INFLUENCE OF TITANIUM ON HAZ MICROSTRUCTURE AND TOUGHNESS OF STEEL WELDS : Literature Review-PART 1

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I. INTRODUCTION

Usually, the toughness of the Coarse Grained Heat Affected Zone (CGHAZ) deteriorates with increasing heat input (decreasing cooling rate). However, developments in steel plate manufacturing may make it possible that improved HAZ toughness can be achieved even at high heat input weldments. Improved steels may achieve this required toughness through balanced additions of microalloying elements such as Al, Nb, Ti, V, B etc.

It is well known that embrittlement in the HAZ is often located in the CGHAZ region adjacent to the fusion line. Therefore, it would only be logical to make attempts to reduce austenite grain growth of this zone. Microalloying with Al and Nb is normally considered to be beneficial in this respect, but the austenite grain boundary pinning effect of Al and Nb is restricted to peak temperatures below about 1100 ^{o}C. The presence of AlN and Nb(C,N) particles in the base material (for example, in Al-killed C-Mn-Nb HSLA steels) does not alter grain size in the region close to the fusion line, but does narrow the width of the grain coarsened region by restricting grain growth at lower peak temperatures. It is posible that the fine AlN or Nb(C,N) particles in the matrix can be dissolved on heating by the weld thermal cycles, particularly at high heat input weldments. Consequently, much of the previously combined nitrogen can be released in the HAZ to influence cleavage resistance (there are certain elements which appear to be detrimental to toughness at any measurable level; these include nitrogen, phosphorus and sulphur. Free nitrogen hampers the notch toughness, raises the transition temperatures of the weld metal and HAZ).

When Nb or V is present, it is known that toughness decreases more rapidly than in C-Mn steels with high heat input welds. This decrease in toughness is explained to be associated with niobium or vanadium depressing the austenite transformation temperature and promoting the formation of fine bainitic microstructures that have high hardness due to Nb precipitation clustering.

However, titanium can be used by virtue of its ability to form stable nitrides (TiN) and stable Ti-oxides even at high temperatures (~1350 °C). For this reason appropriate amount of titanium is believed to be effective to prevent coarsening of the austenite grains adjacent to the fusion line.

There have been two interpretations for possible mechanisms of the improvement of HAZ toughness with Ti-microalloyed steels:

1) Refinement of ferrite grains which is improved by TiN particles distributed in austenite (γ) grain boundary pinning effect if TiN and Ti-oxide particles can be uniformly dispersed in γ at high temperature, they can be nucleation sites of ferrite (α) during γ - α transformation in the cooling process of the weld thermal cycle.

2) Decreasing effect of soluble nitrogen in α (This may in some cases play a greater role than its effect on the refinement of ferrite grains).

There are few studies on whether a small amount (0.01-0.02wt%) of Ti can lead to a refinement of austenite grains by forming fine TiN precipitates. It is thought that grain refinement as mentioned before stems mainly from the pinning effects of TiN particles on grain growth of austenite. The pinning effect, of course, depends upon the particle size and distribution of the precipitates. When fine precipitate particles are dispersed in the matrix, the pinning effect can be more effective and produces finer microstructure (It is also known that presence of coarse particles reduce the toughness of HAZ and base material).

It has also been observed from reviewed literature that high titanium-to-nitrogen ratio, Ti/N, exceeding approximately 3 or 3.5 may not improve CGHAZ toughness, but actually cause its deterioration. If Ti present in an over stoichiometric* amount with respect to nitrogen (i.e. Ti/N ratio greater than 3.42), the CGHAZ toughness can expected to be significantly reduced.

*:

$$\text{stoichiometric ratio between Ti and N} = \frac{\text{atomic weight of Ti}}{\text{atomic weight of N}} = \frac{47.88}{14.00} = 3.42$$

This literature review is aimed to examine the development of Ti-microalloyed (coupled with the adjustment of the nitrogen content) steels to achieve a better high HAZ toughness properties particularly with the role of stable Ti precipitates.

This review will also try to demonstrate the fact that titanium can only be effective in suppresing grain coarsening in the HAZ if the method of welding, the ratio of Ti/N and the level or presence of other microalloying elements produce Ti precipitates with appropriate size and distribution. Furthermore, sufficient amount of precipitates should also remain undissolved in the HAZ and these should act as pinning and probably ferrite nucleation sites. Hence, optimum numbered and sized fine TiN particles must exist if improvement on CGHAZ toughness is expected to occur.

II. Ti PRECIPITATES

II-1. CHARACTERISTICS OF Ti PARTICLES

Ti can form various types of particles such as TiC, TiN, Ti_2O, TiO and TiO_2. Sometimes Ti particles with a mixed composition, e.g. (Ti,V)N also exist in steels. Among them, TiN can be distinguished with its hexahedron shape. It often appears in a square or rectangle form and has orange yellow colour under the optical microscope. However, the Ti-oxide particle often occurs in a kind of typical globular inclusion and its color is dark under the optical microscope. The crystallographic data of major Ti particles are listed in Table 1(1). It is clear from Table 1 that TiO and TiN have the lower planar disregistry(3.0 and 3.8 respectively) with α iron. That means that TiO and TiN are an effective nucleating agent for acicular ferrite.

Table 1. Crystallographic data for the effective nucleating agents(1)

Compound	Crystal structure	Lattice parameter(Å)**			Relation of planes between nucleating agents and α-Fe	Planar disregistry (%)
		a_0	b_0	c_0		
TiN	Cubic (NaCl)	4.235	—	—	$(100)n^{*} /\!/ (100)\alpha^{*}$ $[010]n /\!/ [011]\alpha$	3.8
Ti_2O	hexagonal	2.959	—	4.845	$(0001)n /\!/ (111)\alpha$ $[001]n /\!/ [1\bar{1}0]\alpha$	29.3
TiO	Cubic (NaCl)	4.177	—	—	$(100)n /\!/ (100)\alpha$ $[010]n /\!/ [011]\alpha$	3.0
TiO_2	tetragonal (SnO_2)	4.594	—	2.958	$(001)n /\!/ (110)\alpha$ $[010]n /\!/ [1\bar{1}0]\alpha$	8.8

* n : nucleation site
* α : α-Fe

** The effect of lattice expansion was neglected because it is less than a few % at γ to α transformation temperature.

Mori et al(1) reported the presence of TiO in electrolytically-extracted inclusions, and claimed that it is an effective nucleant for ferrite because of the low lattice disregistry between TiO and ferrite, several authors have already reported the presence of crystalline patches containing Ti towards the edges of inclusions. Although complete identity of the constituent is not certain, but it is consistent with TiO (2,3,4,5,6), TiN (2,3,5,6) and TiC (2,5), and thus may contain more than one of these compounds with a f.c.c. structure, a lattice parameter of ~0.42nm and planes of low lattice disregistry with α iron(1,2,6). Mills et al(6) noted that the regions of the Ti-containing constituent are polycrystalline, thereby giving a greater chance of ferrite nucleation ~~than one orientation would do present.~~ So an increased level(in controlled maner) of Ti can be expected to give a higher proportion of acicular ferrite.

It is also known that Ti has a greater affinity for oxygen than for nitrogen(7). As Al has an even greater affinity than Ti for oxygen, (but a lower affinity for nitrogen), therefore it is possible that a substantial excess of Al over Ti may restrict the formation of TiO and thereby encourage TiN formation.

II-2. Ti PRECIPITATE STABILITY

The coarsening and dissolution of precipitates is a diffusion-controlled process which depends on time and temperature. In the case of carbides and nitrides in steels the process is usually complicated by the presence of substitutional elements other than iron. Nevertheless, the stability of precipitate phases is normally expressed in terms of the solubility products of the metallic (M) and interstitial (C) elements, and their stochiometry (a,b). It is found that

$$\log[M]^a[c]^b = A - \frac{B}{T} \qquad (1)$$

where A and B are experimentally determined constants (material dependent) derived from isothermal experiments. T is the absolute temperature. The product $(M)^a(C)^b$ may be expressed in wt% or atomic%.

Figs.1 and 2 show the solubility product of TiN in the austenite temperature range. From these the following formulae were suggested(8,9).

$$\log[Ti][N] = 0.32 - \frac{8000}{T} \qquad (2) \quad (8,9)$$

$$\log[Ti][N] = -2.20 - \frac{3000}{T} \qquad (3) \quad (9)$$

Formula (2) is for steel A (Si 0.31%; Mn 1.54%; Ti 0.023%; N 0.0084%) and formula (3) is for steel B (Si 0.31%; Mn 2.11%; Ti 0.019%; N 0.0088%; Cr 0.50%; Mo 0.42%).

According to formula (2), (Ti) $(N)=4.75*10^{-5}$ will be given at 1450 °C in studied steel. But the TiN steels used give $(Ti)(N)=8.28*10^{-5}\sim1.57*10^{-4}$ (8). That means that a large part of the TiN in the steel should be dissolved at 1450 °C.

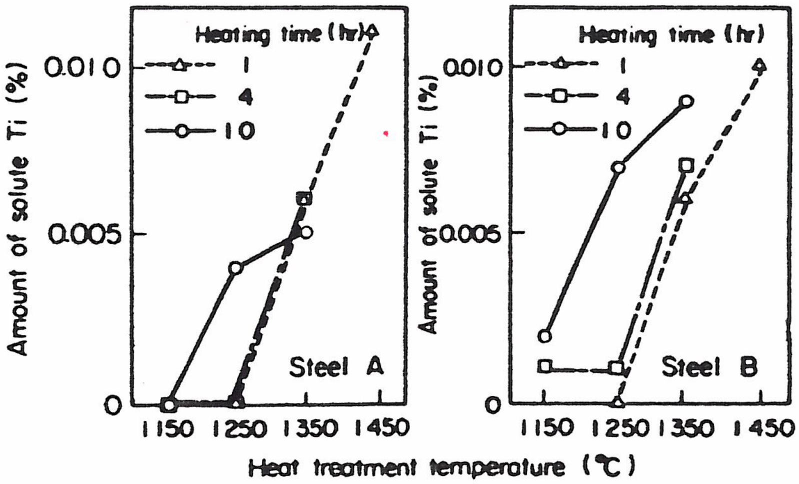


Fig.1 Effect of heat treatment temperature on the amount of solute Ti(9)

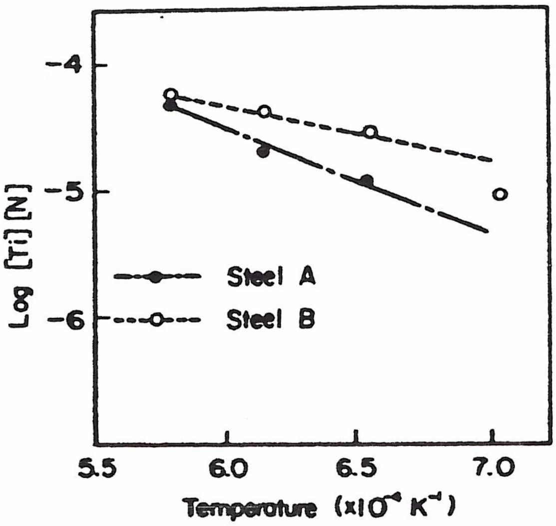


Fig.2 Solubility product of TiN in austenite temperature range(9)

Some published data on the solubility product are compiled in Table 2(10). This table shows also equilibrium concentration of Ti for temperature and a nitrogen concentration that are typical of hot rolling. The equations specified in Table 2 can not be weighted on the basis of the published data.

Table 2. Data on solubility product of titanium nitride in austenite(10)

No.	$\log [\%Ti].[\%N]$	[Ti]-conc. in equilibrium with 0·01%[N] at 1200°C, %	Notes
1	$-\frac{15020}{T}+3.82$	4.2×10^{-5}	Measurements 1200–1300 C
2	$-\frac{6746}{T}+1.28$	5.0×10^{-2}	
3	$-\frac{14400}{T}+5.0$	1.7×10^{-3}	Estimated from free solution and formation enthalpies for Fe_2Ti, N, and TiN
4	$-\frac{13925}{T}+5.15$	5.0×10^{-3}	Estimated as no. 3, but with the free solution enthalpy of titanium[7] in liquid iron

J. Kunze(10) measured the solubility of titanium nitride in γ-iron in the temperature range 1100-1350 °C in nitrogen atmospheres.The experimental conditions and the results are given in Table 3. The regression calculation of the measured solubility products L_{TiN} = (%Ti) (%N) yields the equation

$$\log[Ti][N]_{(\gamma-Fe)} = 5.19 - \frac{15490}{T} \qquad (4)$$

Table 3. Solubility product of TiN in γ-iron:experimental data and results(10)

No.	Temperature, C	N_2 pressure, Pa	Time, h	Solubility product $L = [\%Ti].[\%N]$
1	1350	1.35×10^4	10	$(6.43 \pm 0.55) \times 10^{-5}$
2	1300	6.40×10^2	5	$(1.92 \pm 0.17) \times 10^{-5}$
3	1300	2.28×10^4	6·5	$(2.14 \pm 0.70) \times 10^{-5}$
4	1300	3.57×10^3	8	$(1.89 \pm 0.26) \times 10^{-5}$
5	1250	9.33×10^2	14	$(8.16 \pm 2.40) \times 10^{-6}$
6	1200	1.83×10^3	20	$(6.84 \pm 2.40) \times 10^{-6}$
7	1150	1.33×10^2	22	$(1.03 \pm 0.53) \times 10^{-6}$
8	1100	6.66×10^1	28	$(1.24 \pm 0.55) \times 10^{-6}$

Shizuo Mukae et al (11) also studied the solubility product of TiN in low carbon steels during thermal cycle. Fig.3 shows the relationship between Sol. TiN and Sol.N content of base metal and the thermal cycled samples. Sol.Ti content is inversely proportional to Sol.N and it can be seen from Fig.3 that a solubility product of TiN depending on the maximum temperature occurs in the HAZ. The solubility products, K = (Sol.Ti)(Sol.N), are $6.8*10^{-6}$, $1.9*10^{-5}$ and

$3.1*10^{-5}$ at the maximum temperatures of 1200, 1350 and 1410 °C, respectively. These values are large in comparison with the solubility product, $K=2.5*10^{-6}$, of the base metal. Some of TiN particles dissolve in the austenite matrix at the maximum temperature of the thermal cycle and do not precipitate again in the cooling process of the thermal cycle. Therefore, it seems that both the Sol. Ti and the Sol.N exist in soluble state in structures at room temperature.

