

THE USE OF VANADIUM

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1. Introduction

Vanadium is the 17th most commonly occurring element in the earths' crust and finds wide use as an alloying element in steels, titanium based alloys for aerospace applications, catalysts, ceramics, chemicals and probably, in the future, in batteries both for the storage of electricity generated during off peak times and as power packs for electrically powered vehicles. However, as can be seen from Figure 1,⁽¹⁾ by far the majority of vanadium consumed, presently, is used by the steel industry and it is on giving a broad indication of this use that this paper will concentrate.

2. The Use of Vanadium in Steel

Figure 2 shows the range of steel products where vanadium is used by the steel industries of Germany, Japan and the U.S.A. It appears from this figure that the pattern of use in the three countries is different, only tool steels being consistently categorised in all three. There are, however, other less obvious similarities in the pattern of use. Structural steels recorded in Germany are almost certainly recorded within HSLA / carbon steels in the U.S.A. and in "others" in Japan. Similarly linepipe steels recorded in Japan are almost certainly recorded within special structural steels in Germany and within HSLA steels in the U.S.A. The main point to note, however, is that when vanadium is added to steel it results in a benefit to steel production or to an improvement in steel properties or to both, ultimately leading to a reduction in the cost of producing or of using the steel or of both.

Figure 3 shows vanadium consumption in the World and in the West up to the end of 2000. From this it is clear that consumption has been growing strongly since the early 1990's. Indeed, world consumption of vanadium in 2000 was 84% higher than in 1993 and was, in fact, a record. Similarly, in the West, consumption of vanadium has increased by almost 70% since 1993. The record world consumption, to some extent, reflects the record world steel production of 826 million tonnes observed in 2000. Dividing vanadium consumption by steel production we see that the unit consumption (or the intensity of consumption) of vanadium, in 2000, was also at a record level of just over 0.047kgV / T steel in the world as a whole and 0.053kgV / T steel in the West (Figure 4). The world unit consumption has increased by approximately 60% since 1993 while Western unit consumption has increased by almost 50% in the same period. These increases represent new consumption over and above that which would be expected from the increase in steel production, and reflect the efforts of workers in research and development, worldwide, into the use of vanadium in steel.

I will now examine some of the technical attributes of the use of vanadium, which have led to this significant increase in consumption of vanadium. Many of these attributes will be covered in more detail by other speakers at this conference.

3. Technical Attributes of the Use of Vanadium in Steel

3.1 Steel Production

In steel, vanadium forms stable compounds with both carbon and nitrogen and it is in the way in which these elements interact with vanadium which determines many of the properties of vanadium containing steels.

3.2 Solubility of Vanadium Compounds in Austenite and Ferrite

Vanadium carbides, nitrides (and carbonitrides) exhibit solubility in both austenite ⁽²⁻⁶⁾ and in ferrite ⁽⁷⁻⁹⁾ (Figure 5a & b). In austenite, the solubility of VC is the highest of all of those shown, while that of VN is lower than that of VC and is more equal to that of NbC, NbN and TiC. It is also interesting to note that in the group shown, TiN has the lowest solubility in austenite.

Vanadium carbide also exhibits higher solubility in ferrite than that of the other micro-alloy carbides and nitrides shown. It is important to note that the solubility of all the carbides and nitrides shown reduce as the temperature falls and that the solubility in ferrite is significantly lower than that in austenite.

3.3 Precipitation of Vanadium Compounds in Austenite and Ferrite

The reduction in solubility with decreasing temperature and on transforming from austenite to ferrite leads to the possibility of precipitation of vanadium compounds in steel. However, because of their relatively high solubilities vanadium compounds tend not to precipitate in austenite until relatively low temperatures are reached, usually in the presence of high levels of vanadium and nitrogen (or carbon) and normally in the presence of deformation. Figure 6 shows that in a 0.05%C – 1.2%Mn steel containing 0.115%V and 0.006%N, deformed continuously in compression, the “nose” of the precipitation start curve was below 900°C and the incubation period was relatively long at 30 seconds, or more. It has been suggested ⁽¹¹⁾ that the start of such precipitation can be enhanced by the presence of a suitable substrate and Figure 7 ⁽¹²⁾ shows an example where VN has been precipitated as a cap on existing MnS. However, in most modern clean steels unless special rolling schedules and/or chemical compositions are used such a process is unlikely to make a significant contribution to precipitation of VN in austenite. Even when such special processes are adopted, it is likely that less than 10% of the available vanadium will precipitate, during rolling, in austenite.

This is advantageous as it means that, in the majority of steels, most, if not all, of the vanadium added to the steel is likely to remain in solution up to the start of transformation from austenite to ferrite. Thus, by far the majority of precipitation in vanadium containing steels takes place during ^(13, 14, 15) and after transformation, ⁽⁴⁾ giving rise to precipitation strengthening. The precipitates, which form during transformation, tend to form in rows, while those, which form afterwards, tend to be more randomly dispersed and to have both a smaller particle diameter and interparticle spacing than the row precipitates.

Examples of coarse austenitic precipitation, row precipitation and general precipitation in ferrite can be seen in Figure 8a and b. Some effects of this precipitation behaviour will now be considered.

3.4 Continuous Casting of Vanadium Containing Steels – Hot Cracking

During continuous casting, one of the most common types of defect, which can occur, is that known as transverse cracking. This defect occurs in microalloyed steels, particularly niobium

microalloyed steels, and results from lack of ductility in the region of and just above the temperature at which austenite transforms to ferrite, during slab cooling. If a stress, such as that applied at the straightener of the continuous casting machine, is applied while the temperature of the steel is within the critical region, cracking can occur. This cracking is normally transverse to the casting direction and the cracks are frequently observed to be in association with reciprocation marks. Recent work,⁽¹⁶⁾ using bend tests cooling down from the casting temperature, has examined the crack susceptibility of vanadium and niobium-containing steels. Figure 9a & b shows a comparison of the extent of cracking obtained in 0.1%V steel, with that obtained in 0.03% Nb steel. Clearly there is a greater degree of cracking in the latter case. These cracks were found to propagate mainly along the austenite grain boundaries. These boundaries were frequently, but not always, decorated with ferrite, indicating that the cracking, as noted above, was associated with the transformation. Figure 10 illustrates the effect of testing temperature on the length of the longest cracks for five steels including C-Mn, C-Mn-0.1%V, C-Mn-1%V-0.018%N, C-Mn-0.03%Nb and C-Mn-0.1%V-0.03%Nb steels. The shortest cracks were found to be in the C-Mn and C-Mn-0.1%V steels, indicating that these two steels should exhibit similar behaviour during continuous casting and that they should be able to be cast relatively crack-free. The longest cracks and the widest range of temperature over which cracking occurred were found to be in the 0.03%Nb steel, indicating that this steel would be the most difficult to cast and obtain crack-free slabs. The other two steels fell between these two extremes, indicating an intermediate degree of difficulty in obtaining crack-free slabs. It does appear, however, that vanadium containing steels are less likely to exhibit transverse cracking than those, which contain niobium alone.

3.5 Rolling of Vanadium Containing Steels

As previously noted, the solubility of vanadium carbide in austenite is significantly greater than that of vanadium nitride.⁽²⁻⁶⁾ However, even in the case of the nitride the solubility in austenite is quite high. Figure 11 depicts the equilibrium solubility temperature for steels containing different vanadium and nitrogen contents. From this, for a steel containing 0.1%V and 0.02%N, a relatively high combination, the equilibrium solution temperature is only 1098°C. This relatively low solution temperature permits the use of energy efficient low soaking temperatures with little or no loss of precipitation strengthening capability in vanadium-containing steels. This has proved to be particularly important in the new process of thin slab casting, where the temperature in the equalisation furnace is typically in the range 1050-1150°C, but could also be important in the rolling of reinforcing bar where high furnace pushing rates are desirable.

One potential drawback of these relatively low solution temperatures, especially if soaking temperatures are not reduced, is that austenite grain coarsening can occur during reheating. As has been widely demonstrated, such coarsening can be controlled by an addition of approximately 0.01%Ti, although the fact that this will use nitrogen which would have been used for precipitation strengthening needs to be recognised. Furthermore, the possibility that the presence of TiN, as a substrate, will encourage precipitation of VCN, at high temperatures also needs to be taken into account.

Because vanadium compounds tend to remain in solution during rolling and vanadium only exhibits a small solute drag effect, vanadium steels recrystallise during rolling, even down to relatively low temperatures.⁽¹⁸⁾ Consequently, by the process of deformation, recovery and recrystallisation on a falling temperature scale, it is possible to produce austenite grains, of

high surface area/volume ratio, which transform to fine ferrite on subsequent cooling. In Figure 12 ⁽¹⁹⁾ the ferrite grain size of vanadium microalloyed steels, transformed from fully recrystallised austenite of high surface area/volume ratio, is similar to that obtained for the same steels transformed from austenite, which contained some deformation. Furthermore, at high surface area/volume ratio the grain sizes obtained for the vanadium-containing steels (4-5µm) were similar to those obtained for niobium steels transforming from deformed austenite.

