

# **THE EFFECT OF MICROALLOYING ON HAZ TOUGHNESS**

**P. S. MITCHELL\*, P. H. M. HART\*\* and Dr. W. B. MORRISON\*\*\***

**\*VANITEC, \*\*The Welding Institute, \*\*\*British Steel Plc, Swinden Technology Centre.**

## **ABSTRACT**

The factors affecting HAZ toughness of modern structural and linepipe steels, microalloyed with Nb, V and Ti have been examined. Critical features include solubility, particle coarsening and dissolution rates, austenite grain size, transformation characteristics, microstructure development and precipitation hardening. Data are presented which demonstrate the effects of Nb, V and Ti on the toughness of the coarse grained region of the HAZ. This indicates that at low heat inputs the weldability of Nb and V microalloyed steels is similar to that of C-Mn steels but that vanadium microalloyed steels appear to be more tolerant to increases in heat input. Improvements in HAZ toughness can be obtained by the addition of titanium, which may be as a result of formation of TiN and/or an oxide of titanium.

## **1. INTRODUCTION**

In 1975, it was well recognized that the main beneficial effect arising from the addition of microalloying elements was that a reduction in carbon content (or carbon equivalent value (CEV)) could be achieved whilst parent material properties were maintained or enhanced.

In the case of weldability, the reduction in CEV was welcome in that it permitted a relaxation of some welding requirements, especially those associated with HAZ hydrogen cracking and resulted in an increase in HAZ toughness. It also brought with it some concerns regarding the special effects of microalloying elements on factors such as weld metal solidification cracking and weld metal and heat affected zone (HAZ) toughness.

Consequently, in the intervening years, much work on these topics has been carried out, generating significant numbers of publications. It is the intention of the present paper to examine the effect of microalloying additions of Nb and V, together with Ti treatment, on HAZ toughness alone. Further, as the HAZ passes through a temperature cycle in which its different parts can be heated, held and cooled differently, the paper will concentrate on the grain-coarsened heat affected zone (GHAZ), close to the fusion boundary, which is likely to be the most embrittled region.

## **2. FACTORS AFFECTING HAZ TOUGHNESS IN MICROALLOYED STEELS**

The main factors which affect the HAZ toughness of microalloyed steels include:-

- i) The solubility of the microalloying elements, interactions between them and the effect of welding conditions on the degree of approach to equilibrium.
- ii) The size of any particles present and the rate at which they coarsen under welding conditions.
- iii) The resulting HAZ austenite grain size.

- iv) The effect of microalloying elements on transformation temperatures, rates of transformation and the resulting microstructures.
- v) Precipitation hardening within the HAZ.

The effects of these will now be considered.

## 2.1 Solubility of microalloying elements

The equilibrium solubilities of Nb, V and Ti carbides and nitrides are shown in Figure 1<sup>(1)</sup>. From this figure it is clear that in most modern conventionally microalloyed steels the micro alloying elements should be in solution in the grain-coarsened HAZ, close to the fusion line, where the temperature is of the order of 1450°C, or greater. The only exception to this is TiN where the solubility is quite low.

Additionally, some titanium-containing steels depend on the formation of TiO<sub>2</sub>, rather than TiN for achievement of properties and it has been estimated by Homma et al<sup>(2)</sup>, that the solubility of TiO<sub>2</sub> in austenite, at 1450°C, is of the order of 10<sup>-10</sup>, i.e., extremely low.

In steels where combined alloying additions are made and complex compounds are formed, the equilibrium solubility can be altered, especially if the solubility of one of the pure compounds forming the complex is significantly different from the other (Figure 2). As Gladman<sup>(3)</sup> has shown for Nb-Ti-N steels, at high temperature the compound formed is essentially rich in Ti and N, whereas at low temperatures the equilibrium phase is rich in niobium and carbon. This can, of course, lead to coring of the precipitates.

In welds, equilibrium conditions are rarely achieved and the above can only be taken as a guide. However, Easterling and his co-workers<sup>(4)</sup> have modelled the dissolution of microalloyed carbides in austenite, as shown in Figure 3. Thus, even under non-equilibrium welding conditions, the greatest majority, if not all, of the microalloying carbides and nitrides present would be in solution next to the fusion boundary. Once again the exception is TiN, where only a small portion will be in solution. As noted above, TiO<sub>2</sub> is unlikely to be in solution.

## 2.2 Particle size

The only particles which remain out of solution in the high temperature HAZ are TiN and TiO<sub>2</sub>. As TiO<sub>2</sub>, because of its very low solubility, is unlikely to exhibit significant coarsening during welding most of the work reported on particle coarsening has been conducted on TiN.

Sage et al<sup>(5)</sup> have demonstrated, using laboratory cast ingots, that the initial particle size in V-Ti-N steels is dependant on the post solidification cooling rate (PSCR) during casting (Figure 4). As the PSCR increased from 8 to 50°C/min, the particle size reduced by a factor of five. They also demonstrated that the titanium content of the particles increased with increased cooling rate. Crowther<sup>(6)</sup> has studied the size distributions of Ti-rich particles in samples of commercial offshore plates rolled from continuously cast slabs of Nb-treated steels containing around 0.01%Ti. Table I shows the results of the study and includes values for the austenite grain sizes after a heat treatment of 30 mins at 1300°C. The average particle sizes ranged from approximately 25 to 50nm with the austenite grain size being approximately 50 to 100µm. It is observed that there is a tendency for the smaller particles to be associated with the smaller grain sizes.

During welding, and especially at the even higher temperatures associated with the fusion boundary,

it can be expected that the particles will grow, the extent depending on the heat input and temperature. Easterling and his co-workers have also modelled this behaviour for TiN as shown in Figure 5. However, it should also be noted that Gladman<sup>(3)</sup> has demonstrated that complex Nb-Ti carbonitrides held at 1200°C coarsen more quickly than Ti carbonitrides (Figure 6). While at the short times involved in welding such differences are not likely to be great, it must be borne in mind that at temperatures close to the fusion line, coarsening rates are likely to be significantly greater than shown in Figure 6.

Due to their high stability, arising from their low solubility, no significant change in the particle size of TiO<sub>2</sub> would be expected during welding.

### 2.3 Austenite Grain Size

In modern steels alloyed with vanadium and niobium alone, where the microalloying additions are almost certainly in solution at the fusion boundary, there will be few, if any, particles to impede grain growth and, because of the high temperature, it is unlikely that there will be any significant solute drag effects. Consequently, it would be expected that a relatively coarse austenite grain size will develop and that, as the heat input increases, the time at maximum temperature will increase and the cooling rate will decrease, so increasing the maximum grain size. Figure 7, taken from the work of Lau et al<sup>(7)</sup>, illustrates this for a vanadium and a niobium steel.

Adding controlled amounts of titanium can significantly refine the austenite grain size. Nishio et al<sup>(8)</sup> have demonstrated this for simulated welds ( $T_{\max}$  1350°C,  $\Delta t_{8/5} = 40$  secs), in a C-Mn, aluminium-free, steel containing varying titanium and nitrogen contents. Assuming stoichiometry of formation of TiN and TiO<sub>2</sub>, their data can be used to calculate the excess nitrogen. Their austenite grain size data is shown as a function of this quantity in Figure 8. As the titanium content increases from 0.01% to 0.03%, the austenite grain size is reduced and appears to reach a limiting value of around 50  $\mu\text{m}$  with little, if any, further refinement with increasing titanium level. Furthermore, as the nitrogen content is raised there is also an improvement in grain size with the optimum being approached around stoichiometry between nitrogen, oxygen and titanium in the region of 0.01-0.03%Ti. It does appear, however, that it is better to be slightly hypostoichiometric with respect to titanium.

Zajac et al<sup>(9)</sup> have established similar behaviour for 0.08%V - 0.01%Ti, aluminium killed, 0.09%C - 1.4%Mn steels at nitrogen levels of 0.003 and 0.013% (Figure 9). Here, increasing the nitrogen content also resulted in refinement of austenite grain size, especially at temperatures below 1350°C. However, as the temperature increased above this level grain coarsening occurred, even in the higher nitrogen steel. These workers also reported that at 1350°C the grain size was relatively independent of both cooling time from 800°C to 500°C (in the range 10-100 seconds) and of time at 1350°C (up to 30 seconds). While these results indicate that in the very coarsest area of the heat affected zone TiN grain refinement is less effective, it remains useful as a means of refining the majority of the HAZ and hence reducing the width of the coarse region.

In the case of niobium bearing steels, McCutcheon et al<sup>(10)</sup> have shown that, in submerged arc welded Nb-Ti-Mo linepipe steels welded at 2kJ/mm, the minimum austenite grain size was also achieved as the Ti:N ratio approached stoichiometry. This has additionally been observed by Ferguson<sup>(11)</sup> over a range of heat input from 3kJ/mm to 9kJ/mm. The most comparable data from the two groups of workers have been combined in Figure 10.

### 2.4 Transformation

Crowther<sup>(12)</sup> has used 0.13%C-1.45%Mn steels to examine the effects of both vanadium and niobium

on the transformation temperatures of simulated HAZ's,  $T_{\max}$  1350°C, at reasonably constant austenite grain size, typically 110-130µm. He demonstrated that adding up to 0.1% vanadium had little effect on the start transformation temperature over a range of cooling rates typical of those found in welding, i.e.,  $\Delta t_{8/5} = 5-250$  secs. On the other hand, a steel of similar composition, but containing 0.03%Nb instead of vanadium, exhibited the expected 50 - 60°C depression of the transformation start temperature.

Zajac et al <sup>(9)</sup> also determined transformation start temperatures for their 0.08%V - 0.01%Ti-N steels. Increasing the nitrogen content from 0.003% to 0.013% increased the transformation start temperature by up to approximately 100°C. This is, undoubtedly, due to the refinement of austenite grain size discussed above. They found little or no effect of nitrogen on the transformation finish temperatures.

