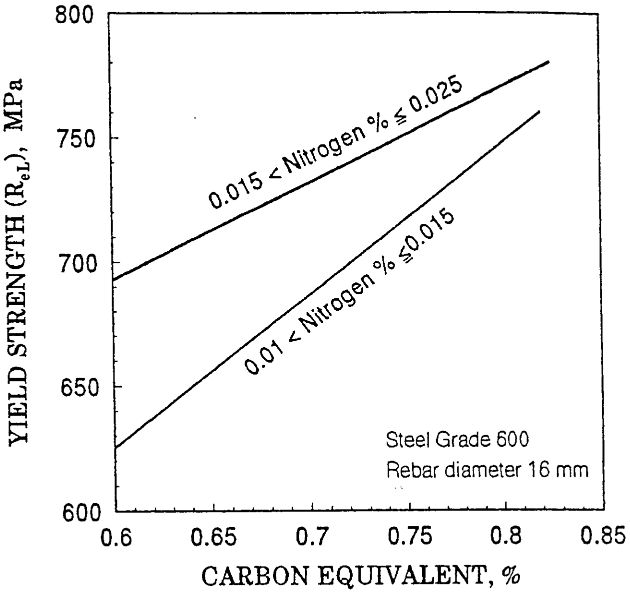

Figure 23. Yield strength of reinforcing bars (steel Grade 600) at two nitrogen levels [48].

5. THE ROLE OF N IN OTHER MICROALLOYED STEELS

5.1 Bar and forging steels

For bar and other long products, hot working is usually carried out at high temperatures in the recrystallisation regime, and in these products microalloying is used to improve properties by precipitation strengthening rather than by grain refinement. A typical product is concrete reinforcing bar. Microalloying has enabled the carbon content to be lowered to 0.15/0.25% with improved ductility, toughness and weldability, and a preferred microalloying combination is V with enhanced nitrogen, which is particularly effective in large diameter bars, Fig. 23 [48]. The V-N addition has also been found beneficial in steels processed by the Tempcore technology [49] in which the bars are water cooled on leaving the final rolling pass to form surface martensite which is then tempered by heat retained in the interior on leaving the water cooling. The centre of the bar thus transforms to a fine grained ferrite-pearlite structure. Control of the process enables varying strength to be achieved in a weldable steel, and it should be possible to obtain increased grain refinement by small Ti additions to a V-N composition, whilst maintaining the precipitation strengthening by VN formed during the transformation on cooling.

The same principle of adding V-N has been used with medium carbon (0.40-0.50%) forging steels in order to produce equivalent properties to quenched and tempered steels, especially by using controlled cooling after hot forging [50-53]. This reduces processing costs and the steels usually have improved machinability. They comprise ferrite-pearlite structures with up to almost 100% pearlite. At higher carbon contents Nb is less suitable due to the very low solubility of NbC. The V-N addition not only gives precipitation strengthening by nitrogen rich V(C,N) precipitates but also refines the ferrite grains and the pearlite colony size giving improved toughness. It has been found that nitrogen rich V(C,N) precipitates by an interphase mechanism in the proeutectoid ferrite and also the ferrite-lamellae of pearlite are effectively precipitation hardened by very fine V-particles. The tensile strength of these steels is directly proportional to (V+5N), Fig. 24 [52], which clearly shows the marked effect of increasing nitrogen content. The main drawback to these microalloyed forging steels is their lack of toughness compared with a quenched and tempered martensite at equivalent strength. This has to a large extent been remedied by refinement of the prior austenite grain size, and thereby a refinement of ferrite grain and pearlite colony size, engendered by Ti and enhanced Al additions combined with close nitrogen control [52]. Lower reheating and forging temperature, together with controlled cooling to optimise the temperature for transformation and precipitation of VN are also beneficial [53]. These principles, and use of V-N additions have also been applied to produce improved rail steels [54], although in such a complex section, control of rolling finishing temperature is not easy.