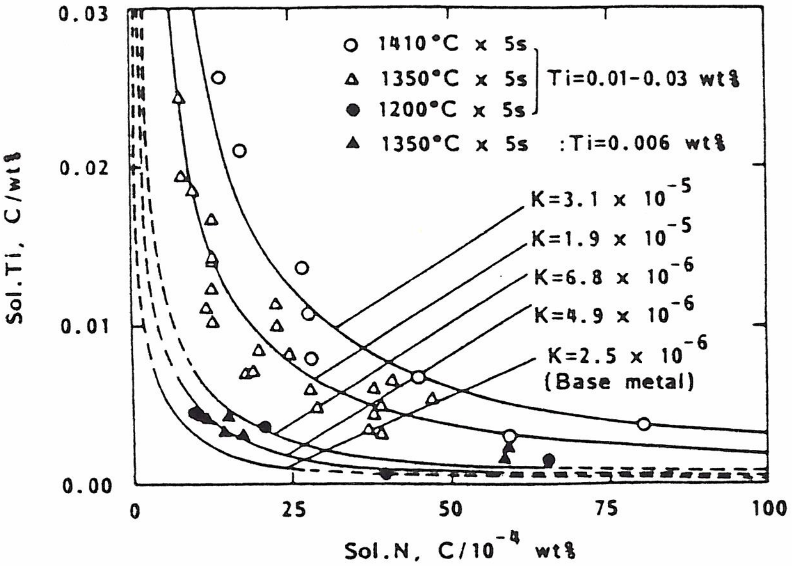


Fig.3 Relationship between soluble Ti and soluble N content on base metal and weld thermal cycled samples(11)

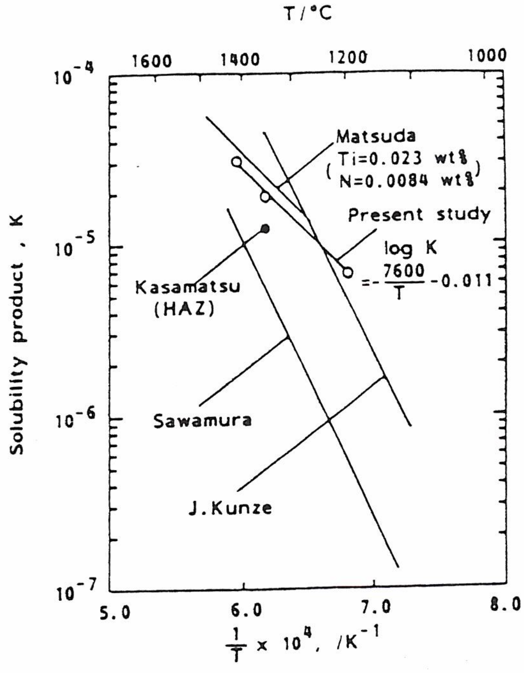


Fig.4 Temperature dependence of solubility product of TiN(11)

Fig.4 shows the plots of the solubility product reciprocally against the absolute temperature in order to clearly demonstrate the temperature dependence of the solubility product of TiN. The following equation is obtained from the result shown in Fig.4:

$$\log[\mathrm{wt\%Ti}][\mathrm{wt\%N}] = -0.011 - \frac{7600}{T} \tag{5}$$

where $0.01 \leq N \leq 0.03$wt%, $20 \leq N \leq 80$ppm and $1200^{\circ}\mathrm{C} \leq T \leq 1410$ °C. Results obtained by other researchers are also shown in Fig.4. It is inferred from the above results that the dissolving of TiN in austenite matrix during synthetic weld thermal cycle nearly reaches an equilibrium state and that it is independent of the cooling time.

Fig.5 also shows generally that the particles progressively dissolve with increasing in temperature. Thus, by knowing the total percentages of the combining elements in the steel involved in the reaction, tne temperature of complete solution of the particles can be obtained from Fig.5

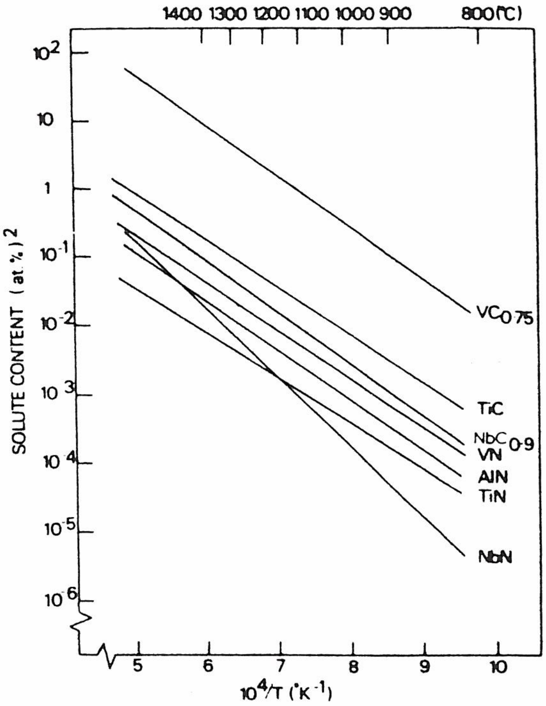


Fig.5 Solubility products of carbides and nitrides in austenite as a function of temperature. After Aaronson B Steel Strengthening Mechanisms, Chmax Molybdenum Co. 1969

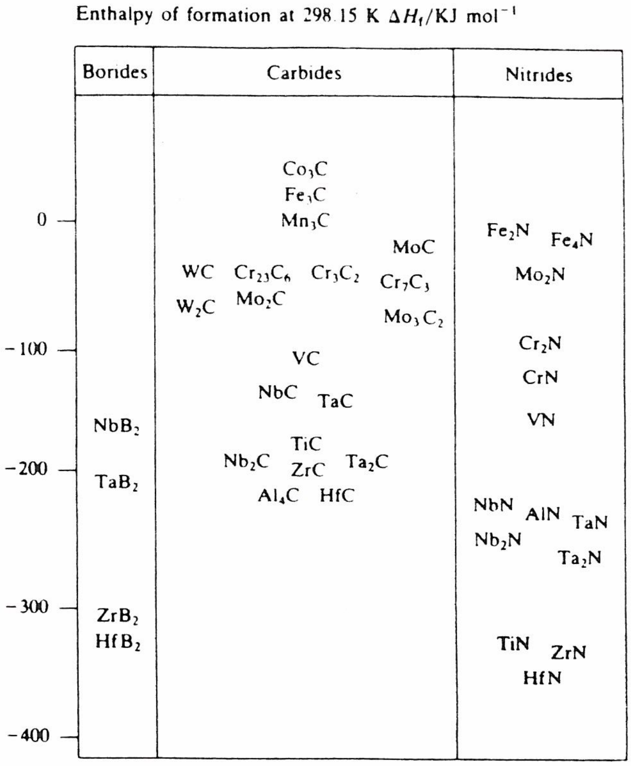


Fig.6 Enthalpies of formation of carbides nitrides and borides. After Schick.H.L. Thermodynamics of Certain Refractory Compounds Academic Press 1966

Fig.6 shows the free energy of formation, ΔH_f, for some carbides, nitrides and borides. In general, the more negative is the ΔH_f, the less soluble the carbides or nitrides tend to be.

It is clear from Figs.5 and 6 that TiN is more stable than most other precipitates even at high temperature. Of course, the solubility product of TiN precipitate increases as temperature increases.

In recent years, Ti-oxides are also efficiently used in improving the toughness of both base and weld metal because of their highly stable nature, According to the literature, the standard free energy of formation of TiN and Ti_2O_3 is approximately -51~-41 kcal/mol and -127~-108 kcal/mol, respectively, at temperatures between 1000 °C and 1500 °C , which means that the standard free energy of formation of Ti_2O_3 is about 2.1 to 2.4 times larger than that of TiN. If it can be assumed that the activity coefficients of O and N are equal, the solubility product of Ti_2O_3 will be given as follows:

$$[Ti]^2[O]^3 = [Ti][N]^{2.1\sim2.4} \qquad (6)$$

Since the solubility product of TiN at 1450 °C is on the order of 10^{-5} where as that Ti_2O_3 is on the order of $10^{-10--12}$, Ti_2O_3, once finely dispersed in the base metal, is considerably more stable than TiN and would not dissolve at the weld interface and in the CGHAZ during a weld thermal cycle(8).

II-3. Ti PRECIPITATE COARSENING DURING THERMAL CYCLE

Particle coarsening is important in steels containing very stable precipitate particles, since these remain undissoved during weld thermal cycling and will affect the mechanical properties. The coarsening rate of binary compound particles can be well described by the Lifshitz-Wagner equation to be

$$\left(\bar{r}\right)^3 - \left(r_0\right)^3 = K\frac{V_m^2}{RT}XEDT \qquad (6)$$

where K is a constant, T is time, $\bar{r}$ is the average particle radius, r_o is the radius at T=0, V_m is the molar volume of the precipitate compound, E is the interfacial energy, D is the diffusion coefficient and X is the solubility of the rate controlling element in equilibrium with the largest particles, and RT has its usual meaning. Generalizing this equation to multicomponent systems is clearly a complex problem, involving a complicated interplay between kinetics and thermodynamics. However, it can be tentatively deduced that dissolving particles may become enriched by the most slowly diffusing element, implying that growing particles become surrounded by a matrix leaner in this element.

Examples of TiN precipitates in a Ti-steel after high energy input weld simulation are shown in Fig.7. Changes in particle size distribution before and after weld simulation are also included in the Figure, which illustrates that the average particle size following weld simulation increases from approximately 8 nm to 14nm. Experiments have shown that the coarsening rate is usually accelerated if the particles have mixed composition, e.g. Ti(V)N.

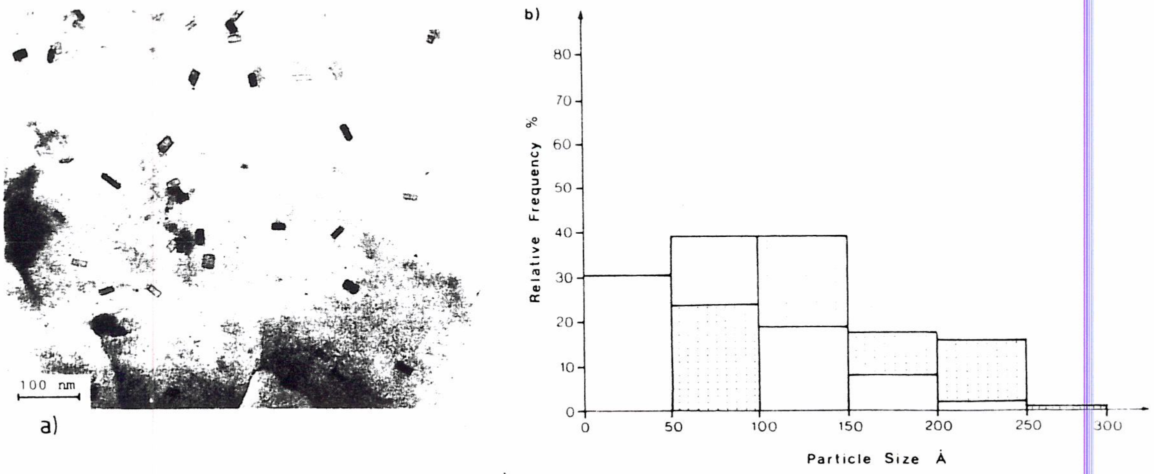


Fig.7 (a) Carbon-extraction replica and (b) measurements (from carbon-extraction replicas) of changes in size distributions of TiN precipitates in a normalized Ti-microalloyed steel. The shaded area refers to particle sizes after weld simulation courtesy of J. Stud and J. Lon University of Lulea

B. Loberg, et al(12) and J. Strid and K. E. Easterling(13) studied the stability of TiN particles and the effects of some elements, such as V, Al, Nb, and N. It has been found that the medium particle sizes in Ti-steels increased by adding extra nitride formers. Alloying elements in the steel which are nitride formers will generally tend to decrease the stability of TiN particles. In particular, Al has a very marked effect in this respect. On the other hand, the medium particle size decreases with an increase in N-level.

S. Matsuda and N. Okumura(9) studied the effect of heating time at heating temperature 1350 °C on the mean particle size of TiN. The following empirical equation was obtained for three kinds of low carbon low alloy steels:

$$r = At^{1/3} \tag{7}$$

where, r: the size of TiN particles
t: the heating time
A: a constant which varies with composition of steels

Equation (7) indicates that the volume (r^3) of a TiN particle increases in proportion to the heating time.

The effect of heating temperature and heating rate on the mean particle size of TiN is shown in Fig.8(9). It can be seen from Fig.8 that the mean TiN particle size at the heating rate of 200 °C/min is about two times coarser, except for heating temperature of 650 °C, than at the heating rate of 1.6 °C/min. There is not much influence of heating temperature in the range of 900 °C to 1150 °C on the mean particle size of TiN as indicated in this Figure.