On the basis of CCT curves determined by Yamamoto et al <sup>(13)</sup>, it would appear that in Ti-0 steels the Ti-deoxidation had little or no effect on transformation start or finish temperatures when compared with more conventional Al-N steels. As will be noted later, they did report differences in the transformation products formed. This lack of effect of Ti-0 on transformation temperatures is somewhat surprising in view of the work of Nishio<sup>(8)</sup> and Zajac<sup>(9)</sup> discussed above. It presumably means that both types of steel examined by Yamamoto et al possessed the same initial austenite grain size.

In addition to having an understanding of transformation temperatures, it is equally important to gain an understanding of the rate at which transformation is taking place as this will, to some extent, determine the number and size of the transformed microstructural units. Crowther<sup>(12)</sup> has determined the effect of vanadium and niobium on transformation rates for different cooling times between 800 and 500°C. The data provided by Zajac et al<sup>(9)</sup> can also be analysed to provide similar information, as shown in Figure 11a and b. As the cooling time decreases, the range of temperature over which the transformation occurs is pushed to lower temperatures, as would be expected. The niobium steel shown in Figure 11a exhibits a peak rate of transformation at temperatures around 50°C below those of the C-Mn and C-Mn-V steels, and its peak transformation rate is always greater than those of the C-Mn and C-Mn-V steels. Refining the austenite grain size increases the temperature range over which transformation occurs and reduces the peak rate of transformation (Figure 11b). The lower the temperature and the greater the rate of transformation, the more likely is the formation of acicular products which traverse complete austenite grains.

## 2.5 Microstructures

Comparison of microstructure is rendered difficult by the tendency for different workers to call the same microstructure by different names and a strong case for rationalization can still be made. However, as will be observed, the different microalloys result in microstructural differences which can be recognized irrespective of what they are called.

In the case of C-Mn, C-Mn-V and C-Mn-Nb HAZ's, a reduction in cooling time results in an increase in the volume fraction of lower transformation products, (Figure 12a)<sup>(12)</sup>. However, in this work clear differences in the nature of transformation products between vanadium and niobium steels were also observed, particularly at longer cooling times, typical of high heat input welding. At cooling times greater than approximately 40 seconds the vanadium steels exhibited more grain boundary polygonal ferrite and less side plate and grain boundary allotriomorphic ferrite than the niobium steel (Figures 12a and b).

Furthermore, the ferrite described as ferrite with aligned second phase (Figure 12c) was different in

the two types of microalloyed steel. In the vanadium steel it tended to be similar to the intragranular ferrite observed in weld metals and to consist of interlocking laths, while the Nb steel tended to exhibit a more classical upper bainitic type of structure (Figure 13). The type of structure observed in the vanadium steel has already been reported by Thaulow et al<sup>(14)</sup> and others<sup>(7,15)</sup>, while that of the niobium steel has also been well documented.<sup>(7,16)</sup>

It has also been suggested<sup>(17, 18, 19)</sup> that both Nb and V can promote the formation of M-A phase in the microstructure. However, as the steels investigated in these papers contained variable boron and/or aluminium levels or were examined under conditions where the opportunity for microalloying elements to influence transformation would be significantly reduced i.e. the ICGHAZ was examined, such a tendency must remain, as yet, unproven.

The effect of austenite grain refinement on the transformation products formed in the V-Ti-N steel investigated by Zajac<sup>(9)</sup> is shown in Figure 14. As expected there has been a reduction in the volume fraction of low temperature phases martensite (M) and ferrite with second phase (FS), accompanied by a corresponding increase in the volume fraction of higher temperature grain boundary ferrite (PF(G)) and of intragranular polygonal ferrite (PF(I)). The greater the cooling time the greater the tendency to form the higher temperature phase.

The main difference between Al-N and Ti-O steels is that, in the latter case, the formation of fine intragranular ferrite, is reported to have been promoted at the expense of side plate ferrite (Figure 15)<sup>(13)</sup>. It is difficult, however, to understand how oxygen contents of the level reported in modern commercial clean steels can produce a sufficient number and volume fraction of relatively large Ti-O particles to significantly influence transformation characteristics.

## 2.6 Precipitation

That vanadium and niobium contributed to precipitation hardening in the heat affected zone was certainly recognized by Hannerz<sup>(20,21)</sup>.

Figure 16, derived from the work of Rothwell<sup>(22)</sup> and the present authors<sup>(23)</sup> demonstrates that in both the as welded and post weld heat treated conditions, vanadium and niobium increase the heat affected zone hardness. The increase is greater in the post weld heat treated condition than in the as welded condition. Likewise, niobium appears to increase the hardness more than vanadium at the same level of addition, although it should be noted that in normal steelmaking practice the level of Nb used to achieve properties will be roughly half that of vanadium. Further, the degree of hardening of the vanadium steel does not appear to have changed significantly within the range of heat input examined, i.e., 2.5-5kJ/mm.

Increasing the heat input reduces the overall HAZ hardness in microalloyed steels. In Figure 17<sup>(7)</sup>, the rate of decrease is similar for all the steels studied within the heat input range 3-6kJ/mm. This suggests that it is the hardness of the matrix which is reducing and not the degree of precipitation hardening per se.

Raising the nitrogen content would also be expected to increase the HAZ hardness. Work by the present authors<sup>(23)</sup> indicates that increasing the nitrogen content in vanadium steels from 0.007% to 0.017% resulted in a 20 - 25HV increase in hardness in both the as welded and post weld heat treated conditions.

### 3. HAZ TOUGHNESS

At the outset it was noted that one of the main benefits gained from the use of microalloying elements was an improvement in HAZ toughness, arising from the reduction in carbon content (or CEV). Initial observations were based on the use of HAZ Charpy vee notch impact specimens and remain correct in modern steels. However, when CTOD tests, the notches of which can be critically placed in the most microstructurally sensitive regions of the HAZ are carried out, there appears to be a limit on the improvement in HAZ toughness which can be achieved by decreasing the carbon content. Terasaki et al<sup>(24)</sup> indicate that this limit may be at a CEV of the order of 0.28 (Figure 18). Fortunately this level is at, or beyond, the minimum CEV likely to be encountered in most modern HSLA steels. However, it should be noted that this limiting CEV would be expected to change with heat input.

#### 3.1 Effect of Niobium on HAZ Toughness - As welded

Hannerz<sup>(21)</sup> carried out extensive studies on the effect of niobium on HAZ toughness in simulated welds at two cooling times, i.e.,  $\Delta t_{8/5} = 300$  and 33 seconds, respectively. He demonstrated that in both relatively high carbon (0.17- 0.23%) - 1.3% manganese and relatively low carbon (0.03- 0.04%) - 2.0% manganese steels, the addition of up to 0.29% niobium resulted in significant increase in impact transition temperatures, with the greatest increases being observed at the longer cooling time. Such increases have been attributed to precipitation strengthening and to the formation of brittle microstructures.

Subsequent work carried out mainly by Dolby<sup>(25)</sup>, Rothwell<sup>(22)</sup> and Wang et al<sup>(26)</sup> tend to confirm the effects of niobium at high heat input but also indicate that at lower heat input<sup>(22,27)</sup> and lower carbon contents<sup>(22,28)</sup> niobium, up to about 0.06%Nb, is not significantly detrimental to HAZ toughness. As shown by Hulka and Heisterkamp<sup>(29)</sup> (Figure 19), increasing the niobium content to a level of 0.08%Nb in 0.08%C - 1.5%Mn steels, welded at 2kJ/mm resulted in a slight deterioration in HAZ toughness, as measured by both Charpy and CTOD testing.

More recent work by Shiwaku et al<sup>(30)</sup> indicated that further reduction in carbon content to 0.03%C resulted in tolerance to niobium (in the range 0.01% to 0.05%Nb) at higher heat inputs, (Figure 20). Such reductions are made possible by modern processing techniques such as accelerated cooling.

The effects of niobium on as welded HAZ toughness are almost certainly due to a combination of precipitation hardening coupled with the development of embrittling, lower transformation, products, particularly as the heat input increases, as described in the previous section. It is notable that the best properties have been obtained under conditions where suppression of precipitation may have been encountered and where the carbon content of the transformation product was low thus ensuring relatively few large, brittle, carbides or islands of coarse M-A phase in the microstructure. Furthermore, the relatively small effect of niobium on toughness at low heat input<sup>(29)</sup> suggests that under these conditions the effect of niobium on M-A phase is small.

#### 3.2 The Effect of Niobium on HAZ Toughness - after PWHT

As was demonstrated in Figure 16, one of the main effects of niobium is to result in an increase in hardness after post weld heat treatment. This increase is about a factor of two greater than in the as welded condition. Depending on the basic microstructure of the HAZ, this hardening can result in embrittlement or it can be mitigated by tempering of brittle phases in the microstructure. In the example shown in Figure 21<sup>(28)</sup>, the former was obviously taking place and the fracture transition temperature increased significantly as the niobium level increased to 0.08%Nb.

### 3.3 The Effect of Vanadium on HAZ Toughness - As Welded

Hannerz<sup>(20)</sup> also investigated the effect of vanadium on the HAZ toughness of synthetic welds at three cooling times, i.e.,  $\Delta t_{8/5} = 33$  secs, 100 secs, 300 secs, respectively. In a steel containing 0.15%C - 1.4%Mn he observed that, at vanadium levels up to about 0.1%, or greater, there was no significant effect on the HAZ toughness at the two lower cooling times. Even at the longest cooling time, the effect of 0.1%V was small and it was only at vanadium levels higher than this that significant reductions in toughness were observed at any of the cooling times. It is also interesting to note that Hannerz found little or no effect on HAZ toughness of increasing the nitrogen level from 0.006% to 0.013%N, at any of the cooling times investigated.