A further effect of the recrystallisation behaviour exhibited by vanadium microalloyed steels is that their rolling loads are similar to those for carbon-manganese steels when measured in the same temperature range.^(20,21) Examples of the effect of rolling temperature on the flow stress during rolling of <3mm thick strip of C-Mn and C-Mn-V steels are given in Figure 13. The flow stresses were calculated from rolling loads and were normalised to account for differences in true strain and strain rate. Also shown in Figure 13 is the well documented increase in flow stress, which occurs in Nb containing steels. In the figure, the flow stress at 860°C of the 0.03% Nb containing steel was some 84% higher than that of the 0.09% V containing steel. These differences were attributed to the differing recrystallisation behaviour of the steels during rolling. This difference in the recrystallisation behaviour of V and Nb steels is particularly important when rolling thin hot rolled coil.

Finally, because the recrystallised austenite grain size of vanadium-containing steels appears to exhibit little variation over a fairly wide range of temperature,⁽²²⁾ the properties of such steels are relatively insensitive to changes in finish rolling temperature.^(23,24) Figure 14 ⁽²³⁾ shows that as the finish rolling temperature increased from 870°C to 1050°C, in steel with vanadium content 0.05-0.23% and nitrogen content 0.009-0.014%, there was no significant change in yield strength and a relatively small effect on impact transition temperature. In this work it was also suggested that the absence of Widmanstätten ferrite in vanadium-containing steels, finished rolled at high temperature, assisted in maintaining impact properties. Thus, in the rolling mill, vanadium microalloyed steels are relatively user friendly and their properties tend to be relatively insensitive to changes in rolling conditions.

3.6 Transformation from Austenite to Ferrite in Vanadium Containing Steels

The transformation of austenite to ferrite and the changes, which accompany this transformation, are amongst the most important factors to be considered during steelmaking. As has already been noted, in vanadium containing steels, precipitation of VCN can occur during this transformation. However, it is equally important to consider the effects of vanadium on the transformation and the transformation products, which result.

Figure 15a ⁽²⁵⁾ shows the transformation start temperature for a steel containing 0.1% V with the relatively coarse austenite grain size of 150µm. A comparison with a C/Mn and a C/Mn/0.03% Nb steel is also given. Clearly the transformation start temperatures of the C/Mn and C/Mn/V steels are similar, that of the vanadium containing steel being, if anything, slightly the higher, while the transformation temperature of the C/Mn/Nb steel is 50 – 60°C below that of the other two steels. Furthermore, on differentiating the cooling curves of the three steels (Figure 15b) a clear difference between the C/Mn and C/Mn/V steels, on one hand, and the C/Mn/Nb steel, on the other hand, can be seen. Not only does the Nb steel transform at a lower temperature than the other two steels, its rate of transformation from austenite to ferrite is also faster. This has a significant effect on the microstructure which forms, particularly at the high cooling rates associated with quenching or with welding, with the C/Mn and C/Mn/V steels likely to form different, less acicular, microstructures from that of the C/Mn/Nb steel.

Recently, there has been significant interest in the effects of vanadium on the formation of intra-granular ferrite during transformation. That second phase particles (TiO_2) can act as substrates for the nucleation of such ferrite have been well known, in weld metals, for many years. The presence of intra-granular ferrite in the coarse grained heat affected zone of vanadium containing steel weldments has also been reported.⁽²⁶⁾ More recently^(27,28) Japanese workers have indicated that, as has already been mentioned, by the of adoption of suitable rolling schedules which encourage VN precipitation in austenite, it is possible to promote the formation of intra-granular ferrite in vanadium-containing steels and that this, in turn, leads to grain refinement. Figure 16⁽²⁷⁾ shows a comparison of the isothermal transformation behaviour at 700°C and 650°C, of a V-N containing and a niobium containing steel. The microstructure of the vanadium containing steel is finer than that of the niobium containing steel and, particularly at 650°C, there is a significantly greater proportion of intra-granular ferrite in the vanadium steel than in the niobium steel.

Another indication of the effect that vanadium and nitrogen levels can have on refining the ferrite grain size is shown in Figure 17⁽²⁹⁾. Increasing the V.N product gave significant reduction in ferrite grain size. What proportion of this increase was due to normal grain refinement during rolling and what was due to intra-granular ferrite is, however, unknown. Nevertheless, that it is possible to produce fine ferrite grain size in vanadium containing steels is clearly shown.

A final effect of vanadium on transformation behaviour has also been noted in hyper eutectoid steels.⁽³⁰⁾ In the absence of vanadium in these steels, grain boundary cementite tends to form in continuous films around the prior austenite grain boundaries, with the centres of the grains being pearlite. This renders such steels as being particularly difficult to draw. The addition of vanadium appears to break up these continuous films (Figure 18), resulting in a series of cementite islands in a matrix of ferrite. This may have a beneficial effect on the drawability of rod and wire manufactured from such steel.

3.7 Strength and Toughness

In vanadium containing HSLA steels, the two main factors affecting strength and toughness are ferrite grain size and precipitation strengthening. As has already been demonstrated there is a clear relationship between vanadium (and nitrogen) level and ferrite grain size and the ferrite grain size remains reasonably constant over a fairly wide range of finish rolling temperatures. That increasing vanadium and nitrogen levels also increases both yield strength and UTS, via precipitation strengthening, can be seen in Figure 19.⁽²⁹⁾ In this figure the effects of vanadium and nitrogen have been combined into a V.N product. The yield strength increased from a level of 350MPa to a level of 600MPa as the V.N product increased from 0 to 0.002. In the same interval the level of precipitation, or dispersion, strengthening increased from 0 to 230MPa, giving an average increase of 115 MPa / 0.001% increase in V.N product. While this vector may be affected by parameters such as cooling rate and transformation temperature it is broadly correct for steels with a wide range of carbon content.

Refining the ferrite grain size tends to improve toughness in HSLA steels and a typical grain size vector is $11.5^\circ\text{C} / d^{-1/2}\text{mm}^{-1/2}$.⁽⁴⁾ On the other hand, increasing precipitation strengthening increases the impact transition temperature by about 3-4°C for every 10Mpa increase in yield strength.^(31,32) The net effect of these changes on impact transition temperatures is shown in Figure 20. It must be emphasized that the Charpy vee-notch impact test pieces used to compile this diagram were 5mm x10mm in cross section i.e. sub standard, half size. Nevertheless it can be clearly seen that even with high levels of precipitation strengthening (600MPa YS, 230MPa precipitation strengthening) in a steel with a finish rolling temperature

of 850 / 900°C and an aim coiling temperature of 600°C, the level of impact transition temperature was excellent at -50°C and that this improved down to -80 / -100°C as the level of precipitation strengthening reduced. It is also worth noting that, in vanadium containing steels, even with high nitrogen content, no strain ageing due to nitrogen is observed, providing the V:N ratio is maintained at or above the stoichiometric ratio of 4:1.⁽³³⁾

3.8 Weldability

Arguably the two most important regions in a weld heat affected zone (HAZ) are the coarse grained region, close to the fusion boundary, and the intercritically reheated heat affected zone some distance from the fusion boundary. In these regions the properties which receive most attention are the hardness and toughness.

The hardness of the coarse grained HAZ, in the as welded condition, tends to increase with increasing vanadium level, Figure 21,⁽³⁴⁾ the increase being similar for weld cooling times between 800°C and 500°C of 12 seconds and 55 seconds.

Despite this increase in hardness vanadium can have a beneficial effect on toughness in the coarse grained HAZ (Figure 22).⁽³⁴⁾ Increasing the vanadium level from 0.0% to 0.16% led to a 50°C improvement in Charpy vee notch toughness and was accompanied by a modest, 10°C, increase in CTOD transition temperature.

In this work it was noted that the addition of vanadium appeared to promote intra-granular ferrite in the coarse grained HAZ microstructure. (Figure 23) The development of this microstructure is thought to have had a significant beneficial effect on toughness in the coarse grained HAZ.

In the intercritically reheated HAZ the addition of vanadium up to 0.1%V appears to have had little or no detrimental effect on toughness, although an addition of 0.05%V may be beneficial.⁽³⁵⁾ As can be seen in Figure 24 it is the presence of the intercritically reheated HAZ, which contains islands of M-A phase (Figure 25), which matters. Thus, it can be stated with reasonable confidence that in terms of HAZ hardness and toughness vanadium containing steels are readily weldable.