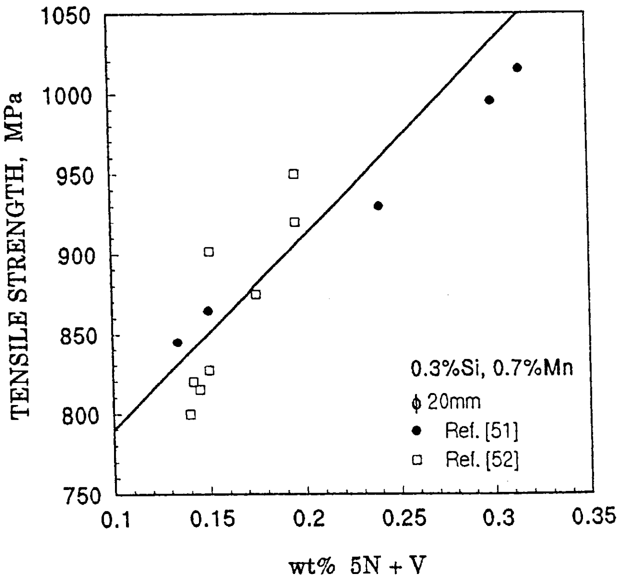

Figure 24. Combined effect of N and V on precipitation strengthening of medium-carbon forging steels.

5.2 Eutectic wire rod, high strength DQ steels

Controlled cooling or hot water quenching, which lower the transformation temperature and produces finer pearlite has largely eliminated the expensive patenting of wire rod. Additional strengthening can be achieved by the precipitation of fine, nitrogen rich V(C,N) particles in the pearlitic ferrite, using up to 0.2%V with or without enhanced nitrogen contents [55]. The enhanced nitrogen seems to be essential if less than the optimum 0.15%V is used, and more rapid cooling rate is required to achieve the optimum transformation temperature. The addition of V and N did not impair the wire drawability and the ductility of the drawn wire is practically unaltered.

The beneficial effects of the V-N addition to eutectoid wire rod steels have now been fully confirmed [56], the work hardening, ductility, reverse bending and torsion properties being largely unaffected, whilst the fatigue strength is improved. For springs made of drawn wire, which is an important application of this steel, it was found that the fatigue strength was raised in accordance with the increase of tensile strength, and furthermore the sag resistance of the springs was improved. Moreover, due to the rapid precipitation of the VN, even under rapid cooling conditions there is virtually no nitrogen dissolved in the pearlitic ferrite and so the steel is less inclined to aging which will minimise variability of properties by variable heating during wire drawing.

In direct quenching and tempering process (DQ-T), performed by quenching after hot rolling from the austenite temperature range, the most important properties are the Bs and Ms temperatures, hardenability and tempering resistance. The effect of nitrogen in DQ-T steels may be considered as virtually identical to effects of carbon. Nitrogen depresses the Ms temperature and increases the hardness of martensite. The effects of normal nitrogen contents on the hardness of martensite in DQ-T steels are almost completely overshadowed by the larger amounts of carbon present.

Early work on the effect of nitrogen on hardenability showed that nitrogen retards the pro-eutectoid ferrite reaction and depress the Widmanstatten ferrite transformation temperature and the Bs temperature [30]. These effects are not quantified due to the generally small nitrogen concentration and because nitrogen interacts markedly with other elements for which it has an affinity. It was postulated that clusters of V atoms with carbon and nitrogen can segregate to the austenite grain boundaries at low austenitising temperature and give very pronounced increases in hardenability, by deactivating sites at which nucleation for transformation occurs [57]. Even more pronounced is this effect when the austenite grain boundaries are immobilised by pinning particles such as AlN and TiN [58]. The complex results of this work led to a hypothesis that the ratio between the rate of segregation of V to austenite grain boundaries and the rate of movement of those boundaries influences the hardenability effect of V and N. Hence according to this suggestion nitrogen plays an important, though indirect, role in hardenability by providing nitride particles which pin the grain boundaries, and by forming clusters with alloying element such as V on austenite boundaries.

6. SUMMARY

All the beneficial effects of nitrogen in HSLA steels lie in its interaction with the microalloying elements which take the form of precipitation reactions involving microalloy nitrides or the formation of clusters. The effectiveness of any precipitation reaction depends on the degree of dispersion and particle size. Since nitrides of the microalloying elements are more stable and show less tendency to coalesce than carbides, an enhanced nitrogen content will maximise the ratio between particle volume fraction and particle size and hence maximise the key microstructural features of microalloyed steels, i.e. grain refinement and precipitation strengthening. The value of nitrogen is particularly recognised in steels microalloyed with V and Ti. It is also demonstrated that high nitrogen steel can have a good weldability, as regards HAZ hardness and toughness, by careful selection of microadditions and the welding parameters and that the toughness of HAZ is not affected by "free" nitrogen, but rather by the nature of the transformation products.

We hope that this review of beneficial effects of nitrogen will stimulate thinking away from our conservative vision of the past and will help to consider nitrogen as an essential and inexpensive alloying element in steel.

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