The present authors have investigated the effect of vanadium on the HAZ toughness of multipass welds<sup>(23)</sup> and Figure 22 a) and b) shows HAZ Charpy transition and CTOD transition data for multipass welds carried out at 2kJ/mm ( $\Delta t_{8/5} = 12$  secs) on 25mm thick plate. In the as welded condition the 40J ITT improved continuously by 40°C as the vanadium level increased from 0 - 0.16%. In the same interval the CTOD transition increased slightly by about 10°C. It is also interesting to note that, as predicted by Hannerz<sup>(20)</sup>, there was little or no effect of nitrogen level observed on either the ITT or on the CTOD transition. Adding 0.03%Nb improved the ITT of the C-Mn steel, but the steel with 0.03%Nb + 0.07%V had a level of ITT slightly above that of similar vanadium-containing, Nb free, steels. Niobium also slightly increased the as welded CTOD transition of these steels by 10 - 20°C, irrespective of the vanadium level.

In the case of vanadium steels, at this relatively low heat input, the improvement in as welded toughness is thought to result from the formation of a favourable microstructure, containing intragranular ferrite, which more than offset any reduction in toughness accruing from precipitation hardening, this being particularly true of the Charpy vee notch transition temperature. As with niobium, it is worth noting that this relatively small increase in CTOD transition temperature indicated that at 2kJ/mm any effect of vanadium on M-A phase formation must have been small.

### 3.4 The Effect of Vanadium on HAZ Toughness - After PWHT

Figure 22 also indicates the effect of post weld heat treatment on the toughness of vanadium-containing steels. The Charpy vee notch transition temperature is now almost a mirror image of that in the as welded condition. At a vanadium level of less than about 0.06%, the toughness is the same as or better than in the as welded condition, while at greater vanadium levels it exhibits a small increase of up to 20°C at 0.16%V. Conversely, post weld heat treatment improved the CTOD transition temperature by 30 - 50°C, the improvement being slightly greater at lower vanadium levels.

These changes obviously reflect the effects of tempering of the matrix and of precipitation hardening which occur during post weld heat treatment as well as the sensitivity of the microstructure to the differences in notch location and strain rate exhibited in the two types of test. The improvement noted in the CTOD tests is indicative of tempering of M-A phase contained in the general matrix.

It is also notable in Figure 22 that nitrogen does not appear to have had a very significant effect on toughness after PWHT of these vanadium-containing steels. Furthermore, the addition of 0.03Nb to a 0.07%V steel has had a greater effect on impact toughness than on CTOD.

### 3.5 The Effect of Heat Input on HAZ Toughness of Niobium and Vanadium Steels

Crowther<sup>(12)</sup>, Wang<sup>(26)</sup> and the present authors<sup>(23)</sup> among others<sup>(21,22)</sup> have investigated the effect of heat input on the fracture toughness of niobium and vanadium-containing microalloyed steels. Figure

23 represents a compilation of results for impact and CTOD testing, in the as welded condition, of steels containing approximately 0.13%C - 1.4%Mn, from the above named authors. It should be noted that these results include single pass bead in groove<sup>(11)</sup>, single pass bead on plate<sup>(26)</sup> and multi pass welds<sup>(23)</sup>.

Increasing heat input resulted in a larger increase in impact transition temperature in the niobium steels than it did in the vanadium steels. Arguably more critically, increasing heat input resulted in an improvement in CTOD transition in the vanadium steels and a deterioration in CTOD transition in the niobium steels.

Reference to Figure 12 indicates that, as the heat input was increased, niobium steels exhibited a higher level of sideplate and allotriomorphic ferrite, in association with ferrite with aligned second phase, than the vanadium steels which exhibited more grain boundary polygonal ferrite, in association with a more intragranular form of ferrite with some alignment of the second phase. The degree of precipitation strengthening is thought to remain relatively unchanged within the range of heat input investigated, or to decrease at a similar rate, in all the steels investigated. It is, thus, the changes in microstructure which are thought to have contributed to the observed changes in toughness.

### 3.6 The Effect of Titanium Treatment on HAZ Toughness

As noted earlier the results of Nishio et al<sup>(8)</sup> can be adjusted to account for stoichiometry between titanium, oxygen and nitrogen and the impact value can be plotted as a function of the excess nitrogen (Figure 24). Reflecting their results for austenite grain size, increasing the titanium level in the range 0.01 - 0.03% also resulted in maximum toughness, particularly when the nitrogen and oxygen levels approached stoichiometry. It would also appear to be advantageous to be slightly hypostoichiometric with respect to titanium. McCutcheon et al<sup>(10)</sup> reported a similar conclusion when studying the weldability of C-Mn-Nb-Mo-Ti linepipe steels welded at 2kJ/mm. As suggested by Pickering<sup>(31)</sup> this should restrict the solubility of titanium at high temperature and consequently reduce the growth rate of any Ti-N particles. It should be noted, however, that the results shown in Figure 24 are based on laboratory heats which would probably have solidified at significantly faster rates than obtained in commercial production. This would have had a major influence on titanium-nitride particle size (Figure 4) which would, in turn, influence the HAZ grain size. In addition, if the titanium and nitrogen levels were sufficiently high to permit formation of TiN in the segregated liquid phase during solidification, then the resultant particles could act as crack nuclei<sup>(32)</sup>. This would significantly increase fracture transition temperatures.

Little systematic data indicating the effect of niobium on the toughness of titanium-treated steels have been published. However Bateson et al<sup>(33)</sup> investigated the effect of titanium treatment on the HAZ toughness of 65mm thick, low CEV, Thermo-mechanically Controlled Rolled (TMCR), steel containing 0.02%Nb. After welding at a heat input of 4.5kJ/mm, their titanium treated steel had a Charpy vee-notch transition temperature some 35-40°C better than that of a similar titanium-free steel (Figure 25).

Similarly Zajac<sup>(9)</sup> examined the effects of nitrogen level and heat input on the Charpy vee-notch HAZ toughness of 0.08%V-Ti steels (Figure 26a). Comparison of his results for a 0.003%N steel with those of the Ti-free 0.004-0.005%N steels, contained in Figure 23, indicates a similar level of improvement to that noted above for niobium steels. However, increasing the nitrogen content of the V-Ti steels from 0.003 to 0.013% led to an increase in impact transition temperature of approximately 30°C. Additionally, compared with the Ti-free steels the Ti-containing steels shown in Figure 26a appear to be slightly more sensitive to the effects of heat input. Above 5kJ/mm the

0.013%N-Ti steel had a higher impact transition temperature than the Ti-free steels, while the impact transition temperature of the lower nitrogen steel at 8kJ/mm was similar to that of the Ti-free steels at 5kJ/mm.

Wang et al<sup>(26)</sup>, using single pass welds, have also reported the effect of heat input on the CTOD transition temperature of Ti-Nb and Ti-V steels. They demonstrated, for the Ti-Nb steel, that increasing the heat input from 3kJ/mm to 6kJ/mm had little or no effect on this transition temperature at a level of 0°C/-5°C. However, Bateson et al<sup>(33)</sup>, using multi pass welds, noted that, while recording a generally acceptable level of CTOD at -10°C, on 65 mm thick, low CEV, TMCR, Ti-Nb steels, the minimum level of CTOD reduced from around 0.6 mm to under 0.2 mm as the heat input increased from 0.8kJ/mm to 5.0kJ/mm.

In the case of the Ti-V steels Wang et al found that increasing heat input from 3kJ/mm to 6kJ/mm resulted in a significant deterioration in CTOD transition temperature from a level of -50°C to around +10/+15°C. This is depicted in Figure 26b which also shows their results for the Ti-Nb steel and for the Ti-free vanadium containing steels taken from Figure 23. From this figure it would appear that it is only at low heat inputs i.e. <3.5kJ/mm, that Ti-V steels have a similar level of toughness to that of Ti-free vanadium-containing steels, when measured by CTOD. This figure also demonstrates that, at heat inputs >4kJ/mm, while the CTOD transition temperatures of the Ti-Nb steel are better than those of the Ti-V steel, they are inferior to those of the vanadium-containing Ti-free steels shown in Figure 23. Thus, at high heat input, it is difficult to see a justification for the addition of titanium when CTOD performance is considered.

## CONCLUSIONS

Our knowledge of the effects of microalloying elements on the toughness of the grain coarsened heat affected zone of welds has significantly increased over the past twenty years. It can be reasonably concluded:-

- 1). At the micro alloying levels normally used, niobium and vanadium carbides, nitrides and carbonitrides are likely to be in solution close to the fusion boundary and only titanium oxides and nitrides are likely to remain out of solution.
- 2). As a result of the low solubility of TiO and TiN, Ti treated steels offer the possibility of achieving austenite grain size control and the optimum Ti level appears to be slightly hypostoichiometric with respect to Ti-N or Ti-O-N.
- 3). Niobium and vanadium appear to affect the transformation from austenite to ferrite in different ways. Niobium promotes the formation of lower temperature transformation products which transform at a relatively high rate to microstructures containing a high proportion of sideplate ferrite and ferrite with aligned second phase which tend to traverse complete austenite grains. Vanadium appears to promote higher temperature microstructures which transform at a slower rate than in niobium steels, to microstructures which contain a higher proportion of polygonal and intragranular ferrite phases.
- 4). Increasing the nitrogen content of Ti-treated vanadium steels raises the transformation temperature, increases the range of temperature over which transformation occurs and promotes the formation of microstructures containing a higher proportion of grain boundary and intragranular ferrite. No comparable data for Nb steels was available.