4. Conclusions

1. Most of the vanadium produced is consumed by the steel industry and this consumption has increased significantly in recent years.
2. The properties of vanadium containing steels are largely governed by the interactions, which take place between vanadium, nitrogen and carbon and the ways in which these interactions affect both precipitation and the transformation from austenite to ferrite.
3. Vanadium containing steels tend to be relatively easy to continuously cast, require low reheating temperatures, can be rolled with no significant increase in rolling load and their properties are relatively insensitive to finish rolling temperature.
4. Vanadium containing steels obtain their properties from a combination of fine grain size and precipitation strengthening, the presence of vanadium promoting both strong, tough, intra-granular ferrite as well as precipitation of vanadium carbides and nitride.
5. Vanadium containing steels have good weldability and the presence of vanadium can improve the heat affected zone toughness.

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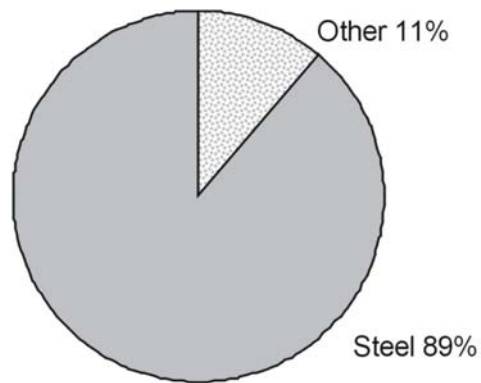


Fig. 1 The consumption of vanadium, by end use, in the USA, in 2000.

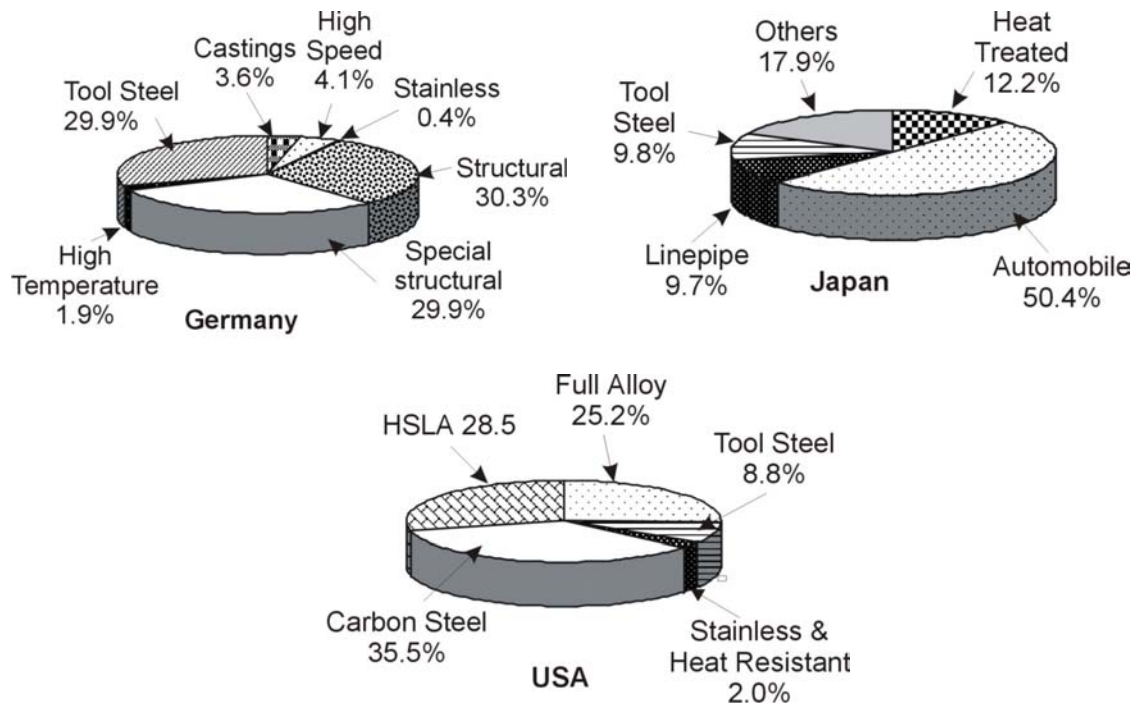


Fig. 2 The consumption of vanadium, by end use, for Germany, Japan and USA.

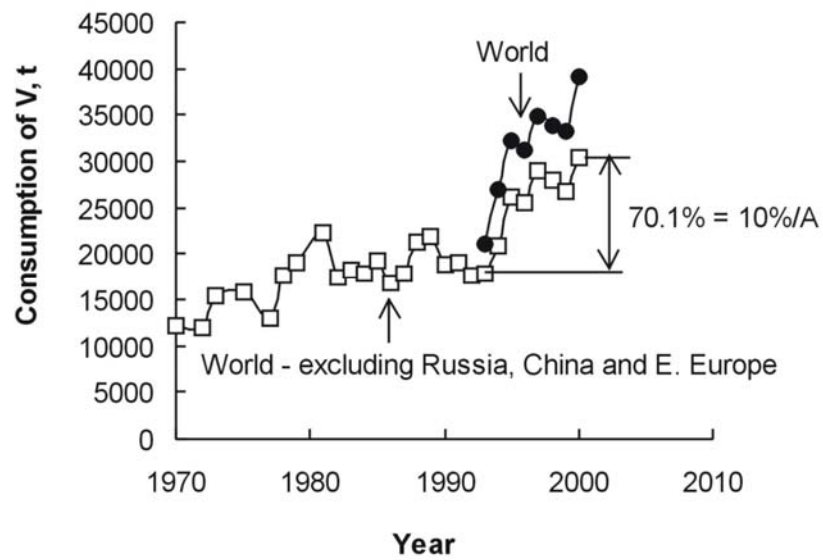


Fig. 3 Vanadium consumption since 1970.

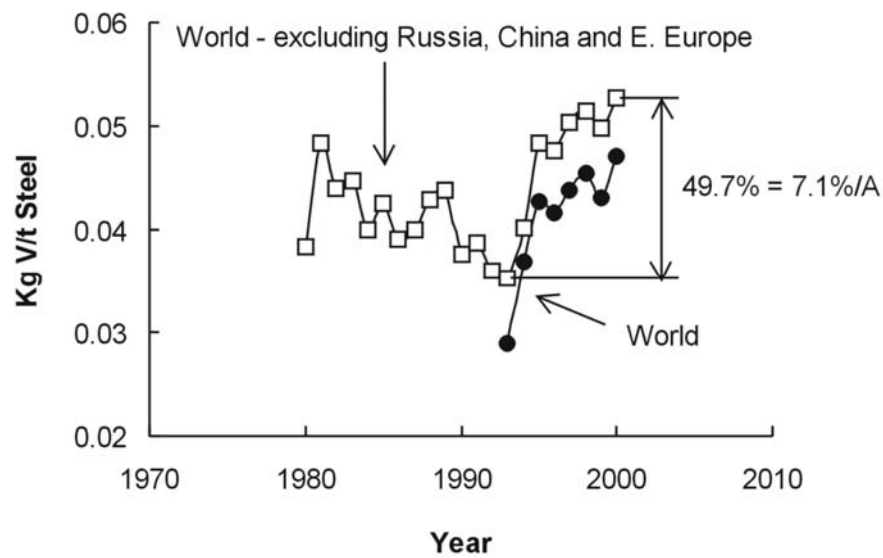


Fig. 4 Change in specific consumption of vanadium since 1970.