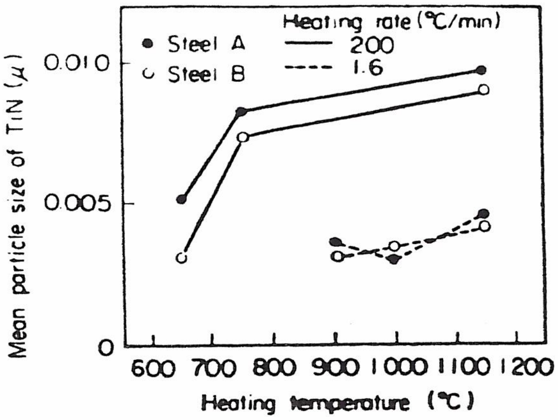


Fig. 8 Effect of heating temperature and heating rate on mean particle size of TiN(9)

II-4. PRECIPITATE DISSOLUTION DURING A WELD THERMAL CYCLE

The theory of precipitate dissolution during a weld thermal cycle is based on the assumption that during a rapid heating cycle the equilibrium solubility of carbonitrides as given by equation (1) has to be modified by a suitable factor that accounts for the superheating of the particles. If the temperature at which full solution takes place is defined as Ts , utilizing equation (1), following equation can be derived:

$$Ts = \frac{B}{A - \log\left(\frac{[M]^a [C]^b}{f^{a+b}}\right)} \qquad (8)$$

where f is the matrix volume fraction. On this basis, the solubility curves for a number of carbides and nitrides can be plotted as a function of heating time and temperature, as shown in Fig.9. It is clear that the mixed Nb(CN) has a lower solubility than, e.g., NbC. However, the highest dissolution temperature is exhibited by TiN.

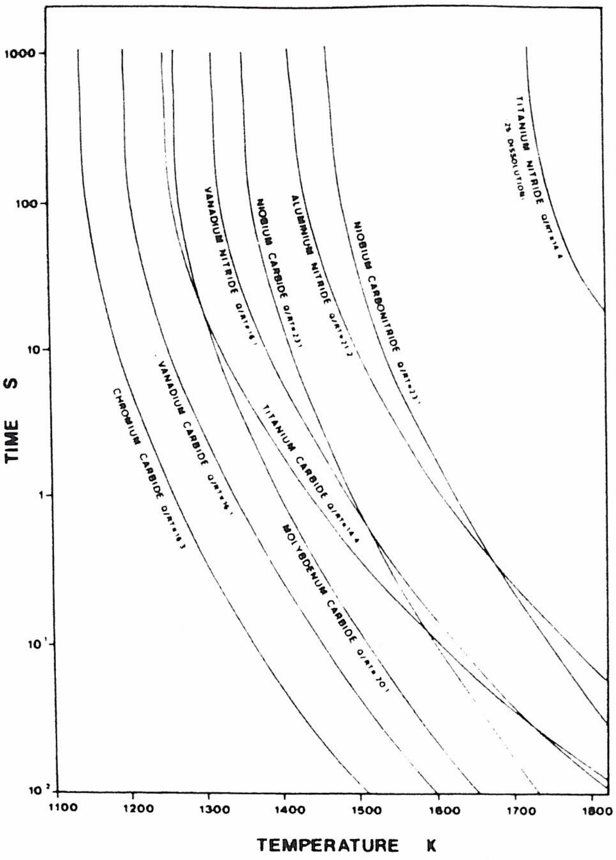


Fig.9 The time of complete dissolution of various carbides and nitrides in austenite as function of temperature. The shorter the weld thermal cycle, the greater the superheating of the carbonitrides. The diffusion data are obtained from Mrowec.S. Defects and Diffusion in Solids-An Introduction. Elsevier 1980

S.Kanazawa(14) studied the TiN dissolution phenomenon during welding. Although TiN is thought to be comparatively stable in a hot steel. Some dissolution under welding heat cycle still can be suspected. Furthermore, because TiN is present in steel in various precipitate sizes ranging from several microns to several hundred angstroms, its dissolving behavior in such short heating cycles as experienced in welding is expected to be very complicated.

Fig.10 shows the variation of soluble Ti and insoluble Ti of quenched specimen with heating temperature on Ti-B containing steels 4# and 6#, which are different in austenite grain growth behavior. The quantity of dissolved Ti was found unchanged up to around 1250 °C, dissolution becoming apparent at 1300 °C, and as much as 0.006% dissolved at 1400 °C. No significant difference was observed between the two steels in dissolution behavior.

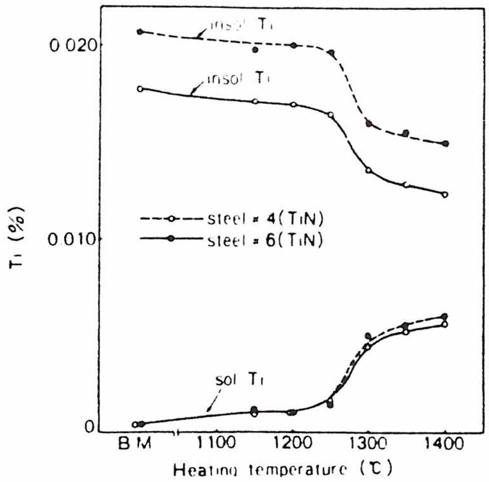


Fig.10 Dissolution of TiN during heating by synthetic thermal cycle(14)

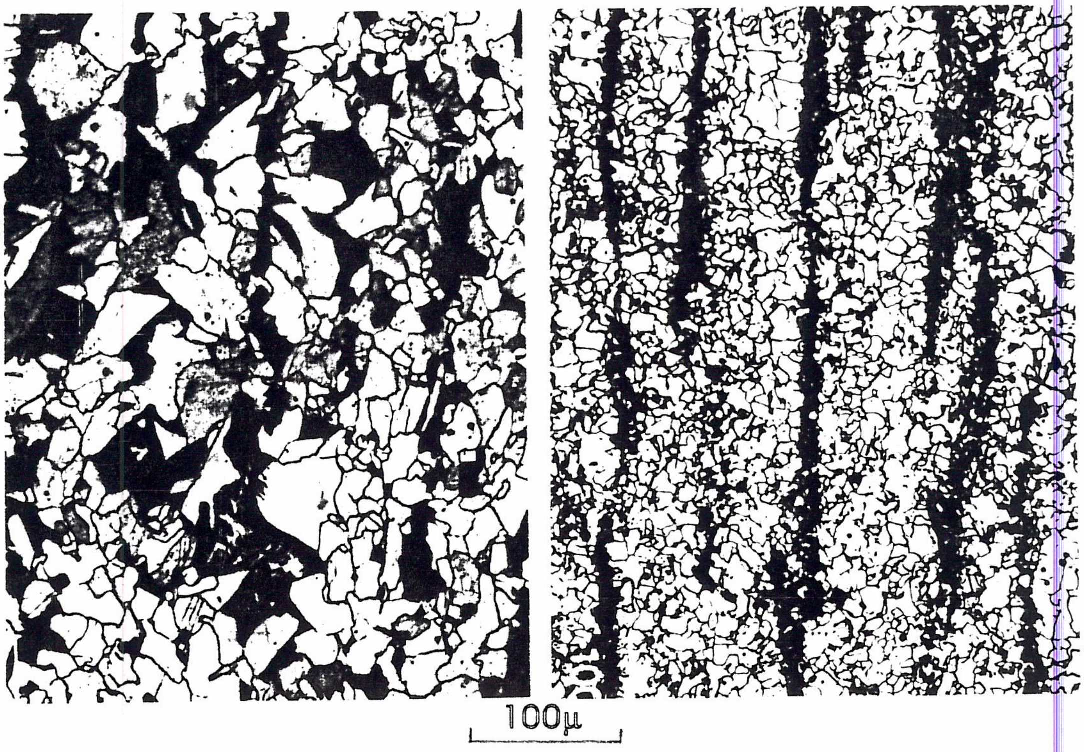
So far particle coarsening and dissolution have been considered as separate processes. In practice, of course, coarsening always precedes dissolution, and this may tend to slightly increase the temperatures of complete dissolution of various carbides and nitrides.

III. THE EFFECT OF Ti PARTICLES ON AUSTENITE GRAIN SIZE

It is apparent that grain size is of paramount importance in metals, by being a key factor in determining the strength and toughness of a material. It has also enormous importance with respect to determining an alloy´s susceptibility to cold cracking and reheat cracking in welds. The weld thermal cycle is such that in the majority of metals some grain growth occurs in the HAZ and this not only affects strength and toughness, but also influences the grain size of the weld metal.

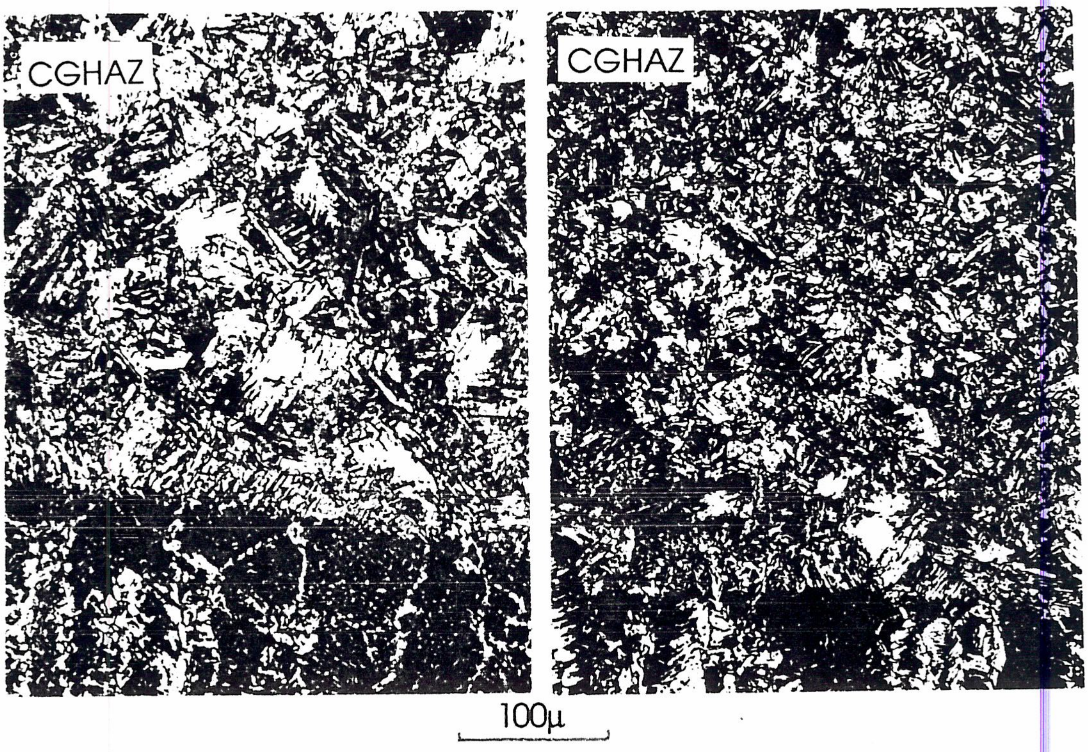
Recent studies have indicated that the best way to control grain size is to use large amounts of very small stable precipitates. As mentioned above the most stable precipitates in steels are Ti-nitrides and Ti-oxides, which only begin to go into solution at very high welding energies. Once particles coarsen and go into solution, there is no barrier to grain growth at high temperatures, and austenite grain sizes of hundreds of microns can occur in high energy welds. As a general rule, coarser austenite grains will tend to produce coarser ferritic structures.

Figs.11 and 12 show that the grain size of Ti bearing steel is much smaller than that of Ti free steel for both base metal and CGHAZ(15)



a) Ti free steel b) Ti-bearing steel

Fig.11 The grain size of Ti free steel and Ti-bearing steel(15)



a) CGHAZ of Ti free steel b) CGHAZ of Ti-bearing steel

Fig.12 The grain size of CGHAZs of Ti free steel and Ti-bearing steel after manual metal arc welding(15)

The effect of various kinds of precipitates on austenite grain growth has been intensively studied by S. Kanazawa, et al(14). The results are shown in Fig.13 and it indicates that TiN particles particularly in steel 4#, 5# and 12# kept the austenitic grain size refined even at 1400 °C. The results suggest the possibility of utilizing TiN to improve the toughness of CGHAZ.

It is well established that the inhibition effect of precipitates on austenite grain growth are dependent on the size and volume fraction of these precipitates. Zener(16) and Gladman(17) proposed the following relationship:

$$d_r = k(r/f) \qquad (9)$$

where d_r: diameter of austenite grains, r: diameter of precipitates
k: constant, f: volume fraction of precipitates

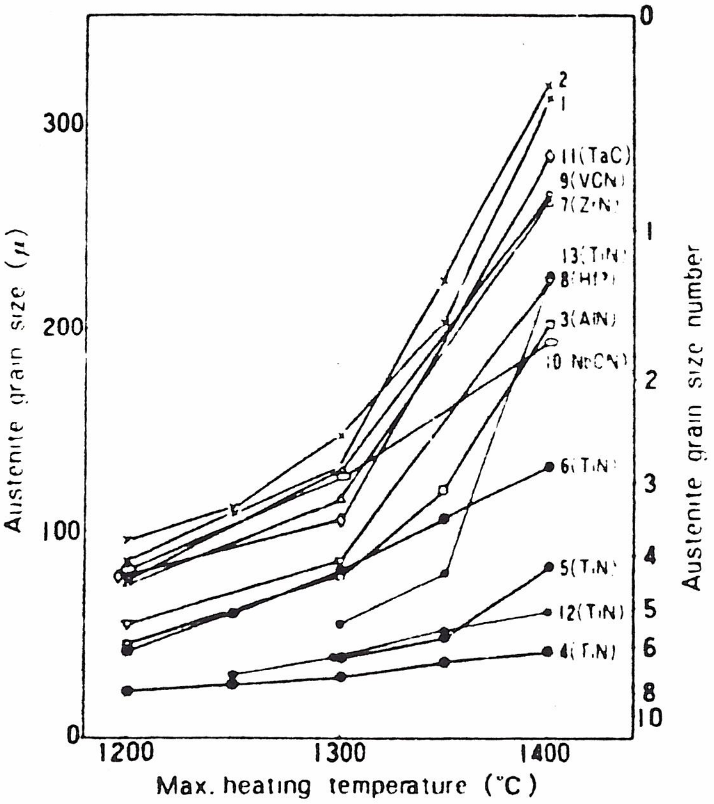


Fig.13 Relation between maximum heating temperature and austenite grain size(14)

Fig.14 shows the correlation between austenite grain size, volume fraction and mean size of undissolved TiN at 1400 °C. Volume fraction was calculated by chemical analysis of precipitates smaller than 0.05μ, 0.1μ, and total TiN precipitates and was designated as f1, f2 and f3 respectively. The volume fraction values of TiN precipitates smaller than 0.05 (the straight-line in Fig.14) were only found to show a significant correlation with the values of d$_r$. when k value was 0.12.