- 5). Both niobium and vanadium result in hardening within the heat affected zone, that in the post weld heat treated condition being significantly greater than in the as welded condition. In both conditions, however, the degree of hardening due to niobium is approximately double that due to vanadium, although for typical alloying levels, the levels of hardening would be similar. Higher nitrogen levels give rise to additional increases in hardness in vanadium containing steels.
- 6). At low heat input (approximately 2kJ/mm) microalloying with niobium or vanadium has little or no deleterious effect on as welded HAZ toughness and such effects as exist can probably be mitigated by reducing the carbon content. There are, however, considerable data indicating that vanadium additions can improve the as welded HAZ toughness.
- 7). At higher heat inputs (approximately 4 - 5kJ/mm) an increase in Charpy vee notch transition temperature occurs in both niobium and vanadium containing steels, with the increase being greatest in the case of the niobium steels. On the other hand, increasing heat input results in an increase in CTOD transition temperature in the case of niobium steels and a decrease in the case of vanadium steels. This difference in performance is thought to be related to the differences in microstructure noted above.
- 8). The effect of post weld heat treatment in both types of steel is to result in a reduction in Charpy vee notch toughness, the extent of the reduction depending on the alloy content and the base composition. In addition, PWHT improves the general level of CTOD transition but within this improvement increasing the microalloying content results in a small reduction in fracture toughness. These effects are consistent with tempering of the matrix accompanied by precipitation hardening as a result of PWHT.
- 9). While there may be benefits to toughness arising from Ti treatment of Al free steels, in more conventional Al killed steels it would appear that the benefits of such treatment are mixed. While Charpy vee-notch toughness in these latter steels can improve as a result of Ti treatment, this is not always accompanied by an improvement in CTOD transition temperature. Indeed, when examining the total picture, it is difficult to note any significant increase in overall HAZ toughness above what can be achieved with conventional C-Mn-Al-V steels.

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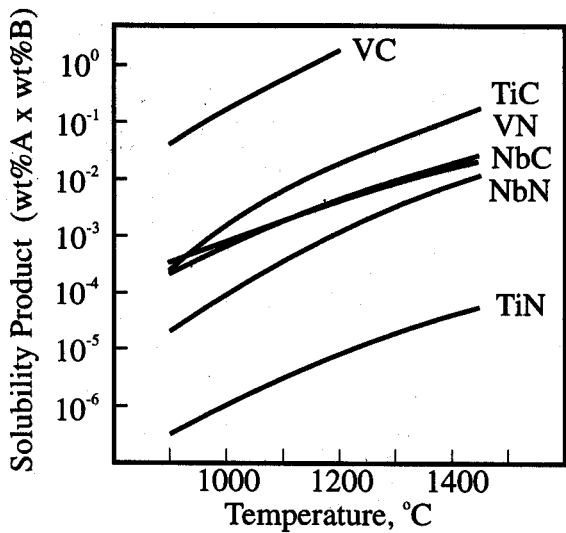


Fig. 1. Solubility Products in Austenite of Microalloy Carbides and Nitrides (Ref. 1).

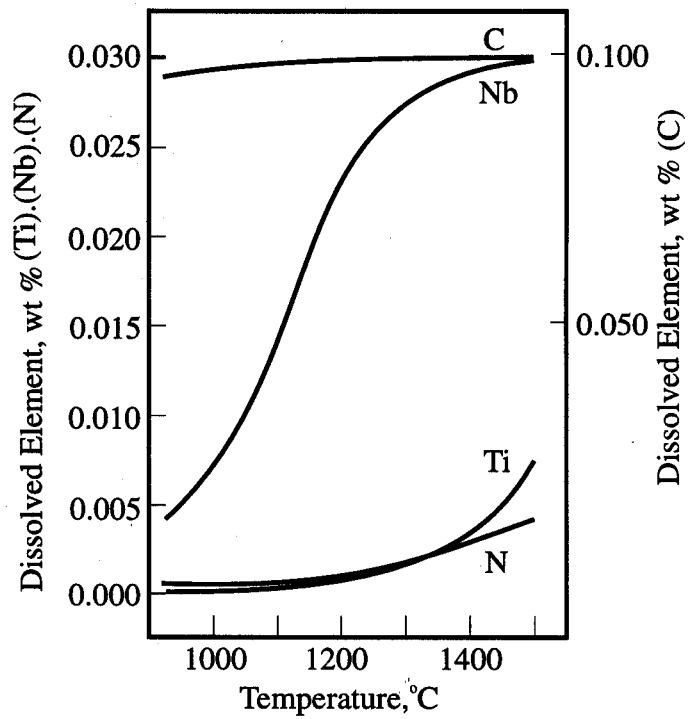


Fig. 2. Dissolution of Complex Nb-Ti Carbo-Nitride (Ref. 3).

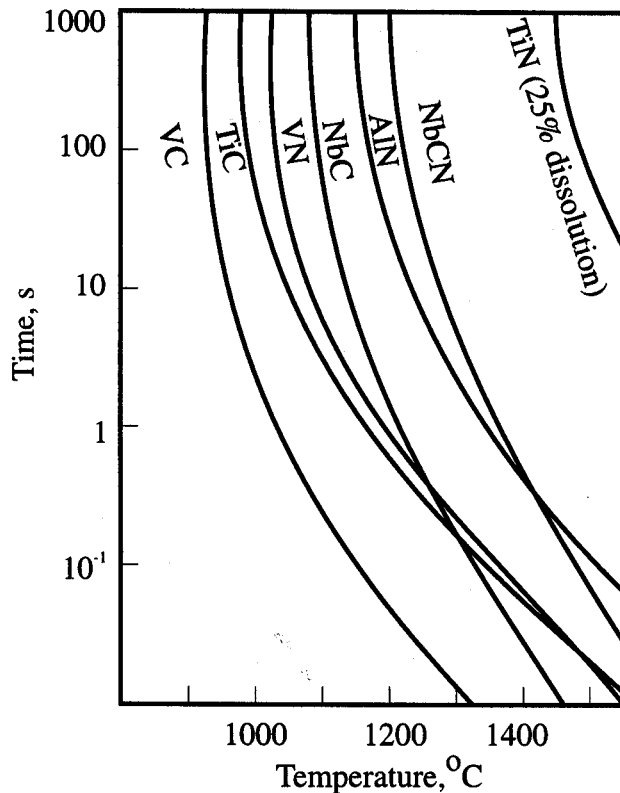


Fig. 3. Times for Complete Dissolution of Various Microalloy Carbides in Austenite as a Function of Temperature. (Ref. 4).

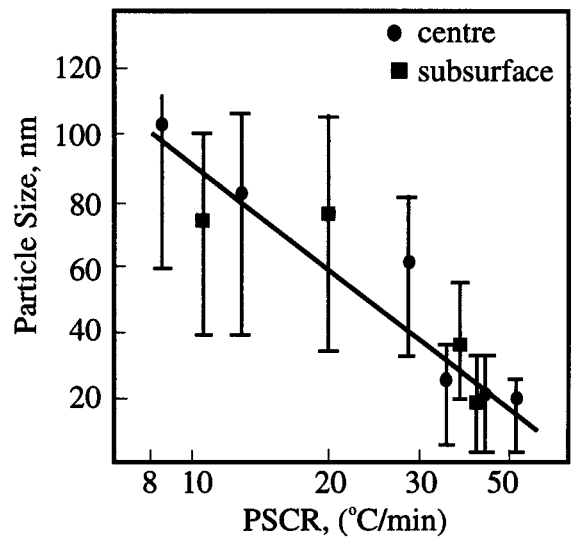


Fig. 4. Effect of Post Solidification Cooling Rate (1470-1100°C) on Particle Size of V-Ti Precipitates in As-cast Ingots. (Ref. 5).

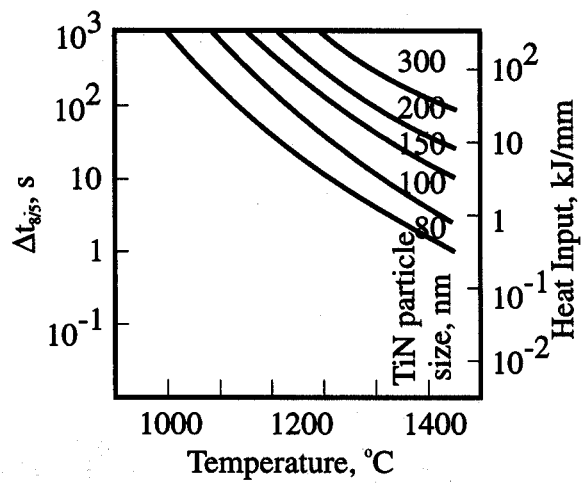


Fig. 5. The Effect of Maximum Temperature and Cooling Rate on Coarsening of TiN Particles in SIS 1217 Steel. (Ref. 4).

Table I Average Ti Particle Size in Commercial Plates of C-Mn-Nb-Ti Offshore Grade 355 Steels (Ref. 6)

Plate thickness, mm	Position		Average Ti content of particles	Average particle size	Grain size after 30 min at 1300°C,
	Width	Thickness	%	nm	μm
20.00	1/4W	1/4T	75.00	30.10	61.00
		1/2T	80.00	37.00	-
	1/4T	1/4T	74.00	24.30	54.00
		1/2T	79.00	25.30	-
50.00	1/4W	SS	84.00	50.50	97.00
		1/4T	74.00	31.40	69.00
		1/2T	77.00	37.60	73.00
		1/4T	72.00	37.40	62.00
40.00	Plate edge	1/4T	72.00	37.40	62.00

SS = Subsurface

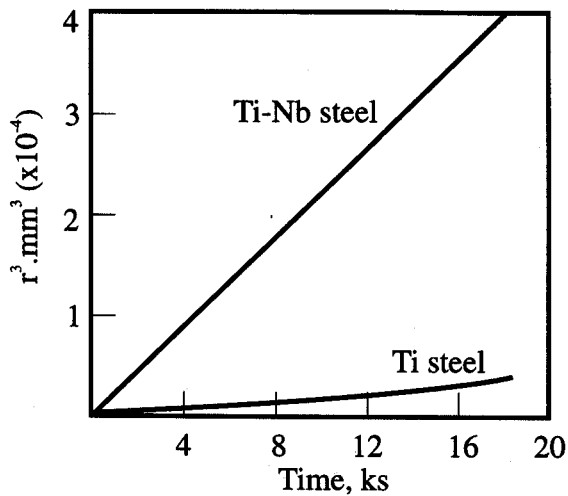


Fig. 6. Coarsening Rates of Carbide-Nitride Particles at 1200°C. (Ref. 3).