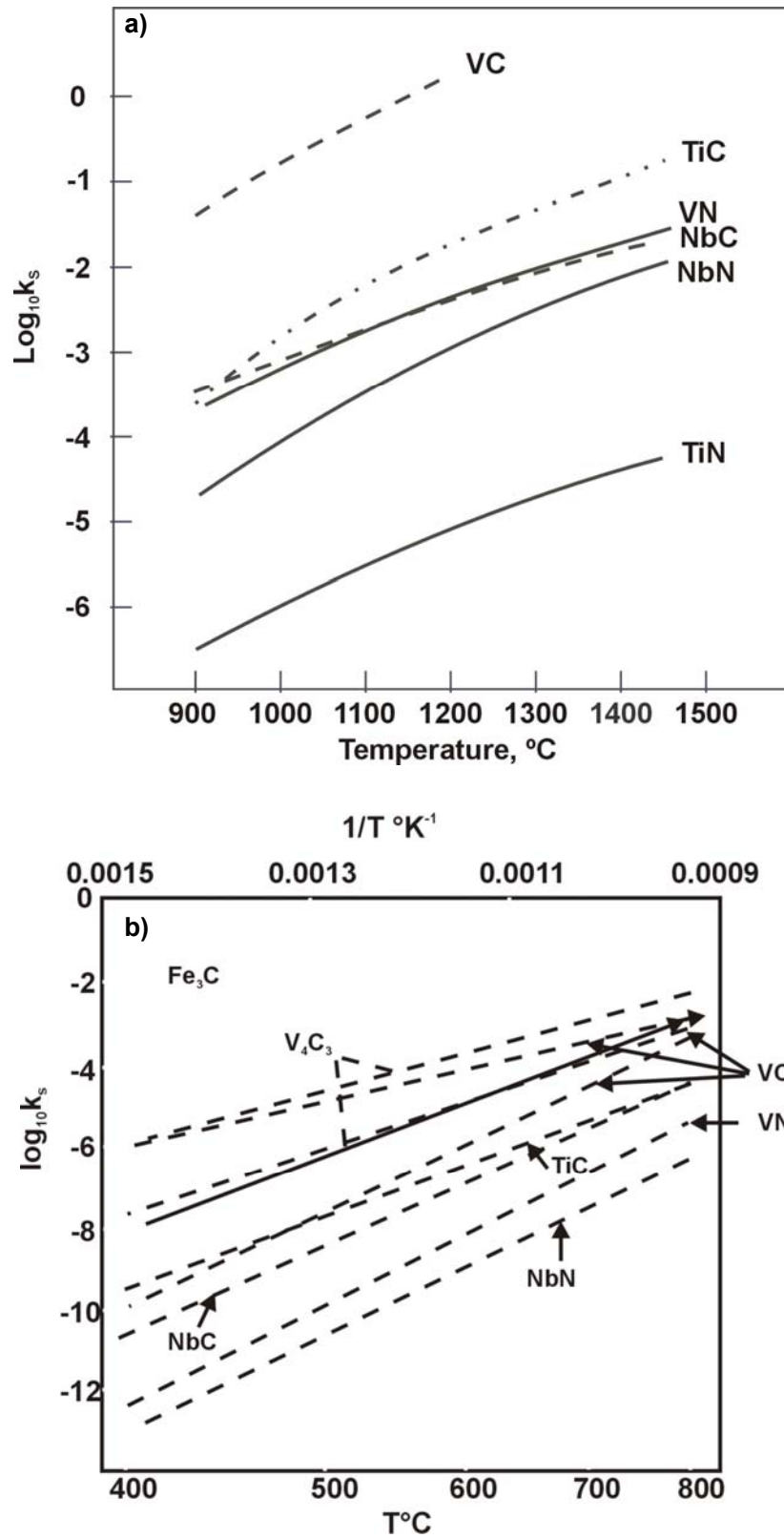


Fig. 5 Solubility of microalloy carbides and nitrides in a) austenite and b) ferrite.

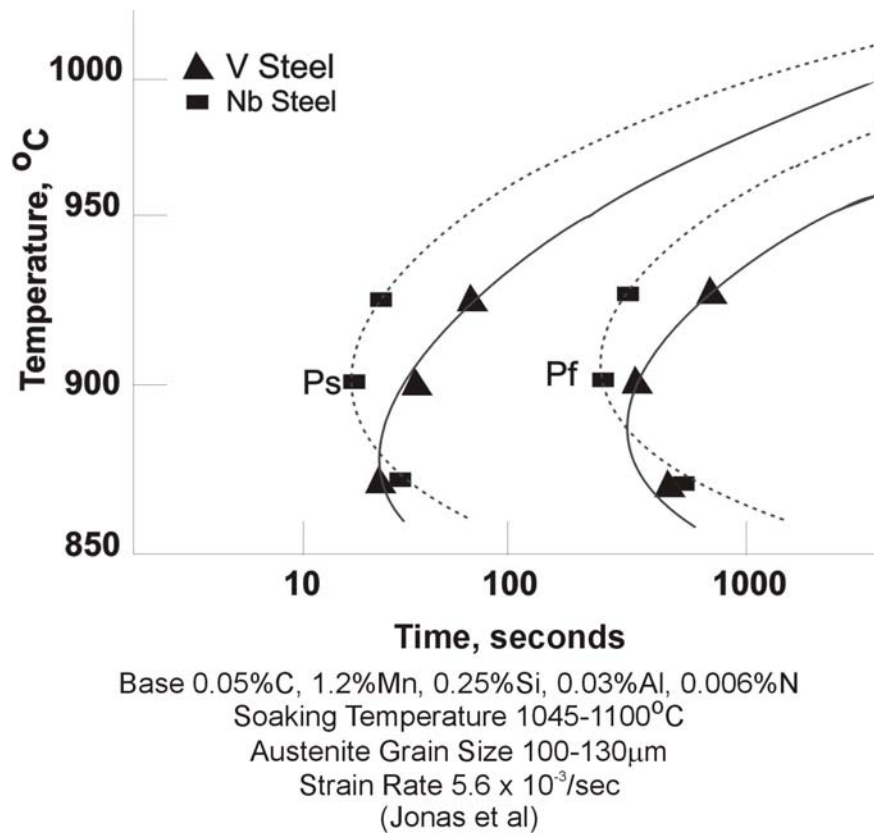


Fig. 6 Dynamic PTT Curves for 0.115% V and 0.035% Nb Steels

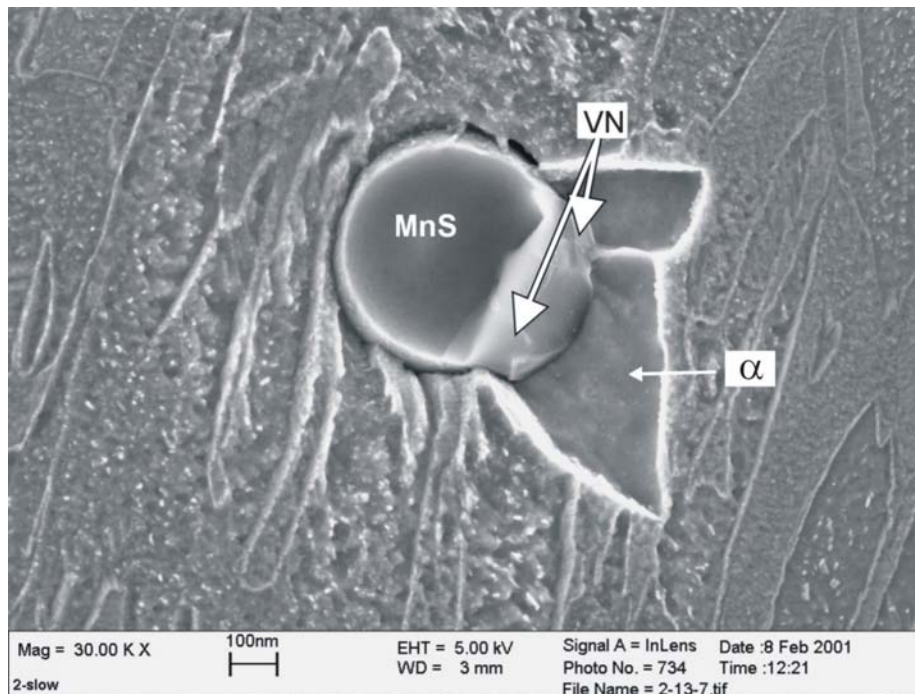


Fig. 7 SEM micrograph showing VN precipitated as a cap on MnS. (Zajal)