Fig.15 shows the relation between austenite grain size at 1400 °C and Ti content of TiN smaller than 0.1 or 0.05μ existing in the plate before welding. This disagrees with the observation in Fig.14 concerning the size of effective TiN precipitates. This phenomenon could be explained by the assumption that among TiN precipitates, smaller ones would dissolve in the course of heating and larger ones would become smaller.

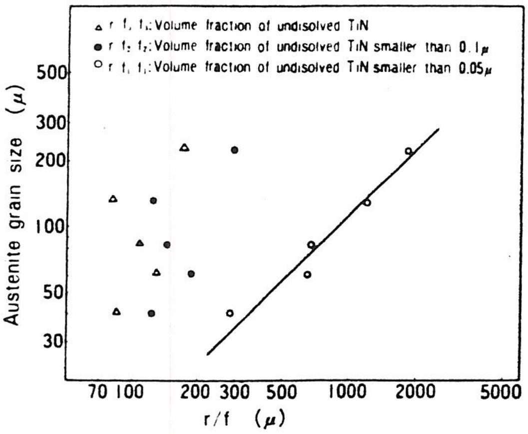


Fig.14 Correlation between austenite grain size,volume fraction and mean size of undissolved TiN at 1400 °C(14)

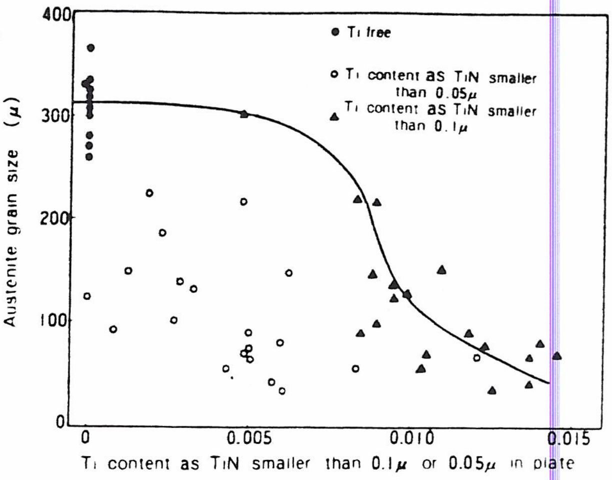
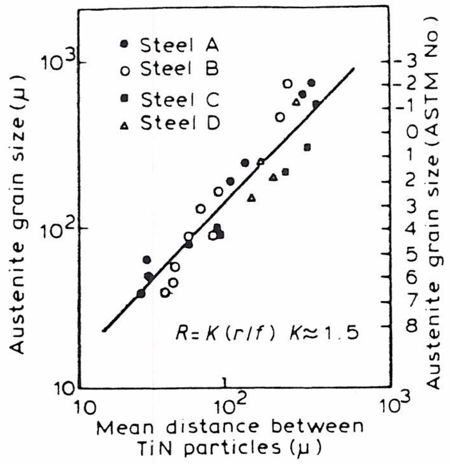


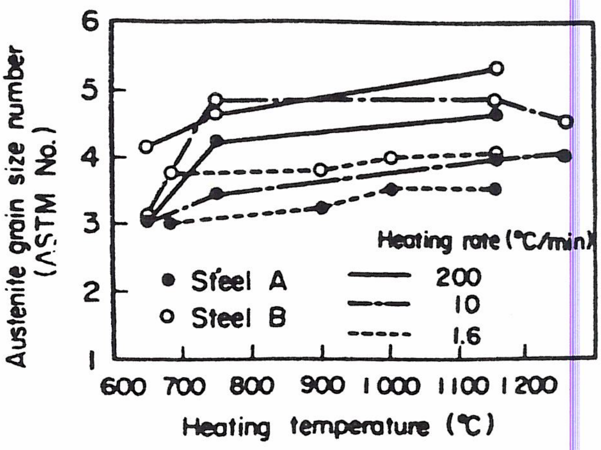
Fig.15 Relation between austenite grain size at 1400 °C and Ti content of TiN smaller than 0.1 or 0.05m existing in the plate before welding(14)

The effect of the distribution of TiN particles on the austenite grain size was investigated in detail in the temperature range of 1430 °C by S. Matsuta and N. Okumura(9). The results obtained from four steels are shown in Fig.16. Fig.16 also indicates that the most effective method to control the austenite grain size is to reduce the mean particle size r for a given volume fraction of TiN.



R: Austenite grain size
f: Volume fraction of TiN
r: Mean particle size of TiN
K: Dimensionless constant

Fig.16 Relation between mean distance of TiN particles and austenite grain size(9)



peak temperature of thermal cycle: 1350 °C

Fig.17 Effect of heating temperature and heating rate on austenite grain size(9)

The effect of some alloying additions on grain size was also studied in reference(9). According to this reference an increase in nitrogen results in smaller as received ferritic grain size as well as a smaller prior austenite grain size after weld simulation. However increased Al-level increases the grain size considerably.

Fig.17 shows the effect of heating temperature and heating rate on austenite grain size. No significant differences of austenite grain size can be observed in the temperature range from 750 °C to 1250 °C. It is also found that a higher heating rate slightly increases the austenite grain size. This grain growth is related to the coarsening and dissolution of precipitate particles.

It is interesting that the maximum increase in grain size occurs at the initial stages of grain growth, because of the higher driving force available at this stage. Research work also shows that the cooling cycle only accounts for about 20% of the total grain growth

IV. EFFECT OF Ti PRECIPITATES ON MICROSTRUCTURE IN WELDMENTS

Some researchers indicated that Ti precipitates were found to have more or less influence on the steel transformation behavior through their austenite grain growth inhibition effect and ferrite transformation acceleration effect. S. Kanazawa et al(14) studied the influence of TiN particles on microstructure.

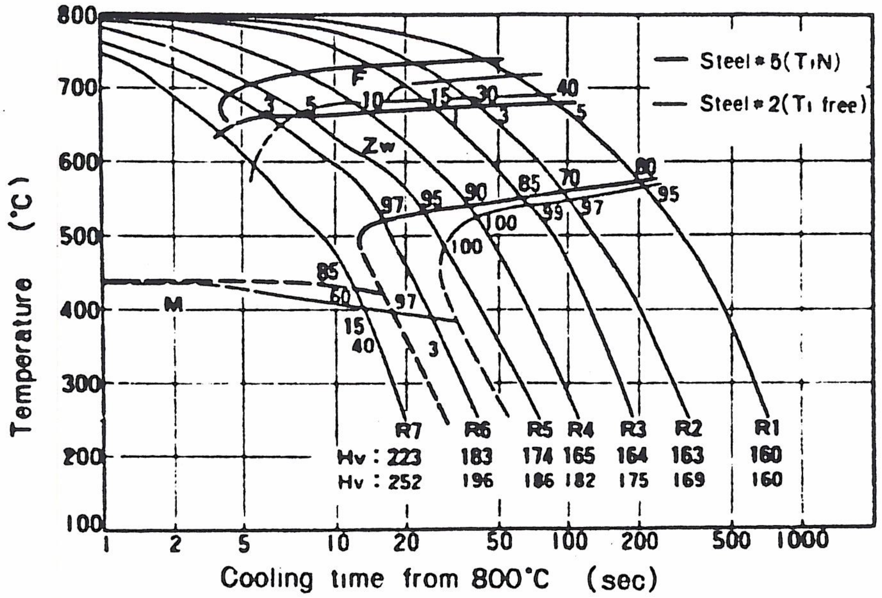


Fig.18a CCT diagram of steels #2 and #5 (max. heating temperature: 1400 °C) (14)

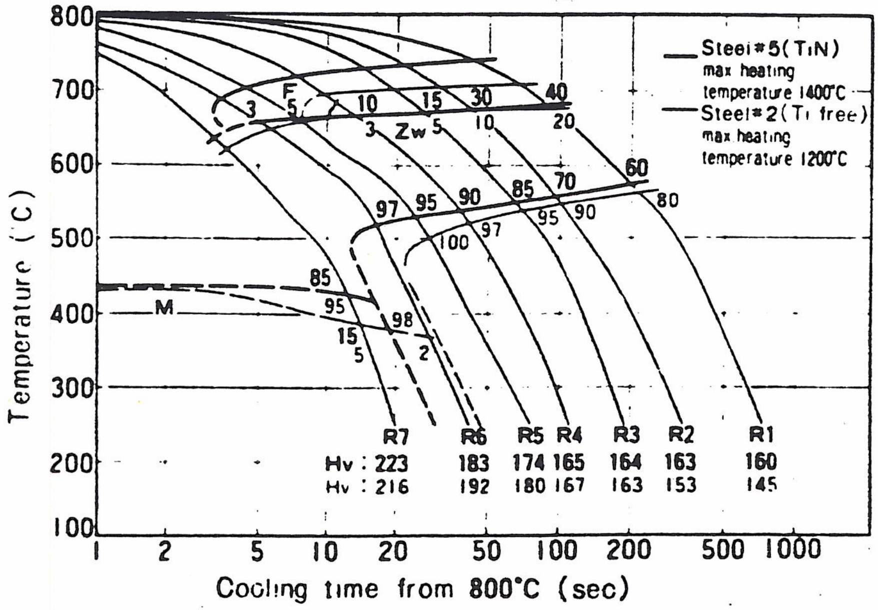


Fig.18b CCT diagram of steels #2 and #5 with same austenite grain size (14)

Fig.18a shows the CCT diagram of steels 2# (Ti free) and 5# (with Ti). It is found from Fig.18 that the steel 5# containing TiN (thick line) had its ferrite noses protruded more towards the short time side than the reference steel 2# with more Fp in the former than in the latter in the same cooling condition. Quenched from different temperatures, the TiN bearing steel 5# was found to contain more Fp and less Fa than the Ti-free steel 2#. Thus TiN was found to have a great influence on steel transformation behavior with TiN particles serving as transformation nuclei.

D. Uwer and U. Lotter(18) found the same phenomimon as S. Kanazwa did. StE 355 TiN (Ti-bearing steel) had its ferrite and Bainite noses protruded more towards the short time side than steel StE 355 (Ti-free steel) as shown in Fig.19.

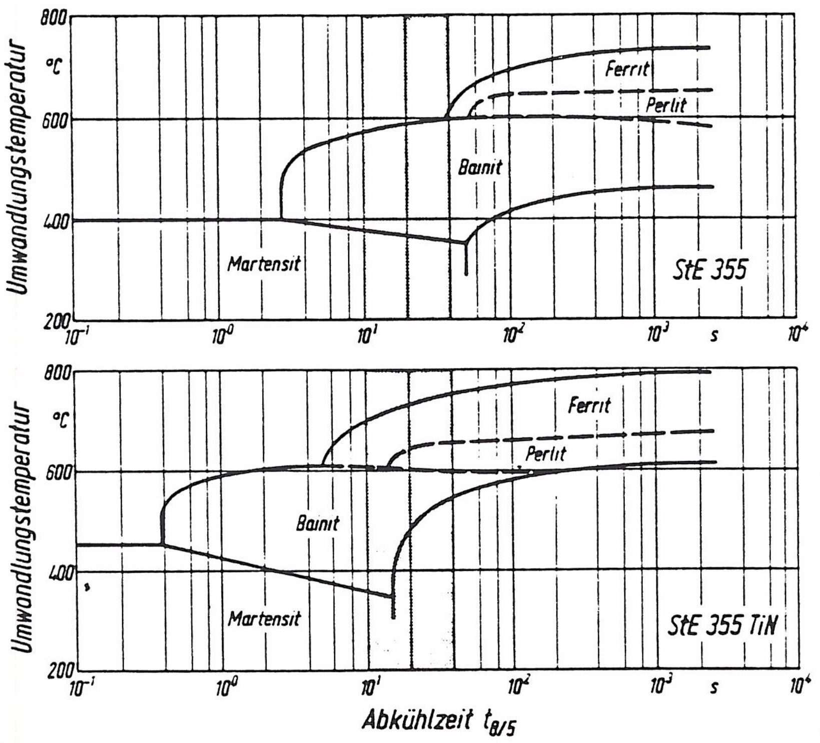


Fig.19 CCT diagram of steels StE355 and StE355TiN. 1s at 1350 °C(18)

The influence of Ti on microstructure in steels containing more and less than 20ppm Ti was investigated by S. Mukae, et al(11). They observed a refining of the grain boundary ferrite, a decrease in ferrite side plates and an increase in fine polygonal ferrite grain with an increasing Ti content when Ti is added to ultra low N steels. When the steel contains 50ppm N and no Ti, the microstructure is composed of boundary ferrites and ferrite side plates. When 0.011 wt% of Ti (Ti/N=2.2) is added, fine ferrite grains precipitate in austenite grains, boundary ferrites are refined and ferrite side plates decrease largely. When 0.02 wt% of higher Ti (Ti/N=3.8) is added, fine ferrite grain further increases and a unformly fine structure is obtained.