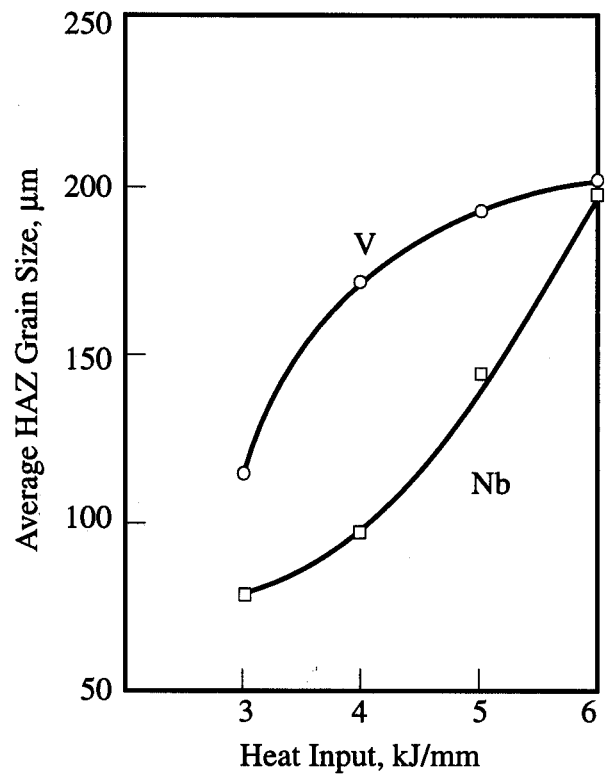


Fig. 7. Effect of Microalloying and Heat Input on HAZ Grain Size at the Fusion Line. (Ref. 7).

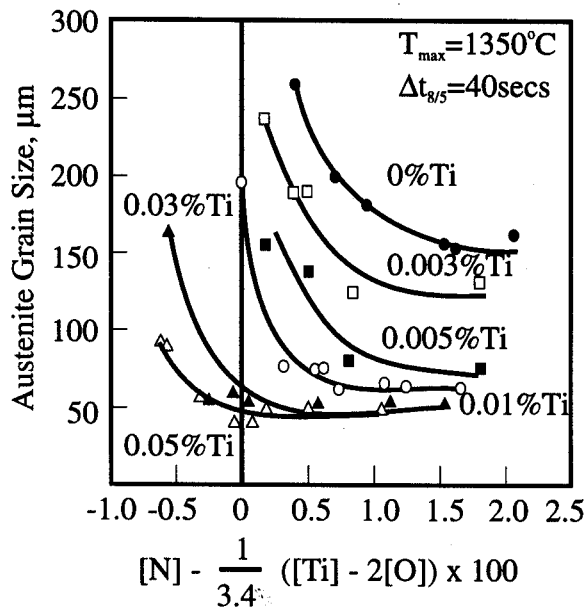


Fig. 8. The Effect of Nitrogen on the Austenite Grain Size of Synthetic HAZ's in C-Mn Steels of Differing Titanium Content. (Ref. 8).

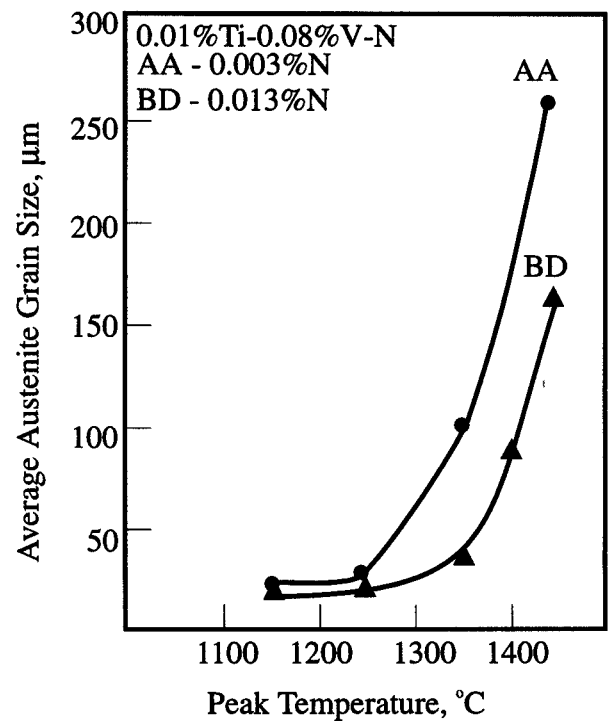


Fig. 9. Grain Growth of Austenite in Simulated HAZ's as a Function of Peak Temperature. (Ref. 9).

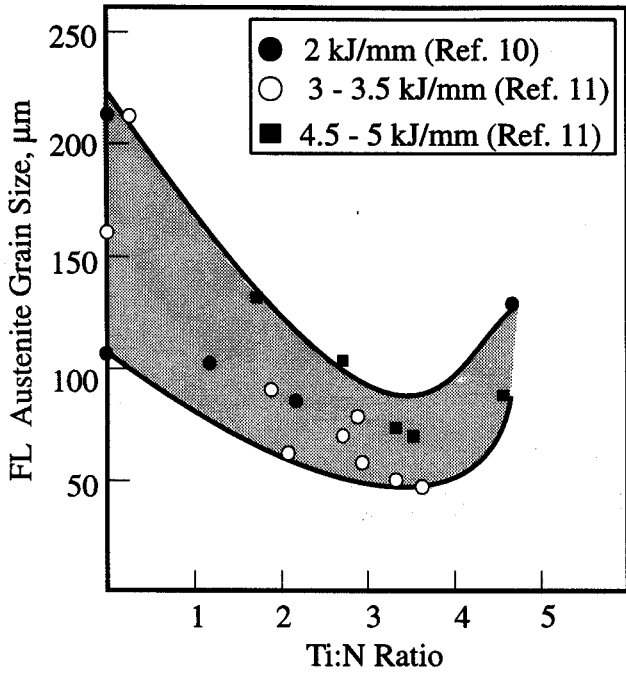


Fig. 10. Effect of Ti:N Ratio on Austenite Grain Size at the Fusion Line in C-Mn-Nb Steels (0.02-0.05%Nb).

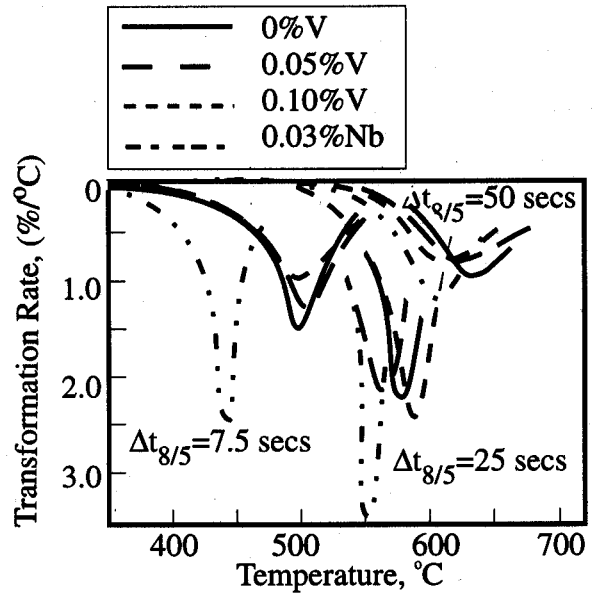


Fig. 11a. The Effect of Vanadium and Niobium on the Rate of Transformation and Temperature Range of Austenite to Ferrite Decomposition at Three Different Cooling Times between 800 and 500°C. (Ref. 12).

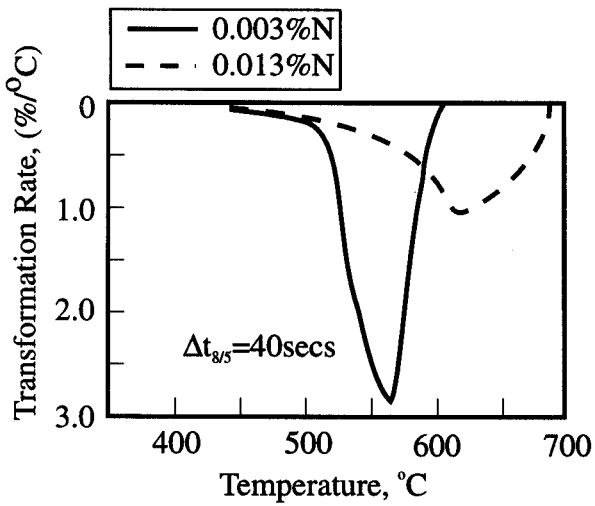


Fig. 11b. The Effect of Nitrogen Level on the Rate of Transformation in Ti-0.08%V-N Steels. (from data in Ref. 9).