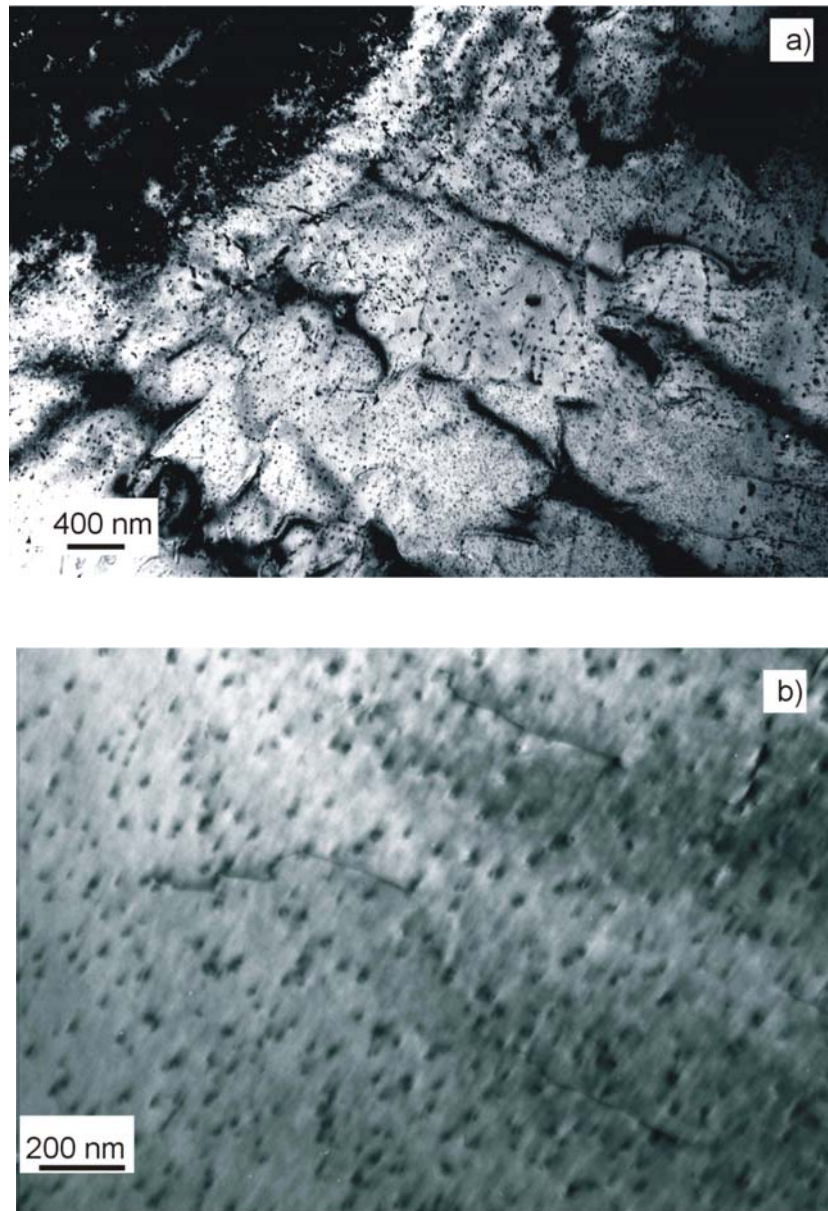


Fig. 8 Examples of precipitation a) coarse precipitation in austenite and row precipitation which occurred during transformation from austenite to ferrite, b) general precipitation in ferrite.

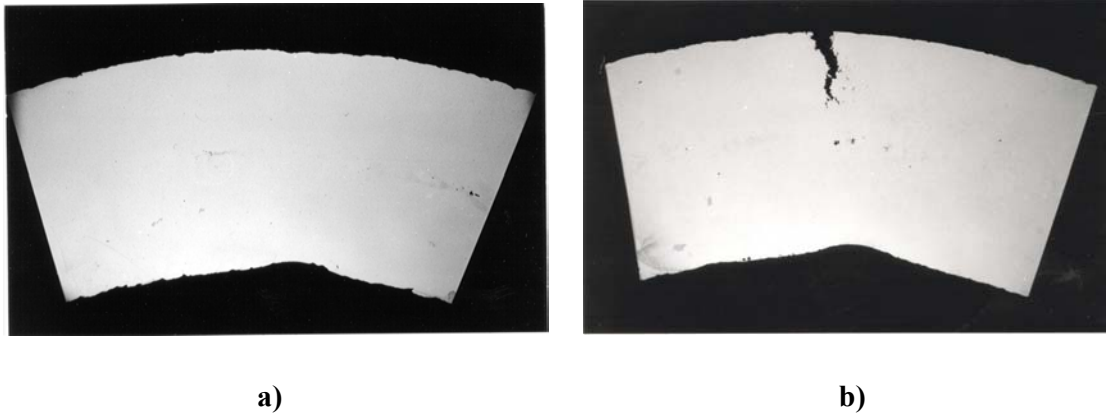


Fig. 9 Bend tests a) 0.1% vanadium steel tested at 850°C, b) 0.03% niobium steel tested at 792°C.

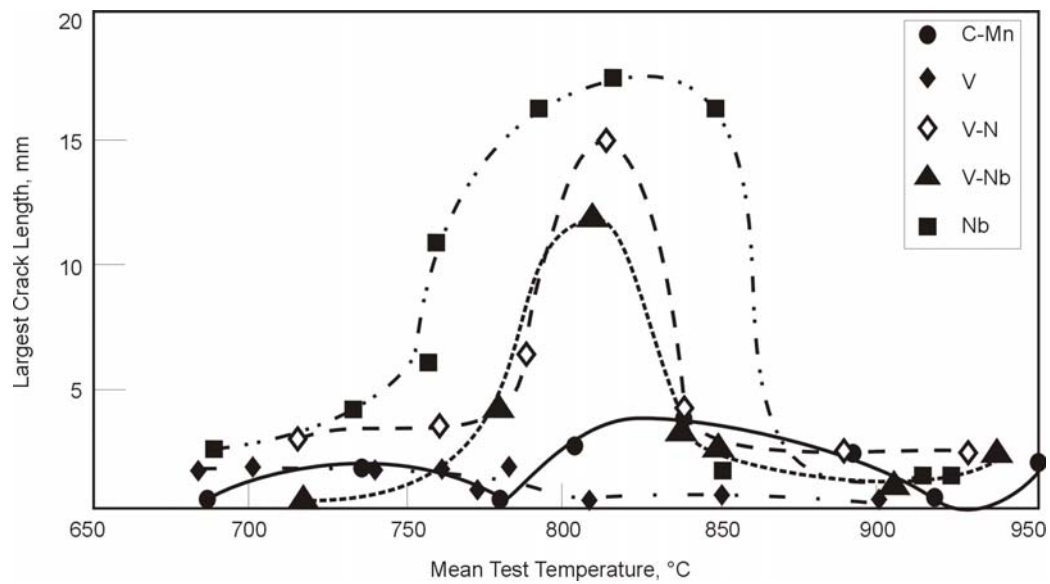


Fig. 10 Effect of temperature on the length of the largest crack observed during hot ductility testing on a range of steels

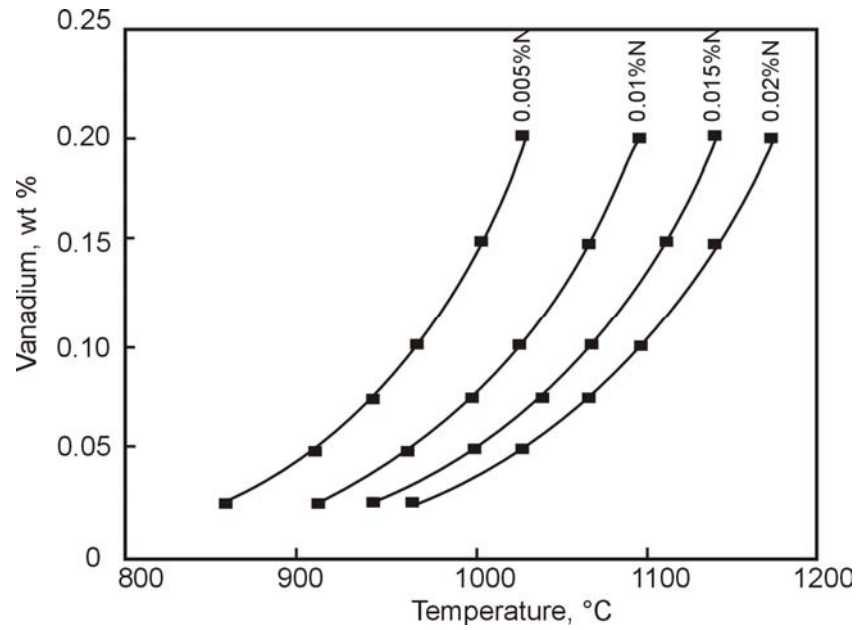


Fig. 11 The equilibrium solution temperature of vanadium nitride in austenite

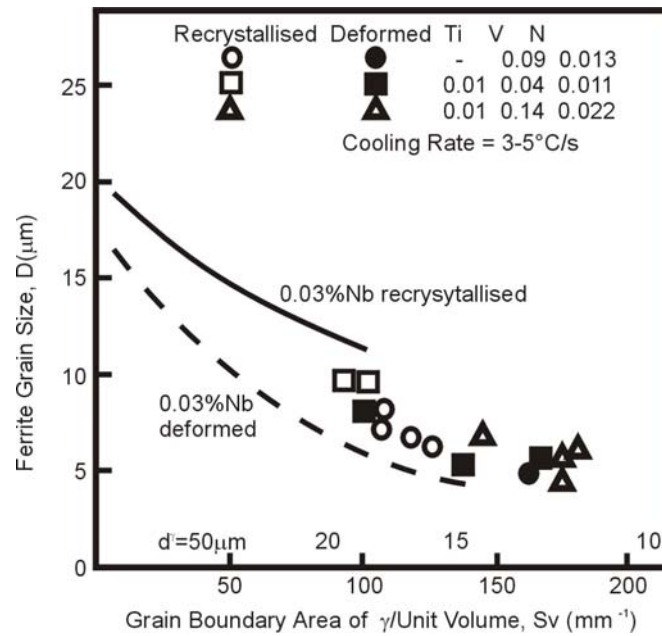


Fig. 12 Dependence of ferrite grain size on the austenite grain boundary area per unit volume. Data points are for Ti-V and V microalloyed steels. Curves refer to Nb microalloyed steels. (Siwecki)