Mutsuo Nakanishi, et al (19) compared the HAZ structure of ultra low S-Ca-Ti and Ti-N treated steels. In case the peak temperature of the heat cycle was 1350 °C, there was more acicular structure inside the prior austenite grain of Ti-N treated steel compared to ultra low S-Ca-Ti treated steel. After Nital then electrolytic etching, the acicular structures were clearly observed in SEM as white needles. The white parts were rising up from the surface of ferrite matrix and were thought to be what is called M-A constituent (or what is called island of martensite).

B. Leberg, et al(12) studied 7 different Ti-microalloyed steels. It was found that in the normalized condition, the microstructure consisted in all cases of a pearlite/ferrite mixture.

Ti-oxides have also been found to affect on the microstructure of the weld metal. It has been established that Ti-oxides increase the proportion of acicular ferrite in weld metal(8,29). Fig.20 indicates that an increased level of Ti would be expected to produce a higher proportion of acicular ferrite. The data in Fig.20 suggest that this is the minimum level of Ti required to give the optimum acicular ferrite content.

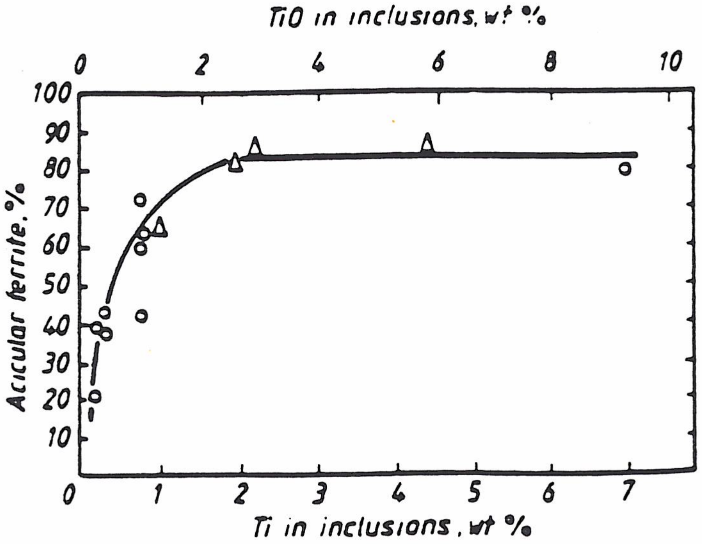


Fig.20 Correlation between the percentage of acicular ferrite and the percentage of Ti (or TiO) in the inclusion in submerged arc welds(20).

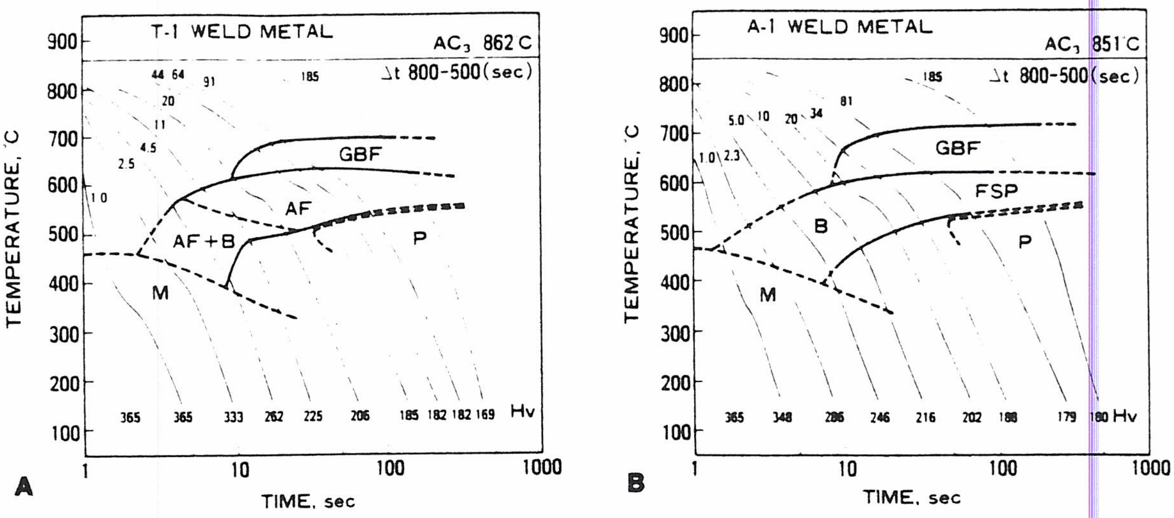


Fig.21 CCT diagrams, A: Ti-oxide-containing weld metal;
B: Ti-oxide-free weld metal (8)

The CCT diagrams of Ti-oxide bearing and Ti-oxide free SAW welds are shown in Figs.21A and B respectively. It can clearly be inferred from Fig.21 that Ti-oxide bearing welds which were reheated rapidly to 1350 °C and then cooled below AC_3 temperatures produced acicular ferrite (AF) when the cooling time between 800 °C and 500 °C exceeded approximately 10s. Ferrite side plate (FSP) and lath like ferrite (LF), but no acicular ferrite, were found in the same condition on the material from Ti-oxide free welds. Analysis showed that Ti-containing inclusions promote the nucleation of acicular ferrite.

Studies were also carried out on the microstructure of the planar HAZ. It is interesting to note that the intragranular microstructure of HAZ with Ti-oxide is almost the same as that of the unrefined weld metal, and consists of acicular ferrite (AF), whereas steels with Ti-free oxide and TiN consist of lath-like ferrite with small amounts of polygonal ferrite, respectively. Recent research indicated that Ti-containing inclusions extensively enhanced intragranular ferrite nucleation, even after they had experienced hot-rolling and were followed by a weld thermal cycle corresponding to a heat input as high as 10kJ/cm. On the other hand, Ti-free oxide inclusions did not nucleate acicular ferrite at all in the same condition.

It has also been found that about 70 to 80% of the microstructure in the Ti-oxide treated steel consists of acicular ferrite with a small amount of proeutectoid ferrite and ferrite side plate, even when the peak temperature was increased from 1350 °C to 1450 °C. On the other hand, in TiN steel, polygonal ferrite started to disappear at 1400 °C, and upper bainite became a dominant microstructure when the peak temperature was increased to 1450 °C, where significant grain growth presumably occured as a result of the dissolution of TiN.

In summary, a schematic illustration of HAZ microstructures in the Ti-oxide treated steel and TiN steel is shown in Fig.22. Ti_2O_3 particles in the former extensively promote intragranular nucleation of acicular ferrite at the weld interface and in the coarse-grained HAZ, while the formation of upper bainite is likely to occur in the latter, particularly in higher heat input welding conditions.

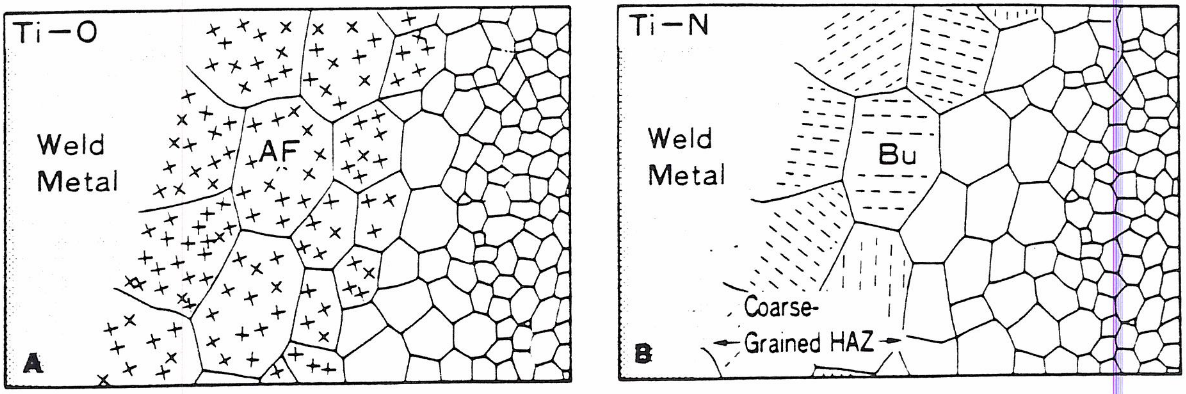


Fig.22 Schematic illustration of HAZ microstructure; A: Ti-oxide-treated steel; B: TiN steel(8)

R. Chijiiwa, et al(21) analyzed the difference between the coarse grained HAZ microstructures of the TiO and TiN steels. Fig.23 shows the changes in the microstructure of a HAZ, the amount of M* (high-carbon martensite) and the mean effective grain size of cleavage fracture surface of specimen tested at -196 °C. Fig.24 presents fotos of microstructures of the HAZ near the fusion line of a weld with heat input of 70kJ/cm. The amount of IFP (intragranular ferrite plate) increased with increasing heat input and the microstructure was observed to be mainly composed of IFP at heat input of 70kJ/cm. In contrast to this, only a small amount of IFP is found in the TiN steel at all levels of heat input and the amount of FSP(ferrite side plate) increases substantially with an increase in heat input. The amount of M* is smaller in the TiO steel than in the TiN steel in the intercritically reheated coarse-grained zone, though this amount was not significantly different between the two steels in the coarse-grained zone. At the heat input of 30kJ/cm, the amount of M* of the TiO steel is much smaller than that of the TiN steel although there is no substantial difference in the main microstructure between the two steels. Therefore it might be concluded that the excellent CTOD properties of the TiO steel is attributable to the HAZ microstructure having a reduced amount of M*, at least in part.

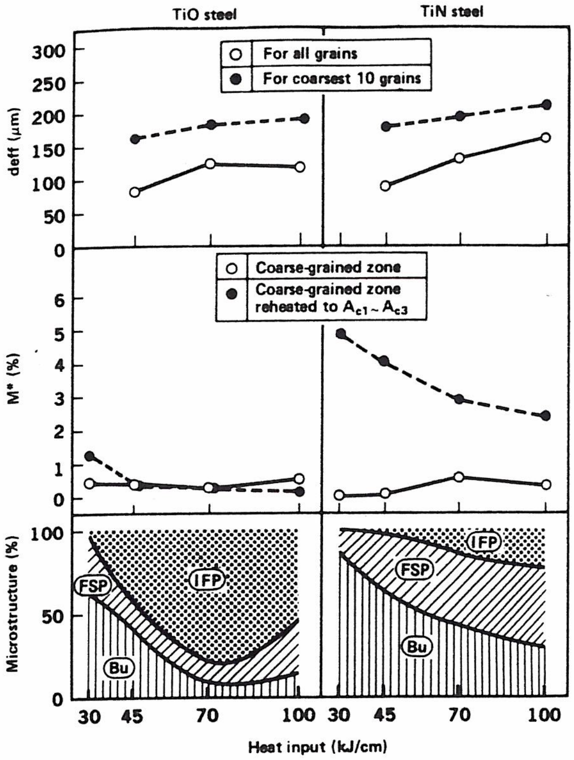


Fig.23 Changes in microstructure (region within 150μm from FL), amount of high carbon martensite and mean effective grain size in coarse grained HAZ with heat input(21)

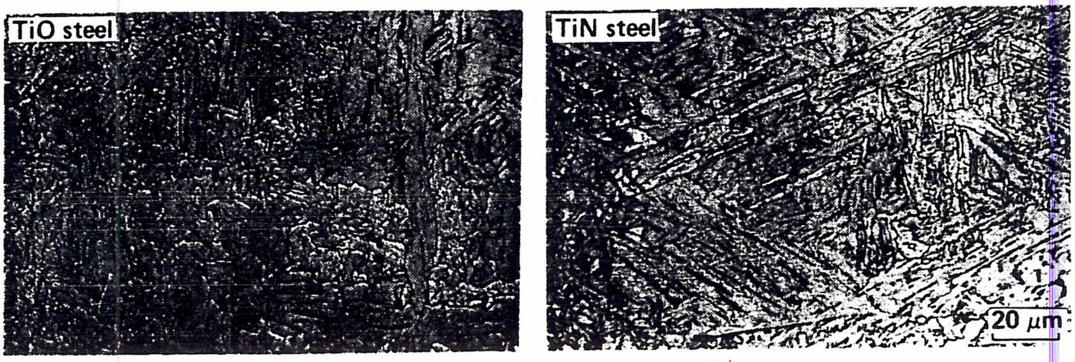


Fig.24 Microstructures of HAZ near fusion line(heat input: 70KJ/cm)(21)

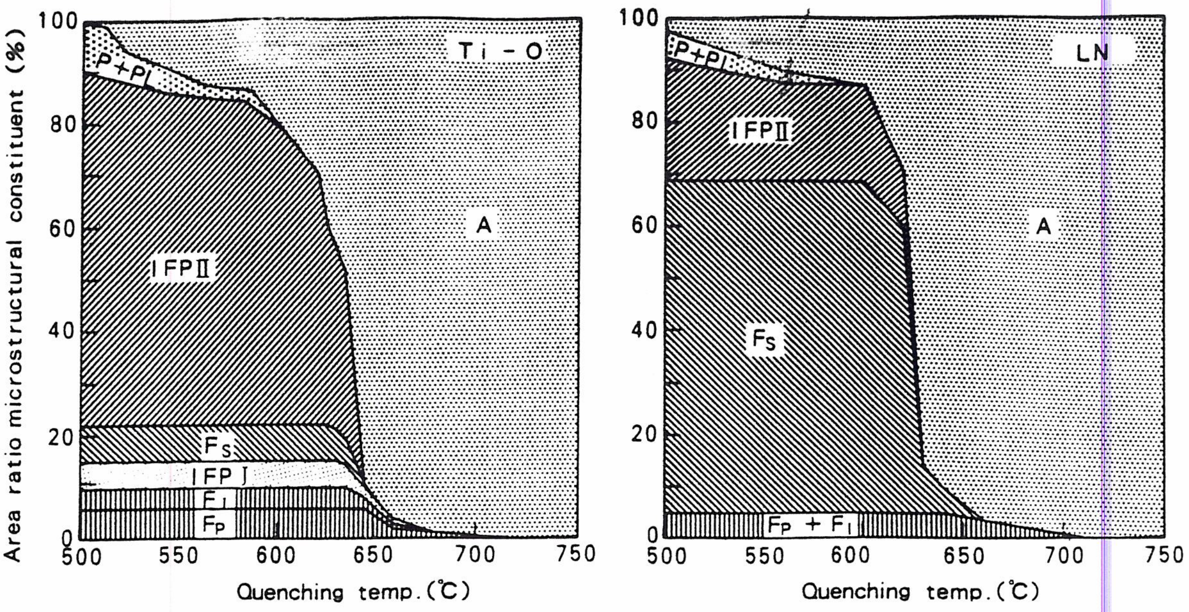


Fig.25 Diagram showing area ratio of microstructural constituents in Ti-O steel and LN steel(22).