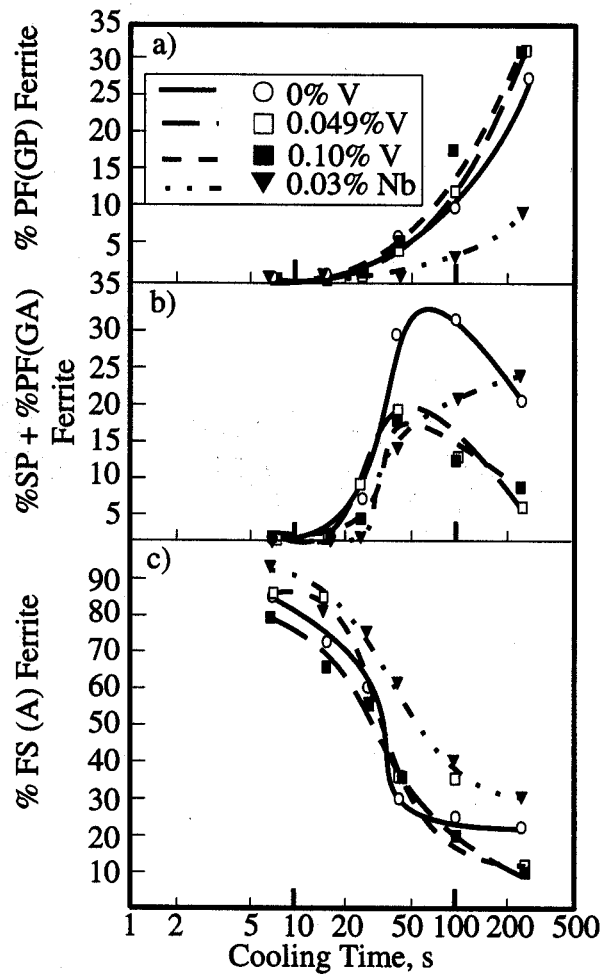
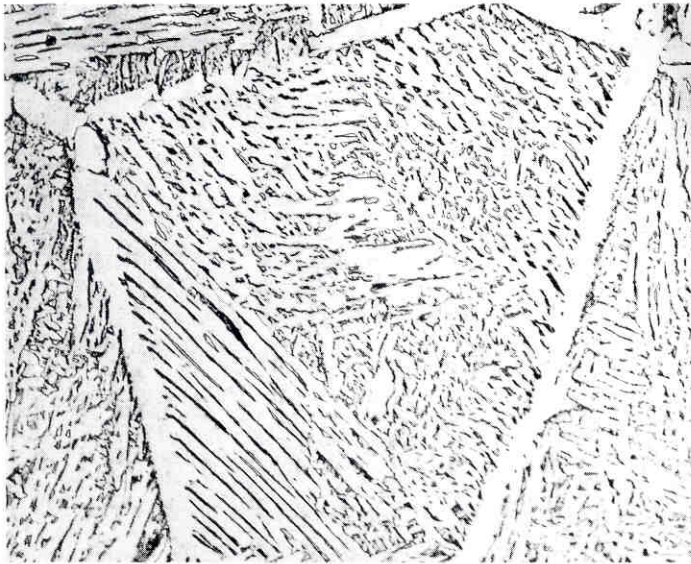


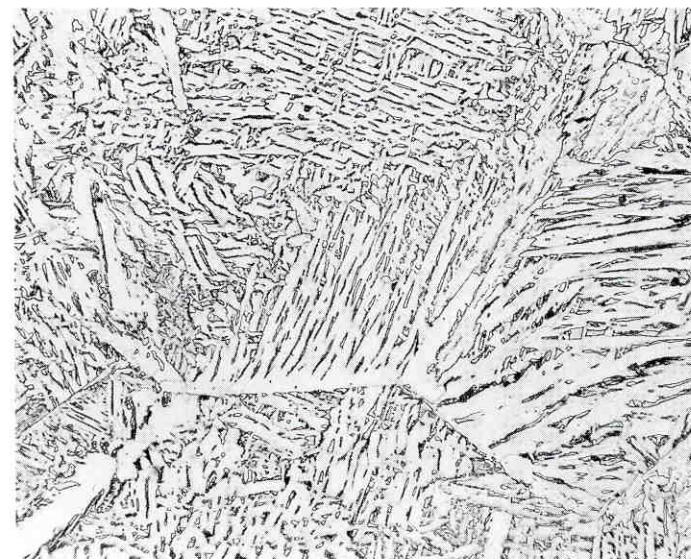
Fig. 12. The Effect of Microalloying and Cooling Time (800-500°C) on the Microstructure of Simulated Welds in 0.13%C-1.4%Mn Steels  
 a) grain Boundary Polygonal Ferrite b) Sideplate + Grain Boundary Allotriomorphic Ferrite c) Ferrite with Aligned Second Phase. (Ref. 12).



C-Mn



C-Mn-0.10%V



C-Mn-0.03%Nb

Figure 13. Simulated HAZ Structures,  
Cooling Rate (800-500°C) 7°C/s,  
x500. (Ref 12)

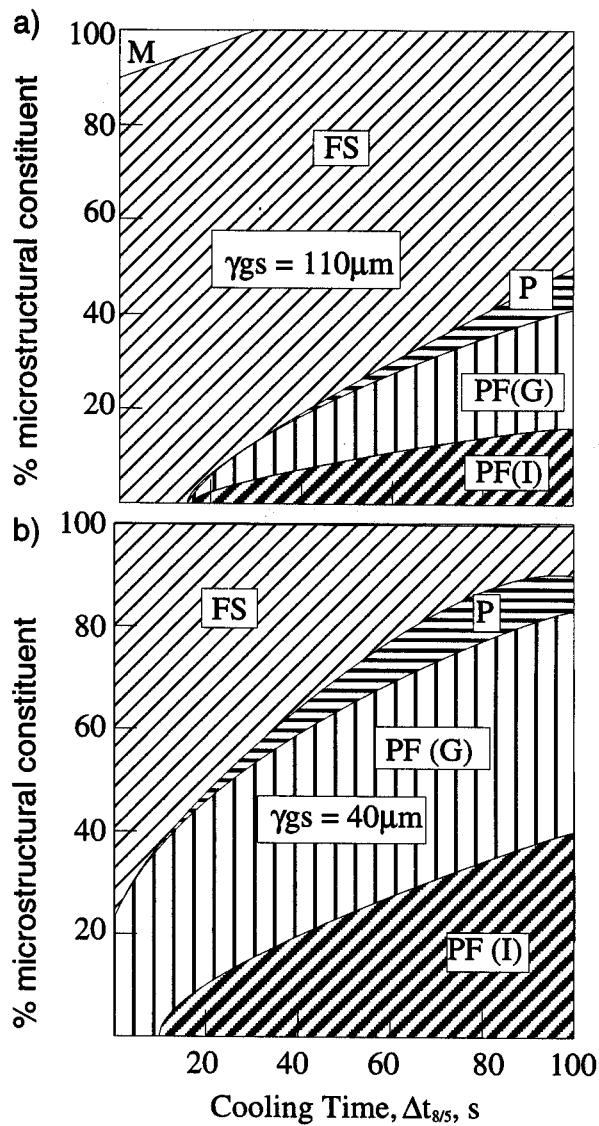


Fig. 14. The Effect of Nitrogen Level and Cooling Time (800 - 500°C) on the Microstructure of Simulated Weldments in Ti-0.08%V-N Steels a) 0.003%N b) 0.013%N. (Ref. 9).

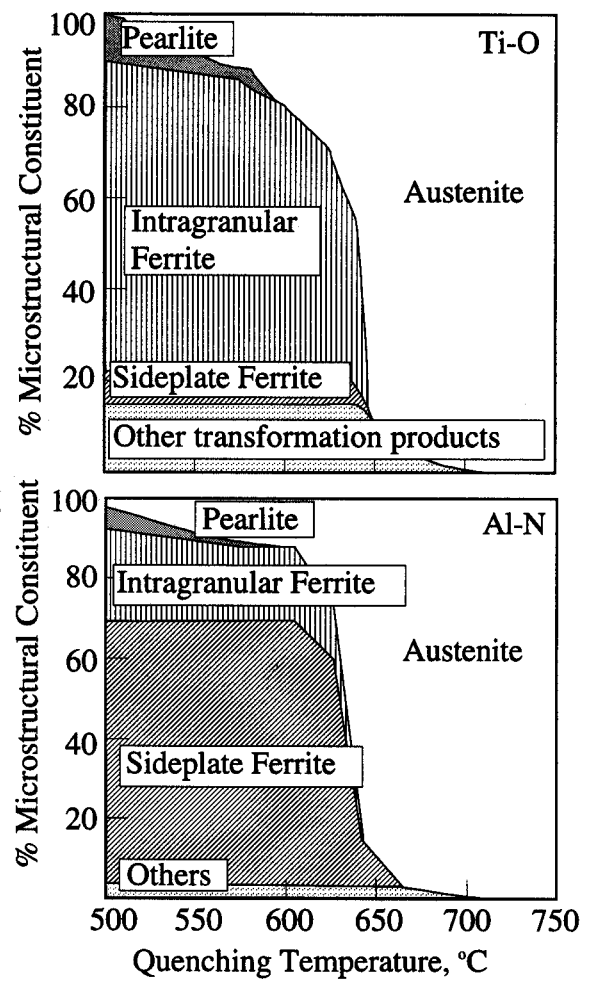


Fig. 15. Diagram showing Area Ratio of Microstructural Constituents in Ti-O Steel and Al-N Steel  $\Delta t_{8/5} = 161$  secs. (Ref. 13).