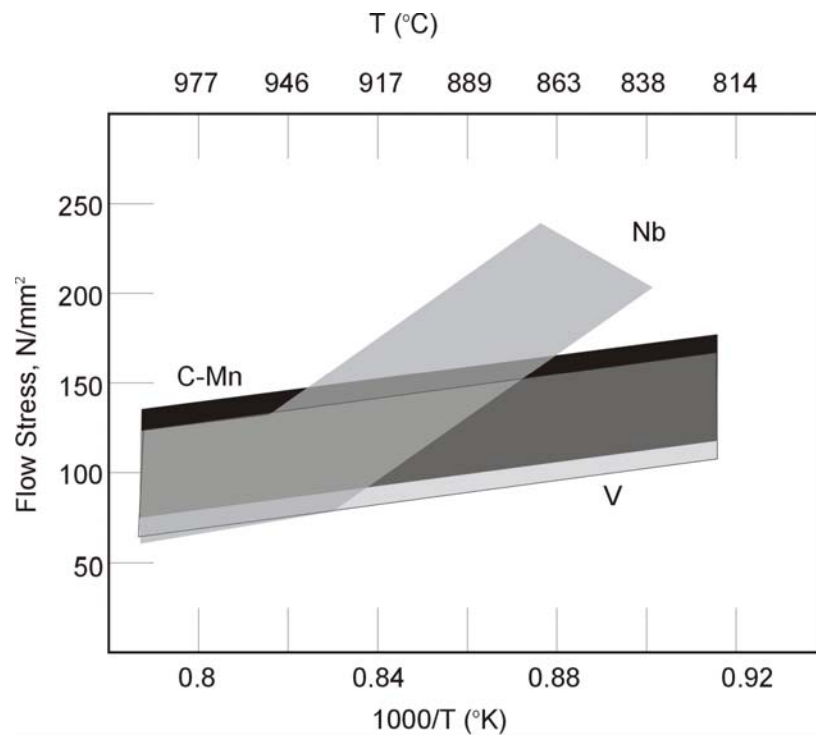


Fig. 13 Mean flow stress as a function of hot rolling temperature at the finishing stand.
(De Lisi)

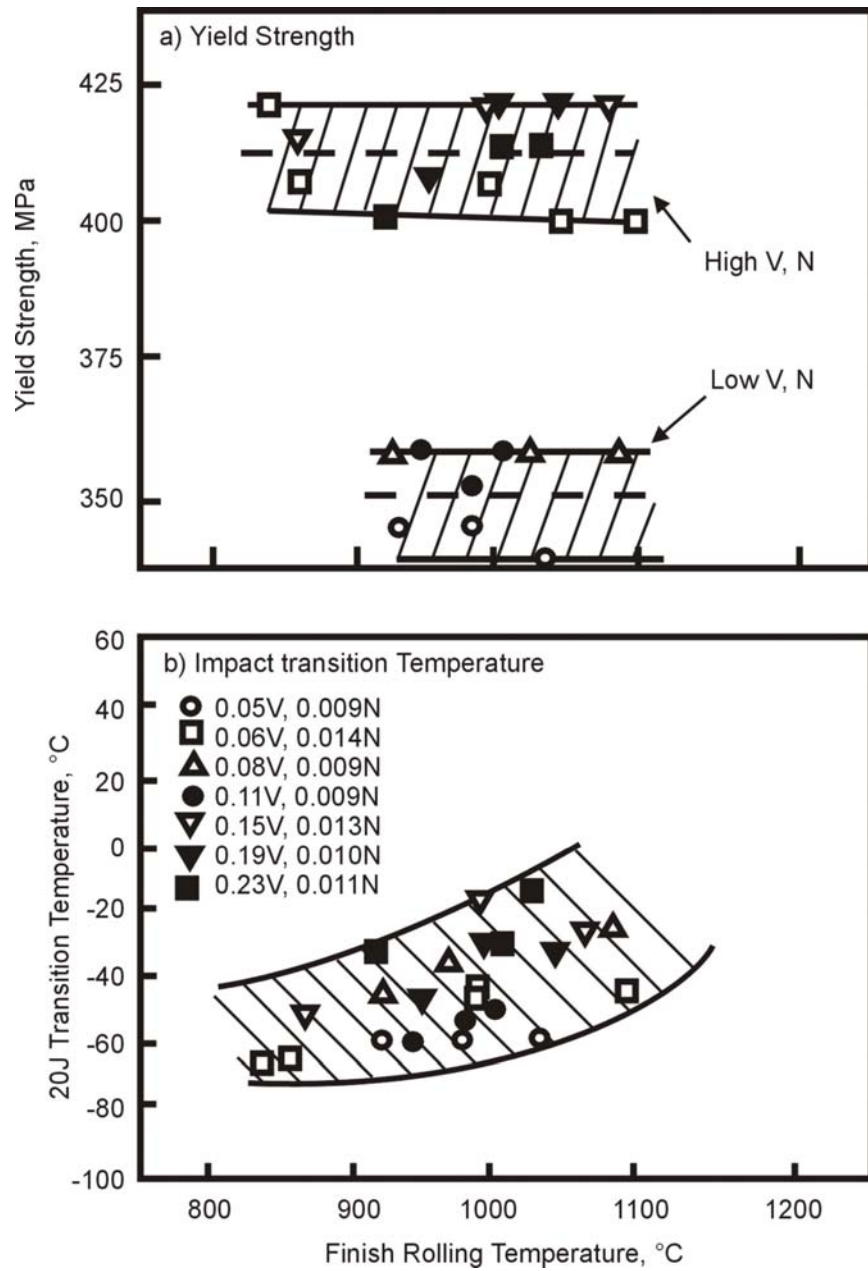


Fig. 14 Effect of finish rolling temperature on mechanical properties of vanadium steels. Soak temperature 1175°C. (Chilton and Roberts)

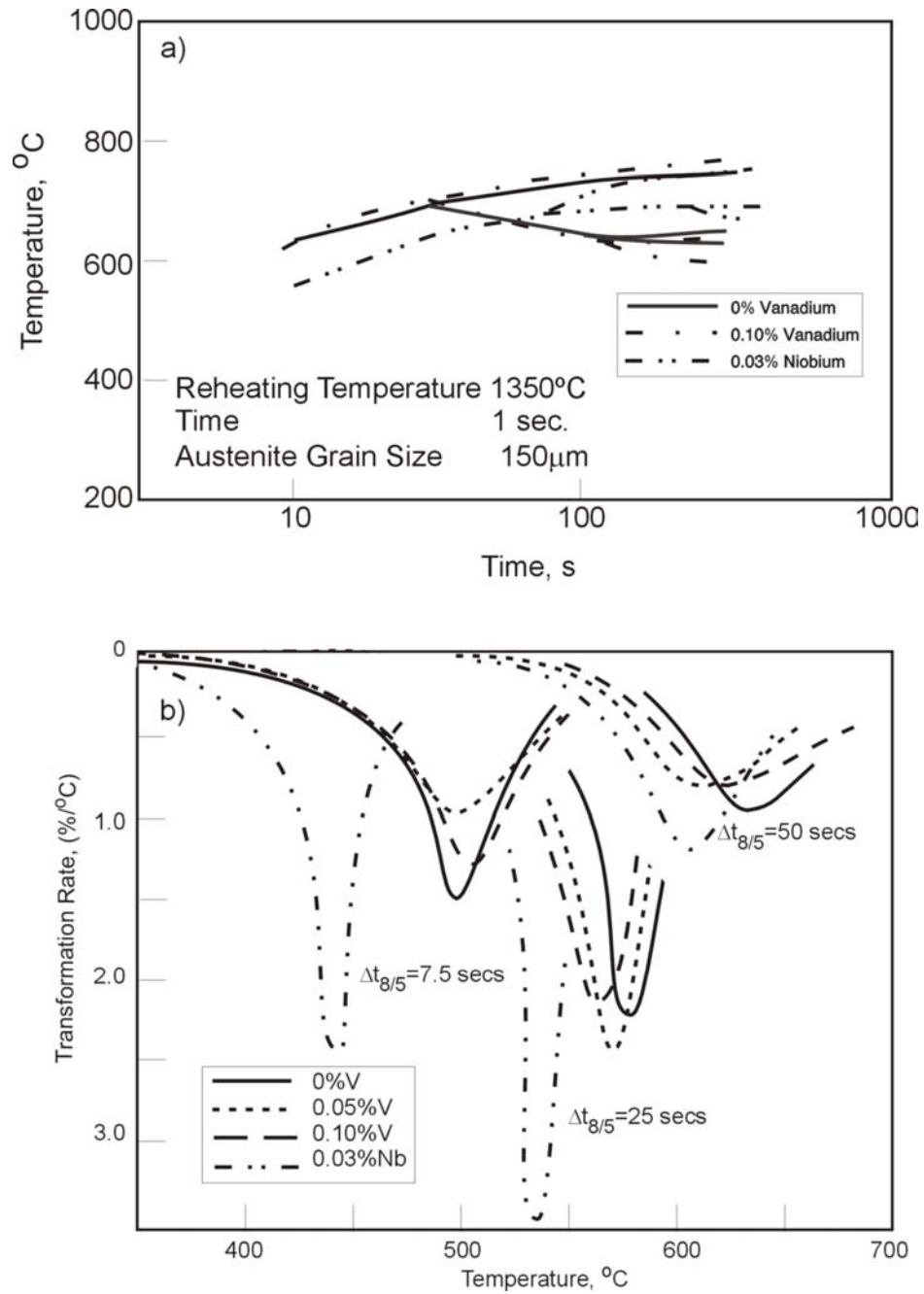


Fig. 15 Effect of vanadium and niobium on transformation behaviour a) transformation start temperature, b) transformation temperature and rate of transformation.