Fig.25 shows the different influence of Ti-oxide and Ti-nitride on microstructure(22). It is obvious that IFPII in Ti-O steel forms in place of Fs(ferrite side plate). In LN steel, Fs prevails, as is the case for usual steels. In other words, Ti_2O_3 particles dispersed in the steel bring about IFP in HAZ, which prevents development of Fs and consequently improves HAZ toughness.

Naomichi Mori, et al(23) found that titanium had also an important influence on the as-welded microstructure of boron bearing weld metals. The weld metal with 0.018% Ti and 41 ppm B, consisted of fine acicular ferrite and grain boundary proeutectoid ferrite, whereas the weld metal with 0.002%Ti and 41ppm B consisted of ferrite side plate and upper bainite with little acicular ferrite.

The influence of Ti on microstructure of Mn-bearing and Mn-Ti bearing weld deposits has also been studied by N.Mori(1). The microstructure of Ti-free deposits was coarse ferrite with aligned carbides surrounded by blocky proeutectoid ferrite at the prior austenite boundaries. On the other hand, the microstructure of Ti bearing deposits was predominantly fine grained interlocking ferrite acicular ferrite, but the prior austenite boundaries were lined with proeutectoid ferrite.

I. Kozasu(25) indicated that fine particles of TiN or other compounds restrict the austenitic grain coarsening and act as nucleation sites for ferrite, resulting in a decreased fraction of upper bainite.

V. EFFECT OF Ti PARTICLES ON TOUGHNESS

In recent years, many researchers and steel manufacturers have successfully improved the HAZ toughness by utilizing finely dispersed Ti particles. However, the optimum Ti content is not being unequivocably agreed upon among researchers and is affected by the presence of other alloying elements. H.Nakasugi(26) found that titanium carbide (TiC) coherently precipitated in the fine ferrite microstructure strikingly increases strength without deteriorating impact properties. Fig.26 shows the change of strength and Charpy V-notch transition temperature as a function of effective titanium (eTi) to carbon ratio (eTi/C) .With increasing amounts of eTi/C, strength increases linearly up to the point where eTi/C=4, accompanied by an increasing transition temperature. Beyond this point strength decreases progressively. (eTi is defined as eTi=total Ti -3.4 * total N).

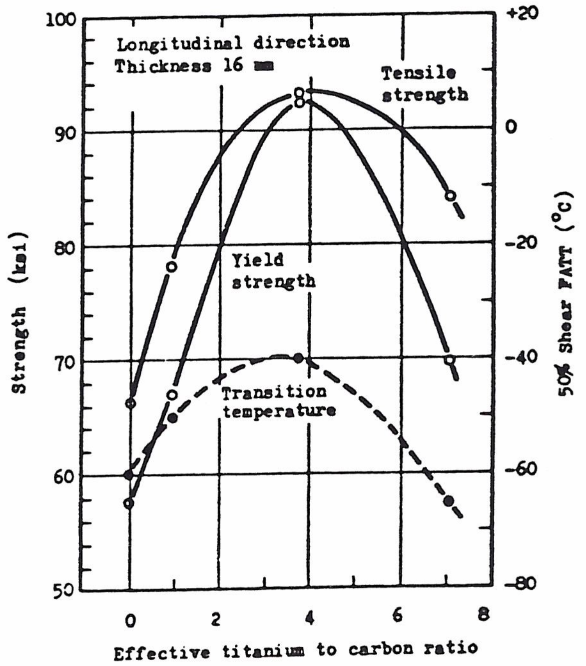


Fig.26 Strength & Charpy V-notch transition temperature as a function of effective Ti to C ratio. The base composition is 0.03%C, 0.27%Si and 1.63%Mn(26).

N.E.Hannerz (27) found that Ti has a favourable influence on implant strength of HAZ of HSLA steel, as shown in Fig.27. Fig. 28 shows the influence of Ti and Al on the impact toughness of HAZ. Each point in this Figure indicates the mean value of absorbed energy for 6-15 test pieces sampled from the welded joints. The toughness of HAZ increases sharply with an increase in soluble Al content and the addition of a trace amount of Ti improvies toughness. Playing a complementary role to Al(28). Naomichi Mori et al(23) studied the effect of Ti, B and N on notch toughness of two pass weld metals. The results of impact toughness tests are shown in Fig.29. It was found that additions of Titanium and Boron significantly improve toughness of the as-welded weld metals. Shogo Kanazawa, et al.(14) also studied the TiN influence on HAZ toughness. The measured fracture appearance transition temperatures VTrs were plotted against cooling rates as shown in Fig.30. The TiN steels #4 and #5 were found to have considerably lower VTrs for all cooling rates compared to the Ti-free steel #2. In order to study TiN effect on toughness without the influence of austenite grain size, a specimen of the Ti-free steel #2 was heated to 1200 °C so as to produce an austenite grain size comparable to the TiN steel #5 as heated to 1400 °C. The measured vTrs values were plotted against cooling rates in Fig.31. It was confirmed that even with a comparable grain size, the CGHAZ toughness of the Ti-free steel #2 was much lower than that of TiN steel #5.

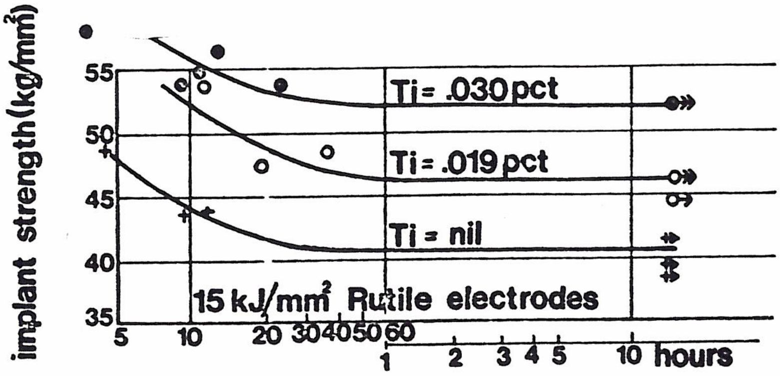


Fig.27 Implant strength of a concast steel with different amounts of Ti added in the casting funnel(27)

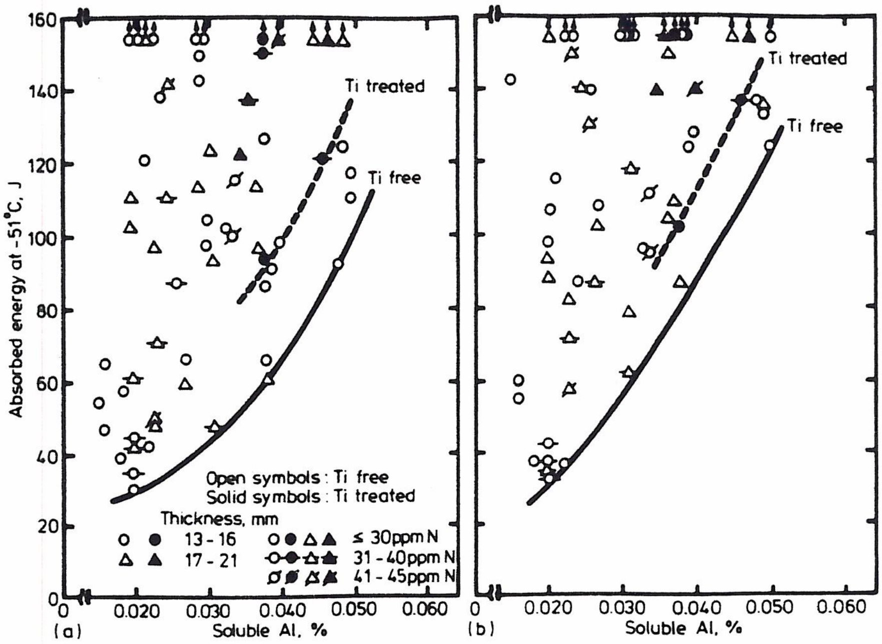
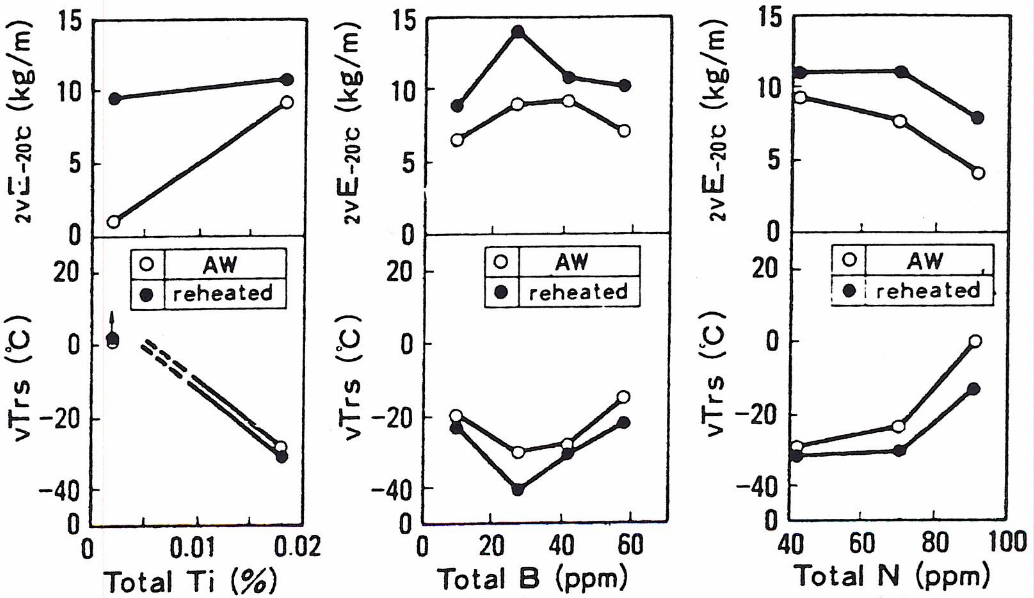


Fig.28 Relation between soluble Al content of steel and impact properties of weldments made by submerged arc welding with large electrode separation: a) Notch on fusion boundary; b) Notched 1mm into HAZ.(28)



(a) (b) (c)

Fig.29 Effect of Ti, B and N on notch toughness of two-pass weld metals (23)

(a) 40ppm B, (b) 0.02%Ti, 40ppm N, (c) 0.02%Ti, 40ppm B

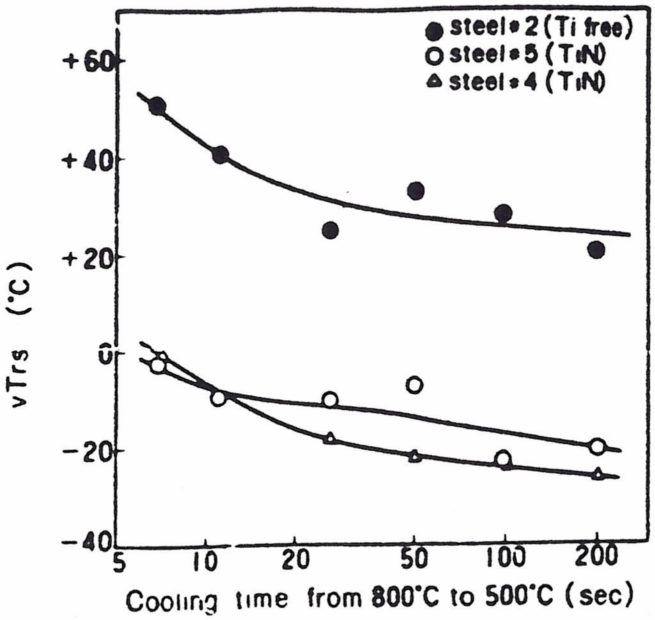


Fig.30 Impact transition temperatures as a function of cooling time from 800 to 500 °C (max. heating temperature: 1400 °C)(14)

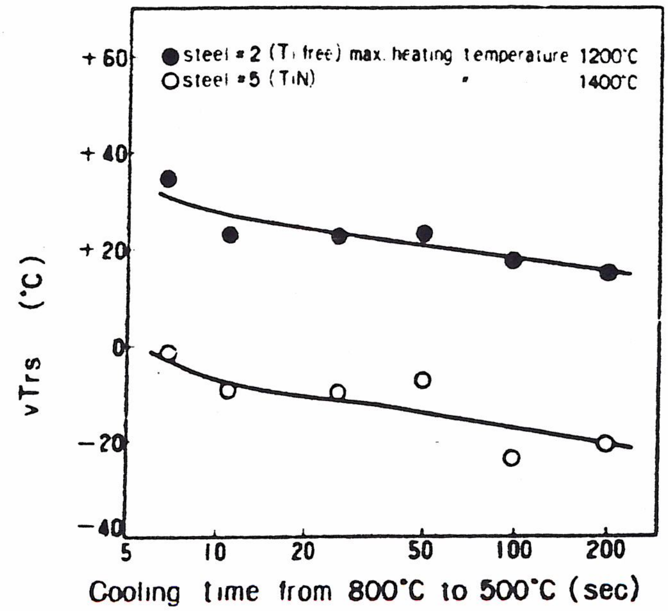


Fig.31 Impact transition temperature as a function of cooling time from 800 to 500 °C in steels #2 and #5 with same austenite grain size(14)

The effect of TiN particle on the toughness of HAZ heated to different maximum heating temperatures was also studied. The measured vTrs temperatures were plotted against the maximum heating temperatures in Fig.32. Again the TiN steel #5 was found to be tougher than the Ti-free steel #2.