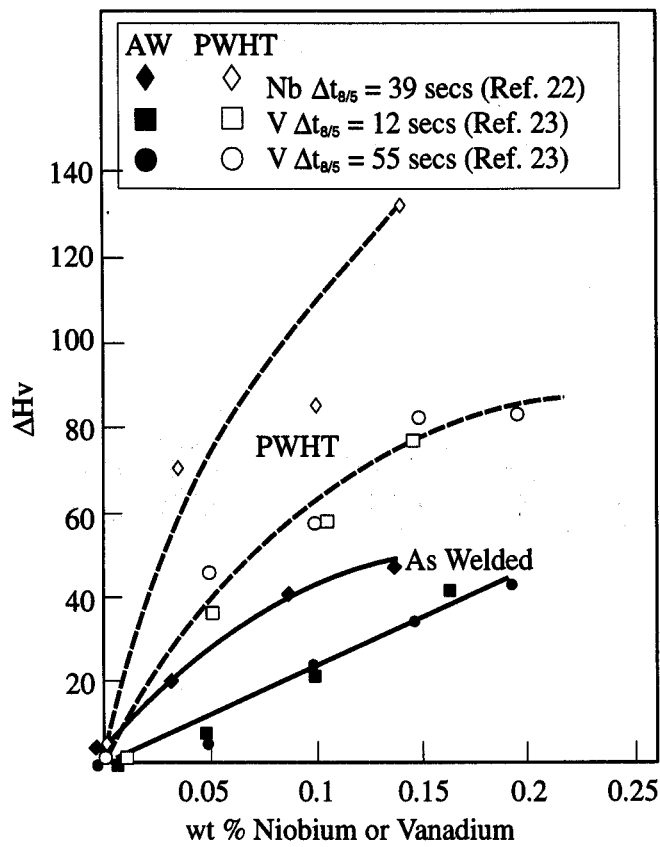


Fig. 16. The Effect of Vanadium and Niobium on the Change in Maximum HAZ Hardness in the As Welded and Post Weld Heat Treated Conditions.

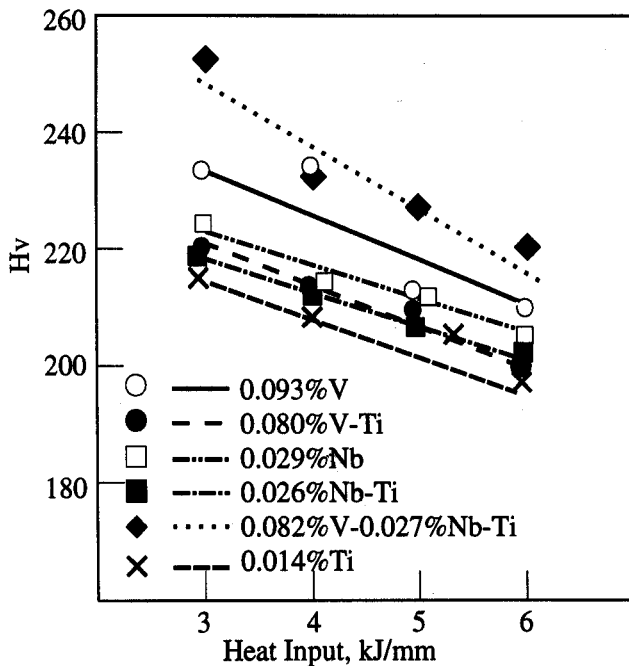


Fig. 17. The Effect of Microalloying and Heat Input on the HAZ Hardness of 0.12%C-1.4%Mn Steels. (Ref. 7).

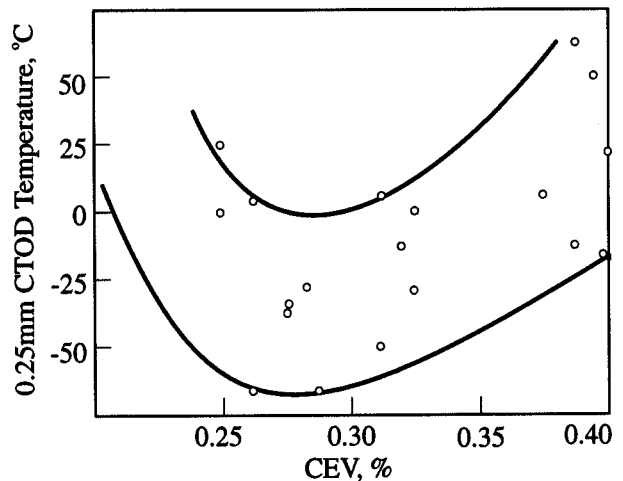


Fig. 18. The Effect of Carbon Equivalent on the Critical CTOD Temperature. (Ref. 24).

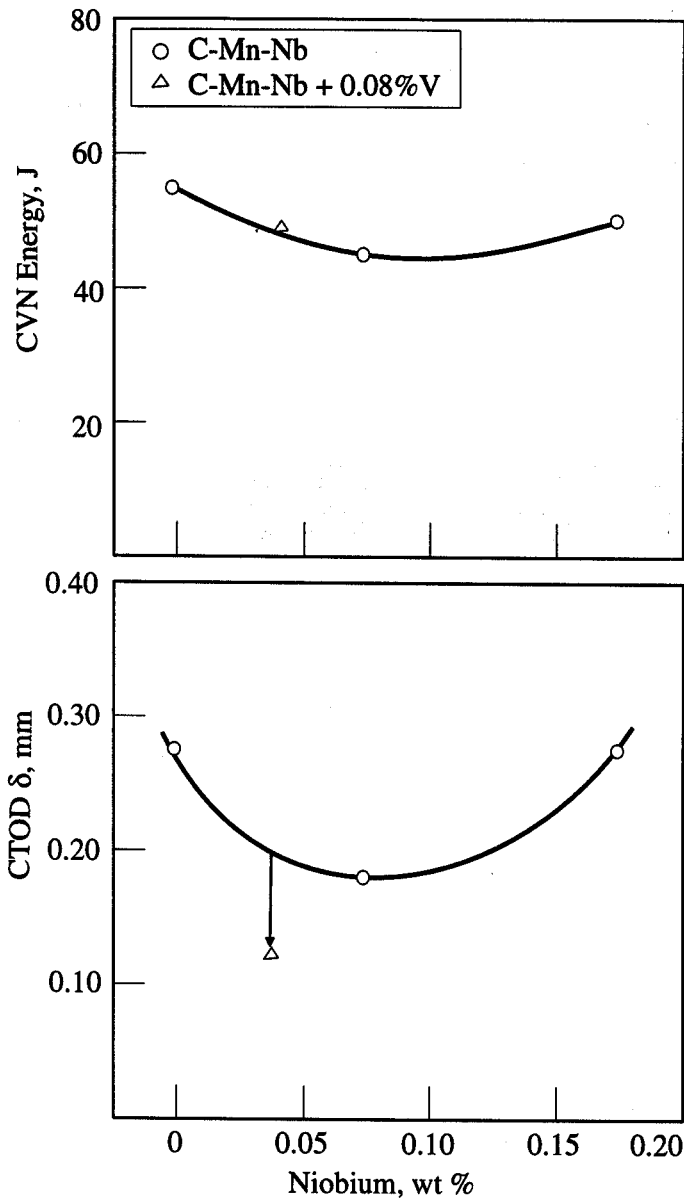


Fig. 19. The Effect of Niobium on the HAZ Toughness of Two-pass SAW Welds in 0.08%C-1.5%Mn, 18mm Thick, Pipeplate Welded at 2kJ/mm (Ref. 29).

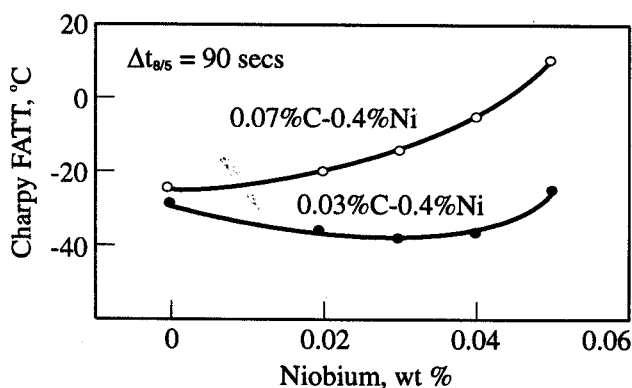


Fig. 20. The Influence of Niobium Content on the Charpy Values of Nickel-containing Steels with Different Carbon Contents. (Ref. 30).

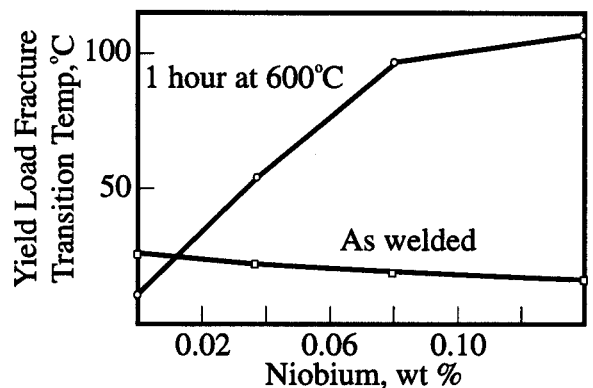


Fig. 21. The Effect of Stress Relief on the HAZ Impact Properties of Niobium Alloyed Low Carbon Base Plates. (Ref. 28). Heat Input 2.4kJ/mm, 12mm Thick Plate, 0.09%C-1.29%Mn.