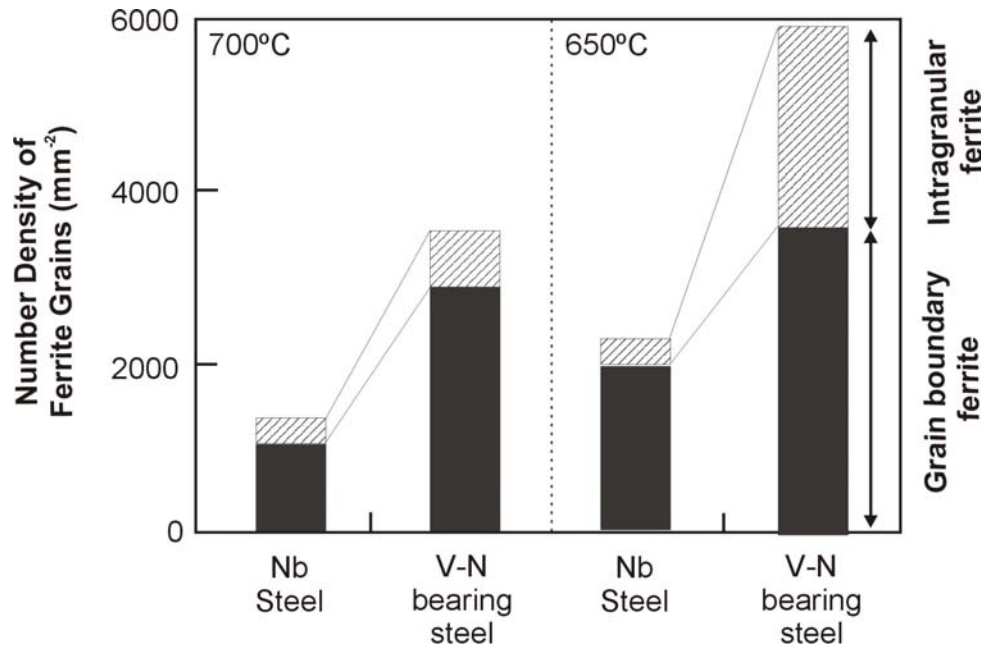


Fig. 16 The number density of ferrite grains during isothermal transformation at 700°C and 650°C.

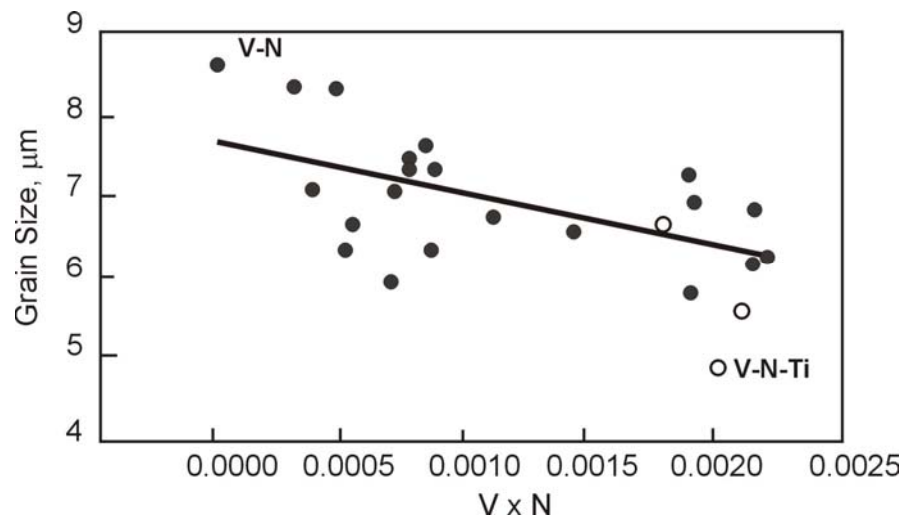


Fig. 17 The influence of VxN on the ferrite grain size, (end cool temperature, 550-650°C).



Fig. 18 TEM bright field image showing the grain boundary carbides of 1.05%C-0.60%Mn-0.23%Si-0.15%V steel partially transformed at 650°C for 3 seconds and then quenched. (Edmonds)

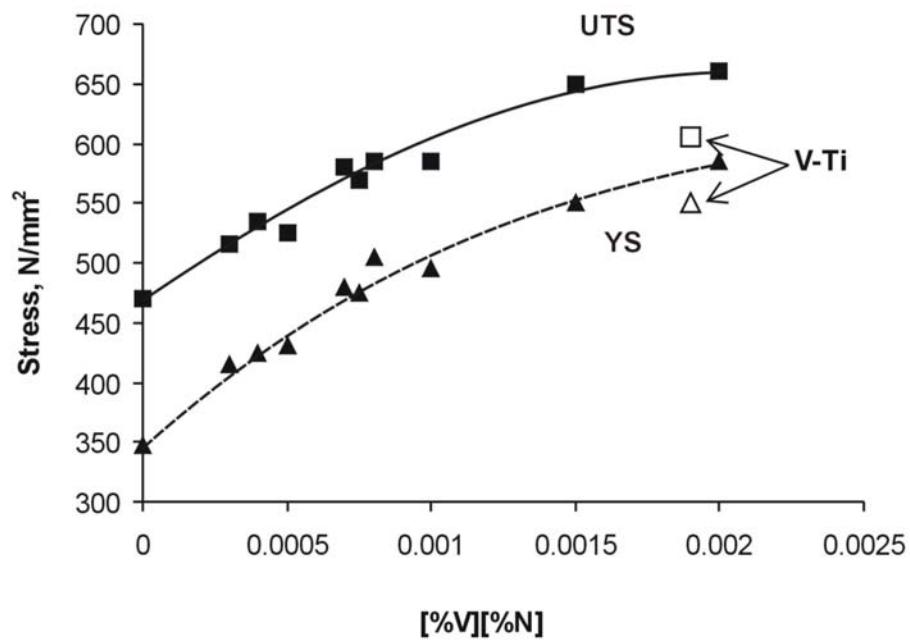


Fig. 19 The effect of vanadium and nitrogen on yield strength and UTS.

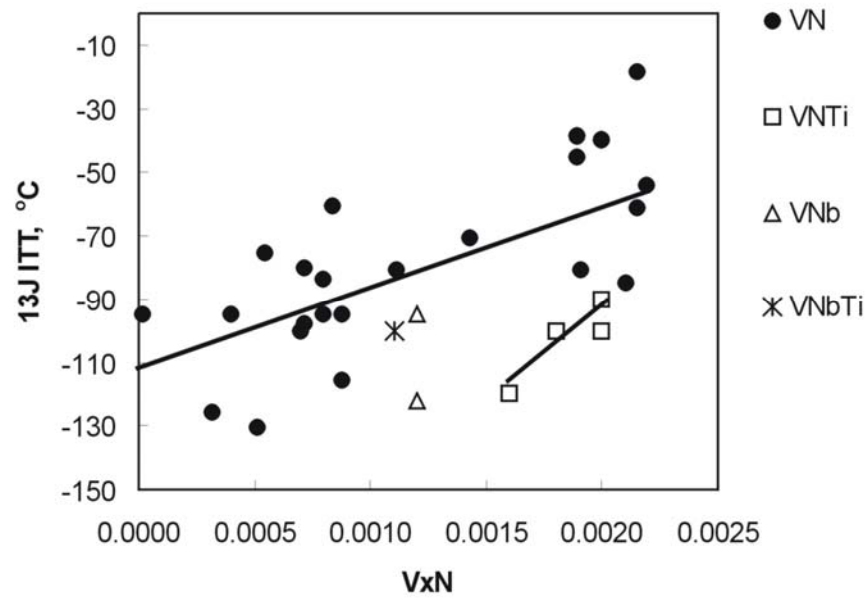


Fig. 20 Relation between impact transition temperature and VxN .