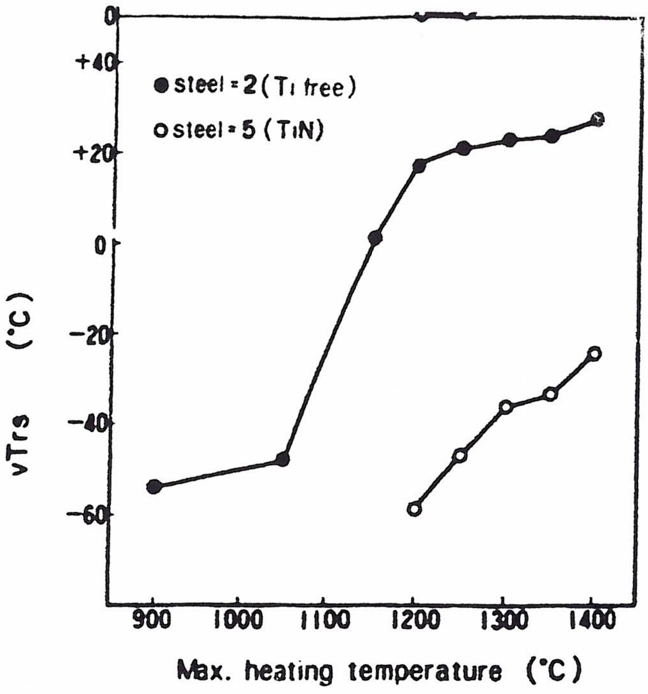


Fig.32 Change of vTrs with max. heating temperature in steels #2 and #5(14)

However, the optimum contents of Ti and N to improve HAZ toughness are not generally agreed issue. The improvement of HAZ toughness is not only affected by Ti and N contents separatly, but also by Ti/N ratio and presence of some other microalloying elements.

In some cases, Titanium additions did not show its usual positive influence on toughness of HAZ. Fig.33 shows the effect of Ti on critical CTOD(δ_c) at -50 °C after PWHT(29).

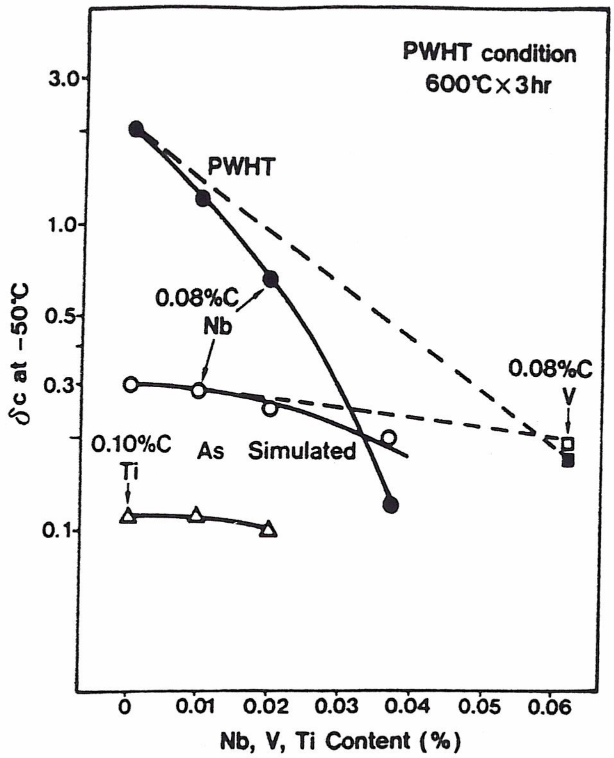


Fig.33 The effects of Nb,V and Ti content on CTOD value(29)

Some researchers(30) think that the optimum Ti to N ratio should be about 2.2. The benefcial influence of 0.005 to 0.011% Ti on the HAZ toughness of X-70 linepipe can be seen in Fig.34. High titanium to nitrogen ratios exceeding 3 to 1 do not improve toughness, but actually cause deterioration of HAZ toughness. Fig.35 shows the effect of Ti/N ratios on the impact toughness properties of HAZ. The addition of 0.009% or less Ti produces little or no effect on toughness of the coarse grained region adjacent to the fusion line heated at a temperature near the melting point. On the other hand, where the Ti content is much higher (Ti/N>3.4) than the N amount, the HAZ toughness shows a tendency to decrease in a sharp curve.

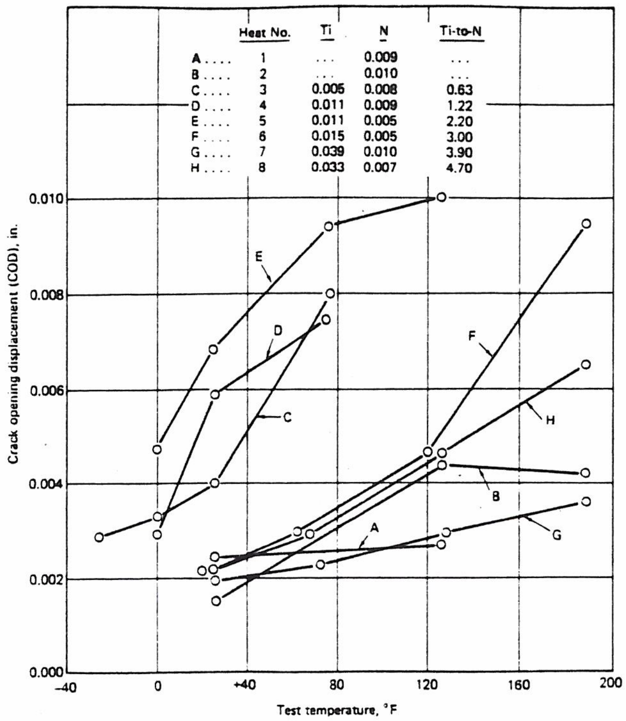


Fig.34 Effect of Titanium-to-Nitrogen ratio on the COD toughness of coarse-grained HAZ material(30)

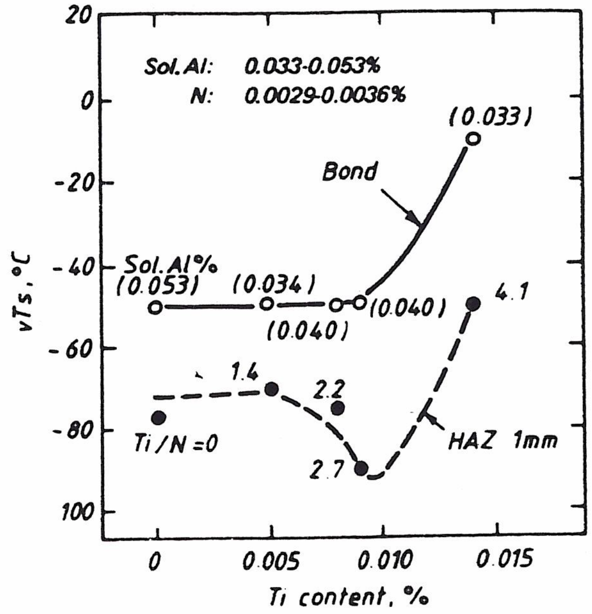


Fig.35 Effect of Ti content on HAZ toughness(31)

Fig.36 shows the results of the investigation on the influences of N and Ti contents at low N content range (N ≤ 80ppm)(19). It was found that the toughnes is the highest when Ti/N content ratio is about 2, and that the toughness is poor when Ti/N ratio is above 3.4 or below 1. It follows that in the range of low nitrogen content (N ≤ 80ppm), the effect of Ti-N treatment is roughly decided by Ti/N ratio.

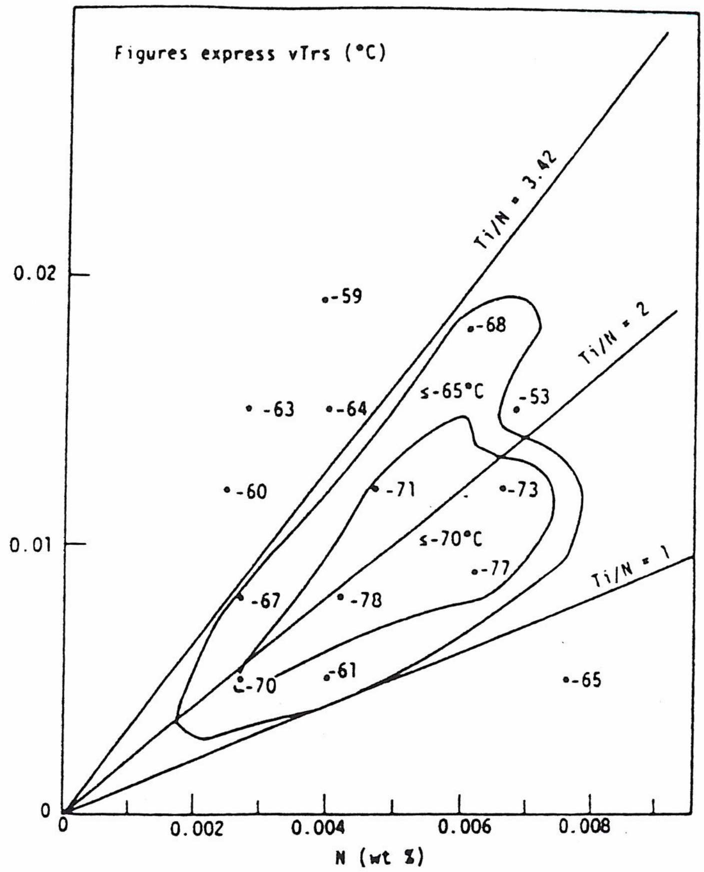


Fig.36 Effect of Ti and N on notch toughness of weld bond(19)

Effects of Ti and Al on the toughness of the steels containing about 15 ppm N have been investigated by Shizuo Mukae, et al.(11). Fig.37 shows the effects of Sol. Al and Ti content on vTrs. VTrs of steels containing high N level (N=34 and 50 ppm) and without Ti are very high as seen in Fig.37. According to this paper, when N level in the steels is low, the austenite grain size becomes greater, the ferrite side plates become coarser and more of the degenerate pearlite develops. However, vTrs decreases to -50 °C when N content in the steel is 13ppm. Thus, it is clear that vTrs drops by 13 to 17 °C with a decrease of 10 ppm in N.

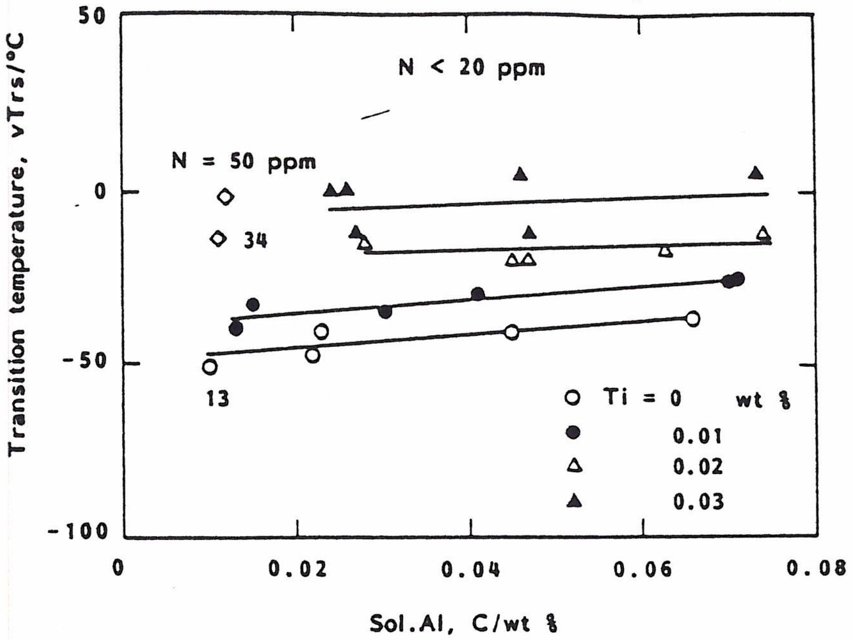
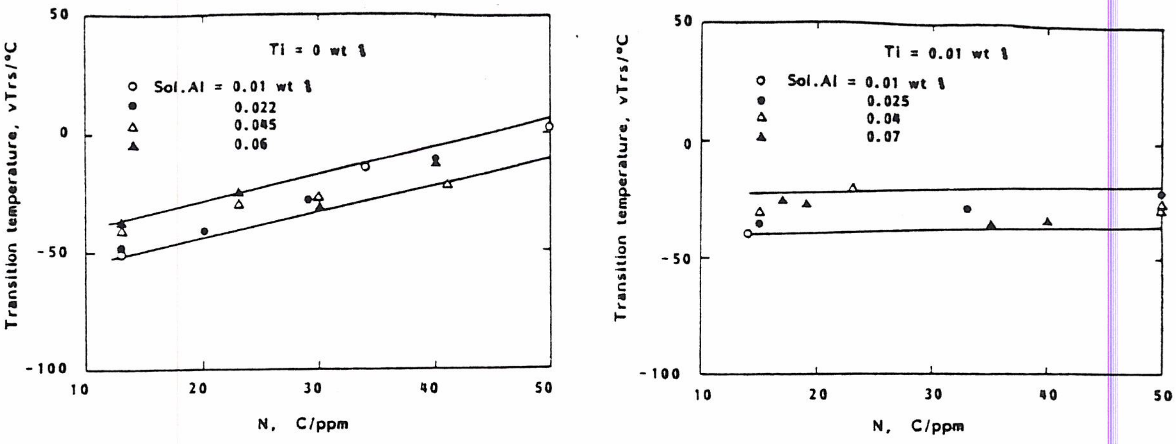