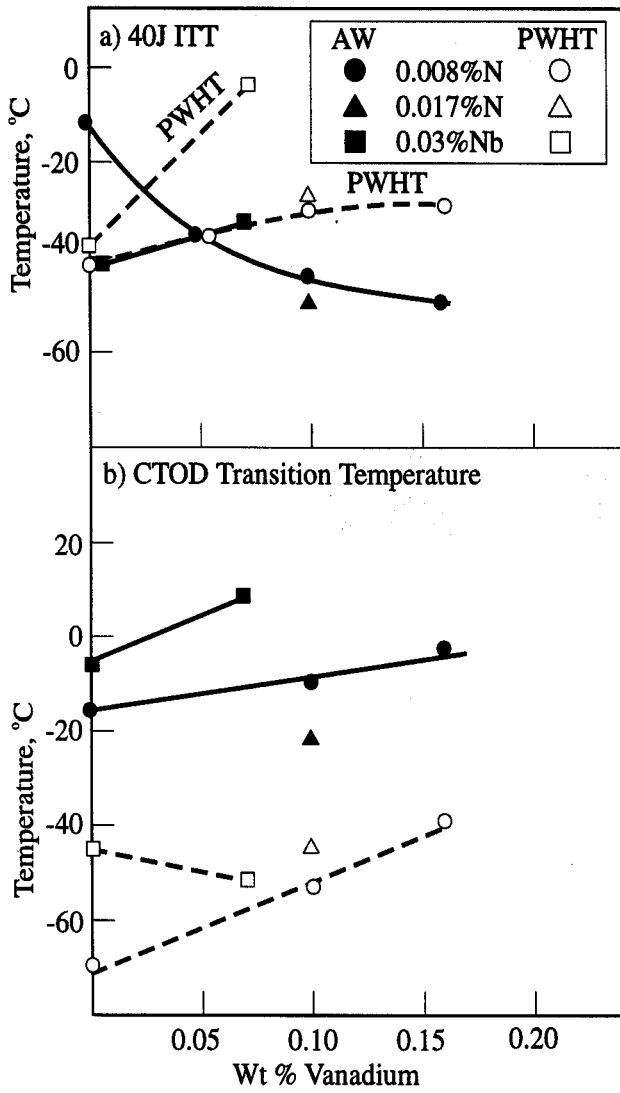


Fig. 22. The Effect of Vanadium on the Fracture Toughness of 0.12%C-1.6%Mn Steels Multipass Welded at 2kJ/mm. ( $\Delta t_{8/5}=12$ secs)(Ref. 23).

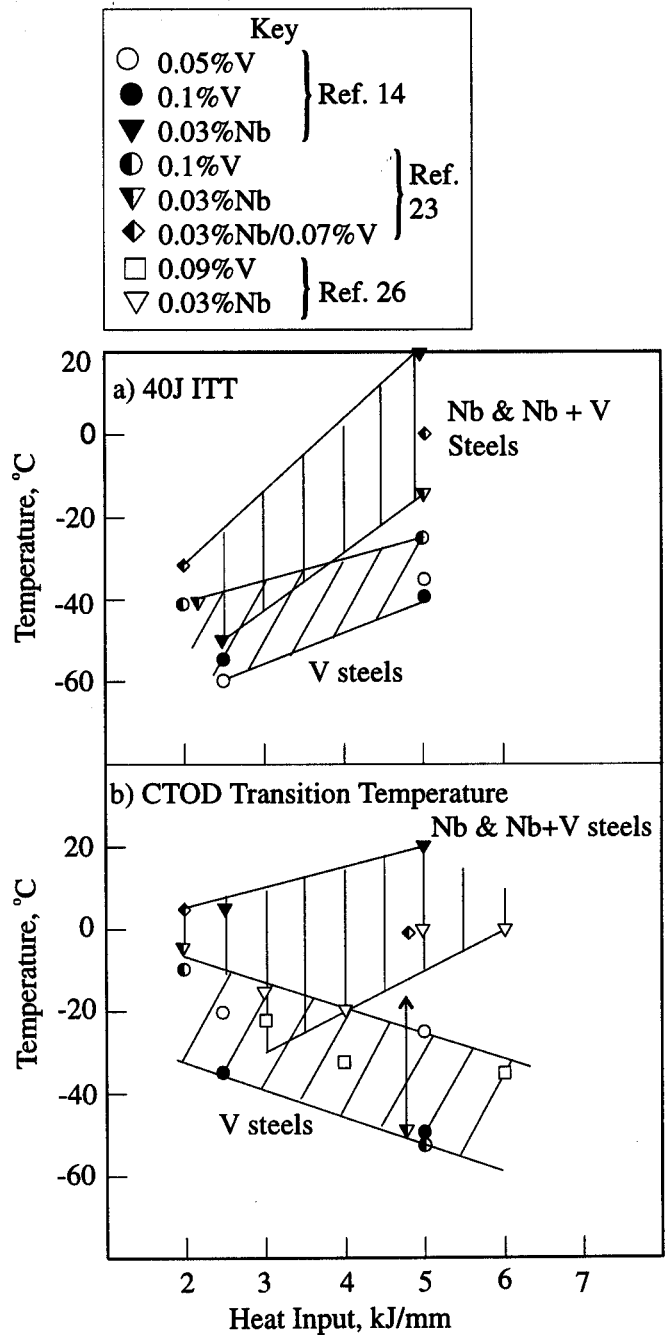


Fig. 23. The Effect of Heat Input on the As-welded HAZ Toughness of V, Nb and V+Nb Steels.

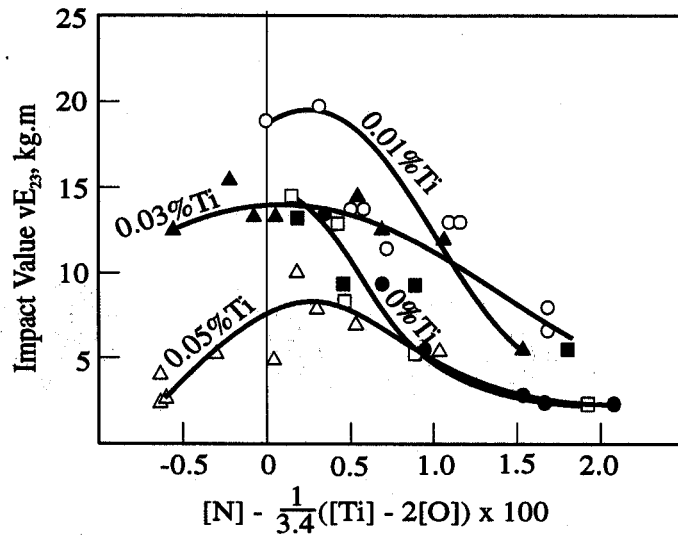


Fig. 24. The Effect of Nitrogen on the Energy Absorbed at 23°C in Synthetic HAZ's of C-Mn Steels of Differing Titanium Content. ( $T_{max} 1350^{\circ}C$ ,  $\Delta t_{8/5}=40secs$ )(Data from Ref. 8).

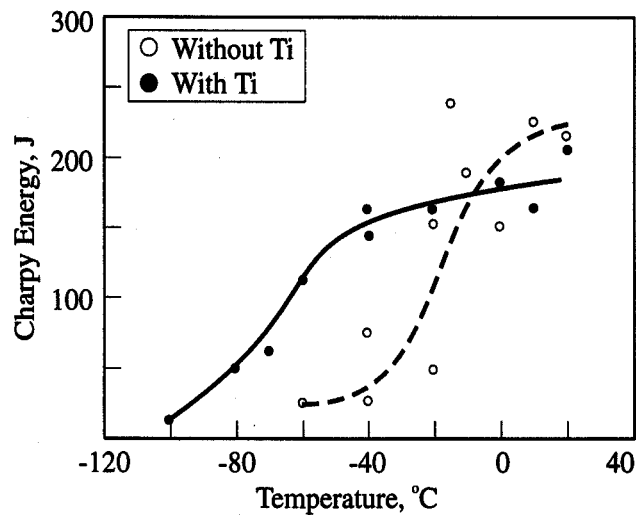


Fig. 25. The Influence of Ti on HAZ Charpy Transition Behaviour in a 0.02%Nb Steel Welded at 4.5kJ/mm. (Ref. 33).

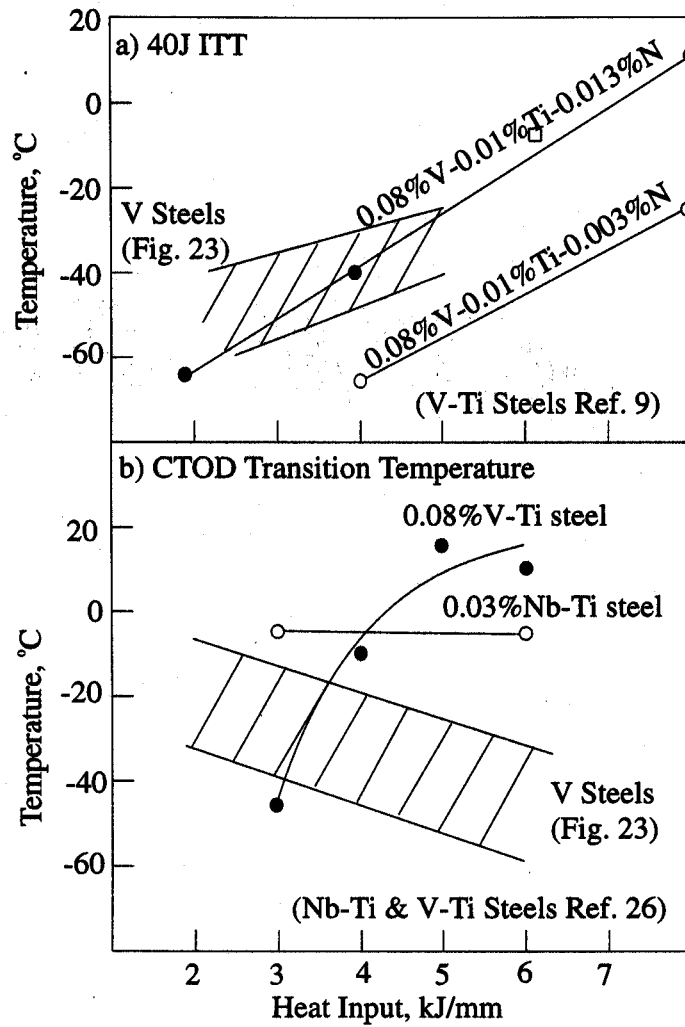


Fig. 26. The Effect of Heat Input and Titanium Addition on the HAZ Fracture Toughness of C-Mn-V Steels.