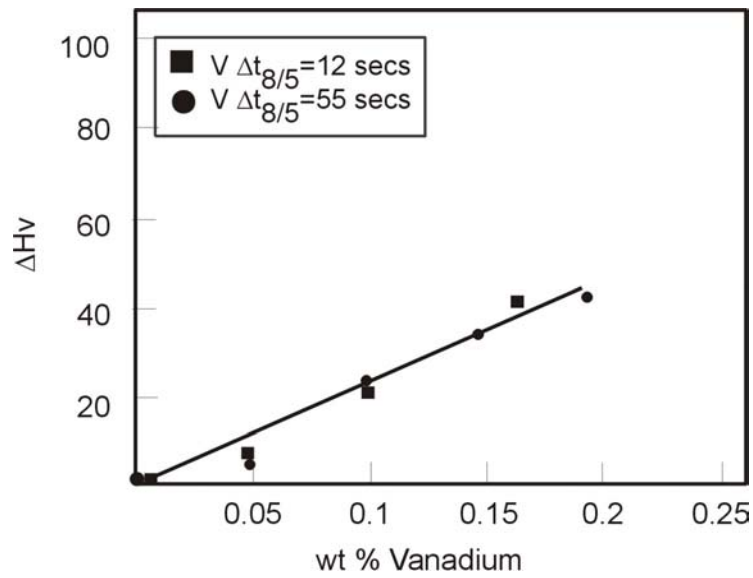


Fig. 21 Effect of vanadium on the change in maximum HAZ hardness in the as-welded condition.

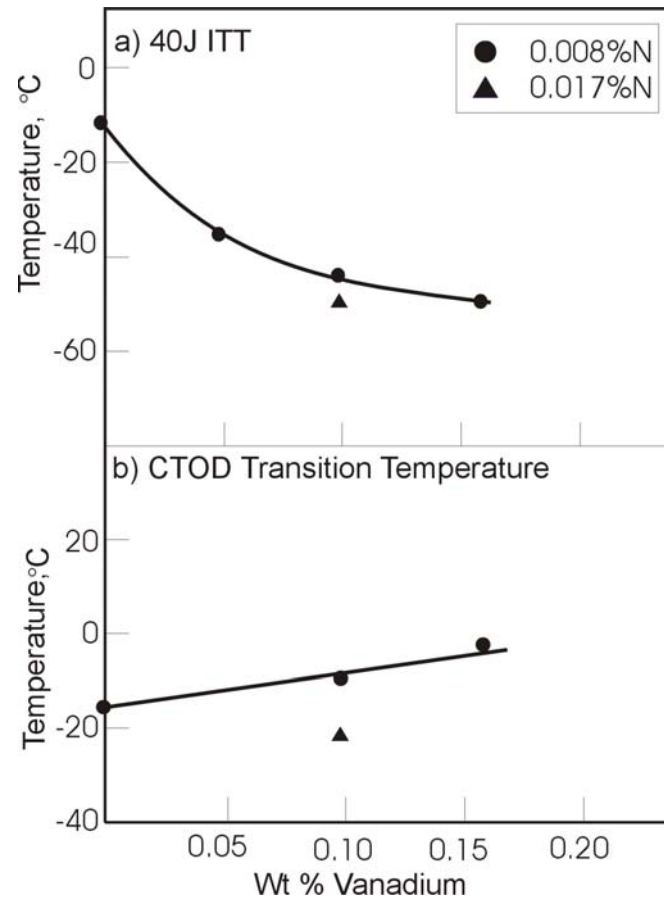
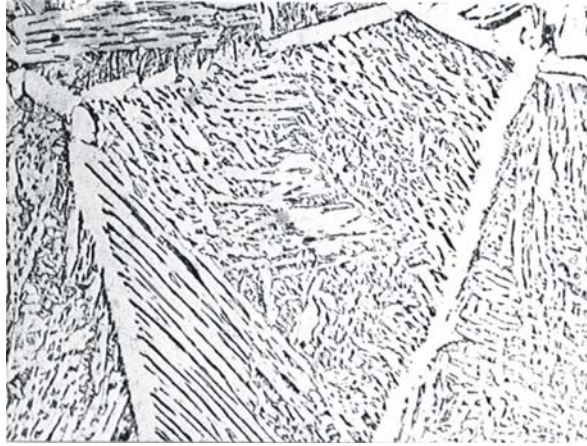


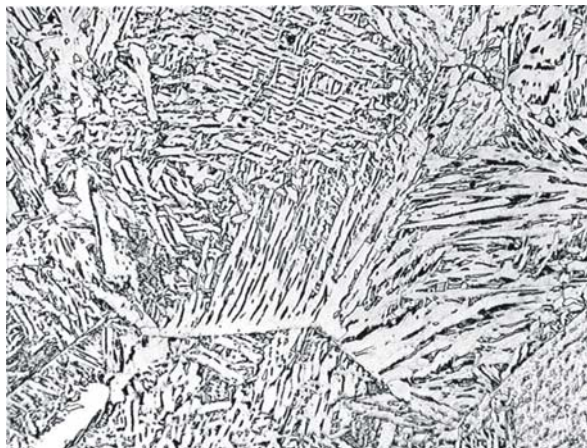
Fig. 22 Effect of vanadium on the fracture toughness of 0.12%C-1.6%Mn steels multipass welded at 2 KJ/mm ($\Delta_{8/5} = 12$ secs) in the as-welded condition.



C-Mn



C-Mn-0.1%V



C-Mn-0.03%Nb

Fig. 23 Simulated HAZ microstructure, cool rate = (800-500) 7°C/s, X500.

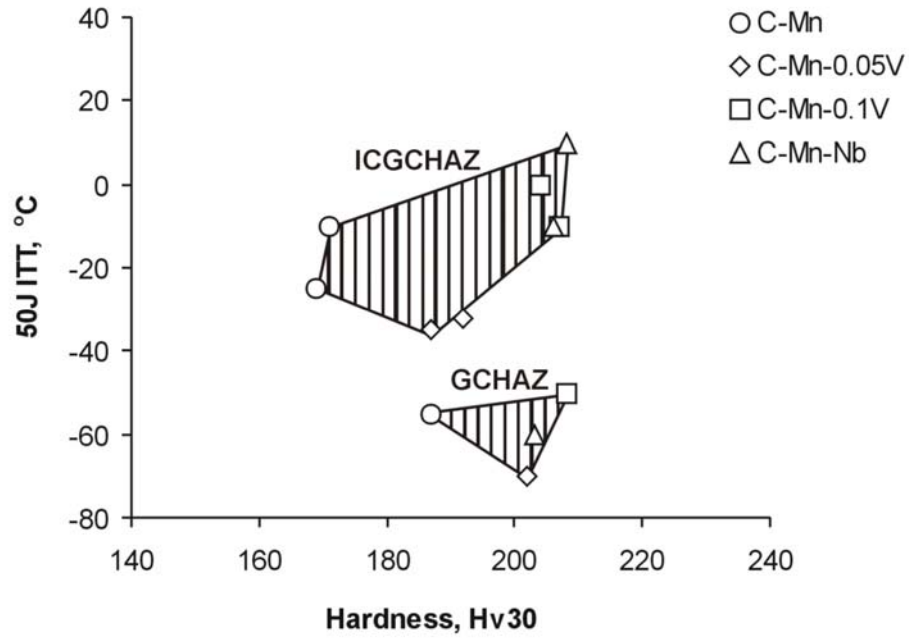


Fig. 24 The effect of hardness on the 50J ITT of the ICGHAZ in V and Nb steels.

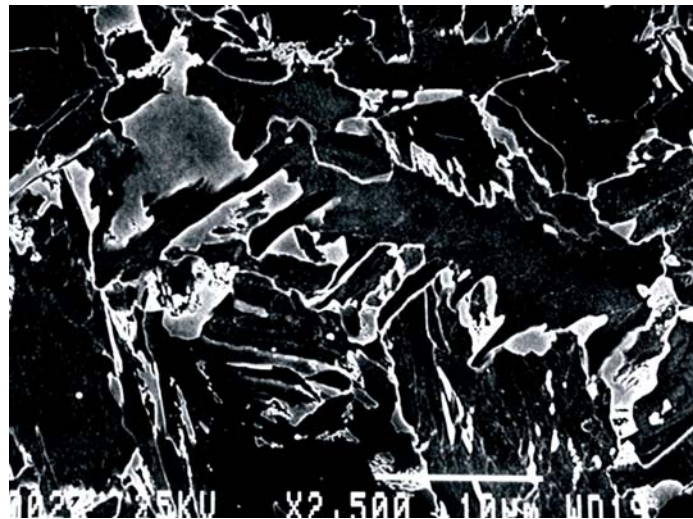


Fig. 25 Typical SEM micrograph showing islands of M-A phase.