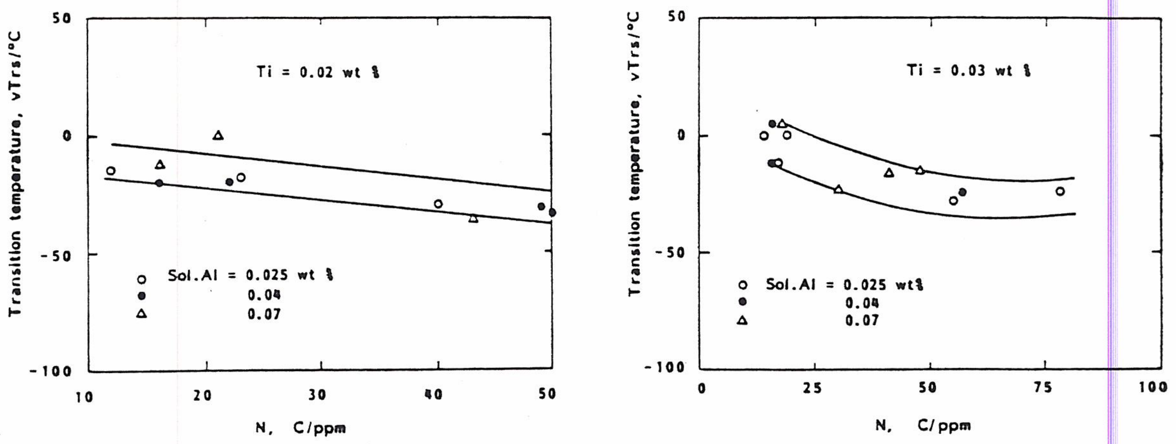
Fig.37 Effects of sol. Al and Ti contents on Charpy transition temperature of steels containing less than 20ppm N(11)

Fig.37 indicates further that the additions of Al and Ti to the ultra low N steels could not improve the HAZ toughness, which, however, was improved very much by decreasing N content in the steels. This can be explained by following reasons: 1) the HAZ microstructure was not refined by the addition of Al, and 2) when Ti was added, not only most of Ti but also N dissolved in the steels because of ultra low N content though the microstructures were refined a little. As a result the HAZ toughness could not be improved. For the improvement of the HAZ toughness of the ultra low N steels having less than 20ppm N, it is necessary to control the Ti content to less than 0.01 wt% in order to decrease both Sol. Ti and Sol. N content.

A remarkable improvement of the HAZ toughness by the addition of Ti tends to lower the toughness a little in steels containing N less than 40 to 50 ppm as shown in Fig.38.



(a) Ti=0 wt%　　(b) Ti=0.01 wt%



(c) Ti=0.02 wt%　　(d) Ti=0.03 wt%

Fig.38 Effects of N and sol. Al on Charpy transition temperature(11).

The optimum Ti content to improve the HAZ toughness has also been investigated by S. Mukae(11). Fig.39 shows the relationship between the optimum Ti and N content. The optimum Ti content is zero wt% when the N content is as low as about 10 ppm. The optimum Ti content increases linearly with an increasing stoichiometric ratio of Ti/N=3.4 when TiN is formed. The ratio of the optimum Ti content to the N content is a little lower than the stoichiometic ratio when the N content is small but it agrees nearly with the ratio for higher N content. The effect of Sol. Al content on the optimum Ti content is slight, and the optimum Ti content decreases a little when the content of Sol. Al is increased in the steels with a higher N content.

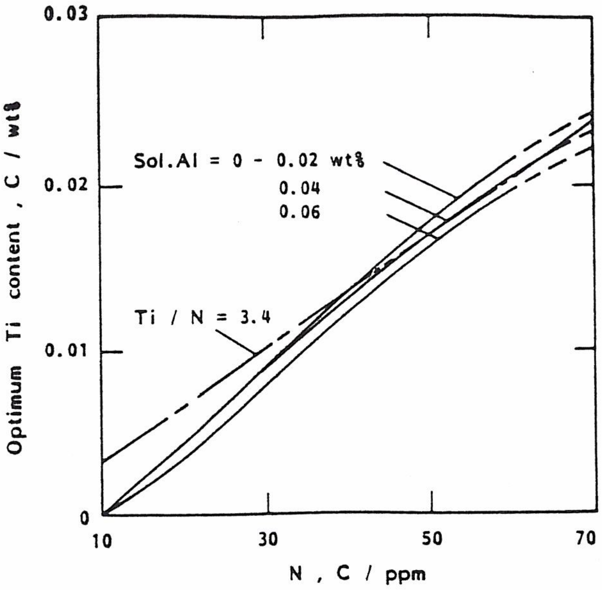


Fig.39 Relationship between the optimum Ti content and the total N content(11).

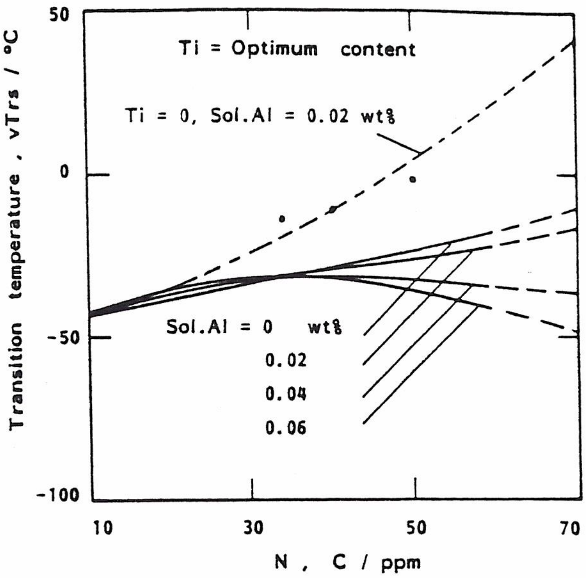


Fig.40 Relationship between Charpy transition temperature and total N content when Ti is added in the optimum amount(11)

Fig.40 shows the relationship between vTrs and N content when the optimum content of Ti is added as shown in Fig.39. It is observed that vTrs of the steels without Ti increases with an increasing N content. However, when the optimum content of Ti is added for the N content, the effect of the addition of Ti improving the HAZ toughness is predominant as the content of N increases, while the effect is slight in the steels containing lower N. Furthermore, in the steels containing higher N the composite addition of Ti and Al was effective to improve the HAZ toughness. It seems, however, that vTrs in this case is not lower than that in the case of the ultra low N steel.

Ti-oxides as mentioned earlier have successfully been used to improve the HAZ toughness because of their high stability at very high temperature(8,21,22). As shown in Fig.41, the welding thermal cycle of 1450 °C heating temperature gave serious deterioration to Ti-B steel and Ti-N steel but no recognizable damage to Ti-O steel. Therefore, it is assumed that the superior property of Ti-O steel is due to the high stability of Ti_2O_3 particles at high temperature.

The effect of C or Nb content on toughness of simulated HAZ of both Ti-oxides steel and Ti-nitride steel was studied(22). As shown in Fig.42, in LN steel and Ti-LN steels, the vTrs of simulated HAZ was raised by about 50 °C due to the increase in C content from 0.04% to 0.12%. On the other hand, the corresponding rise of vTrs in Ti-O steels was only about 20 °C. Therefore, Ti-O steel can maintain good HAZ toughness even with a high C content.

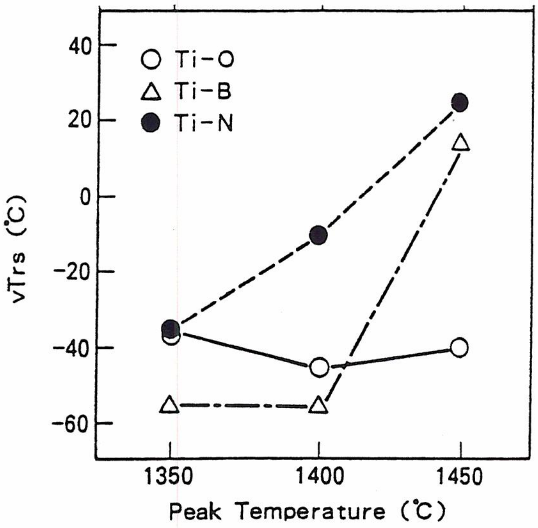


Fig.41 FATT of Charpy impact test(vTrs) as a function of peak temp. in simulated HAZ of Ti-O,Ti-N and Ti-B steels (22)

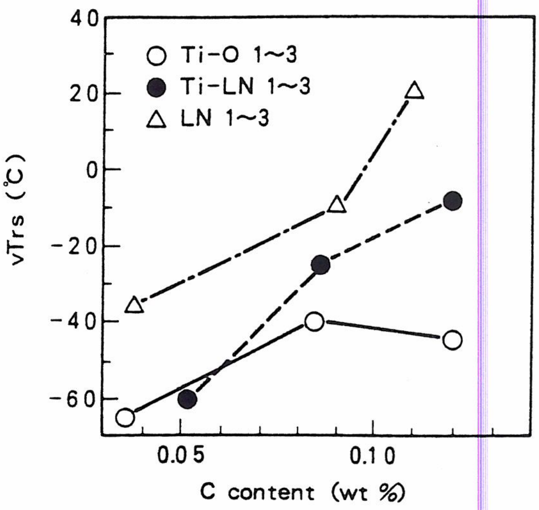


Fig.42 Effect of carbon content on vTrs in specimens subjected to simulated thermal cycle of HAZ (P.T.=1400 °C, $t_{8/5}$=161s)(22)

The effect of Nb addition in Ti-bearing steels was examined as shown in Fig.43. In Ti-N steel, vTrs of simulated HAZ rose in proportion to the amount of Nb with a rate of 40 °C/0.01%Nb. In Ti-O steel, vTrs was nearly independent of, or rather improved by, an addition of Nb. The reason of such different influence by Nb addition is that an Nb addition of 0.01% to Ti-O steel did not prevent the formation of IFP (Intragranular Ferrite Plate) at all and decreased grain boundary ferrite, while an addition of the same amount of Nb to Ti-LN steel prohibited almost all IFP formation and induced a coarsened structure consisting mainly of Fs (Ferrite side plate). The cause of variation in toughness can be attributed to IFP formation.

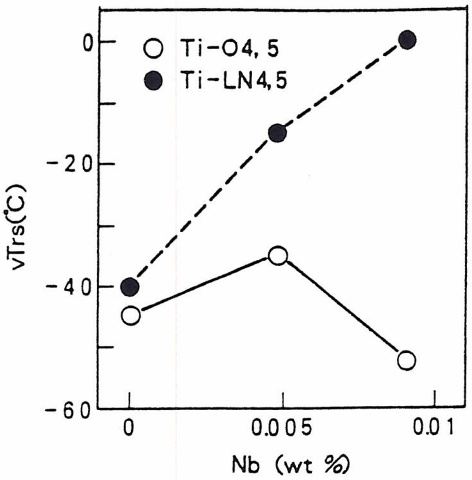


Fig.43 Effect of niobium content on vTrs in specimens subjected to simulated cycle of HAZ.(22)

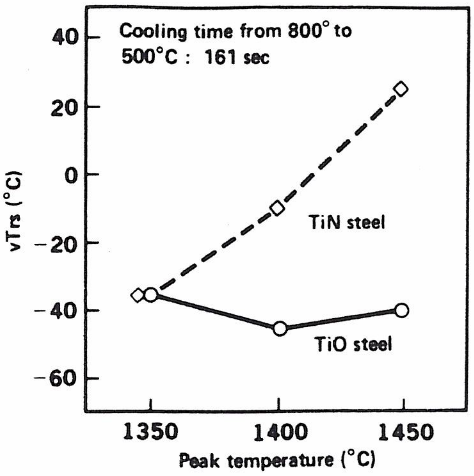


Fig.44 Change in Charpy V-notch transition temp. of simulated HAZ with peak temperature.(21)

Rikio Chijiiwa(21) compared the effect of TiN and TiO on the toughness of simulated HAZ at high input welding. The impact results are shown in Fig.44. In the TiN steel, the vTrs remarkably rises as the peak temperature rises because TiN begins to dissolve at a temperature higher than 1400 °C. In contrast to this, the vTrs of TiO steel changes little with peak temperature because the Ti-oxide is chemically stable at a high temperature such as 1450 °C. Also in the TiO steel, an excess of Ti other than the Ti contained in the Ti-oxide combines with N to form TiN. These TiN particles suppress the coarsening of γ-grains at and below peak temperatures of 1350 °C and improve low temperature toughness.

Critical CTOD values for various heat input levels of welding are shown in Fig.45. The CTOD value is high in the TiO steel irrespective of heat input, whereas in the TiN steel low values appear frequently at large heat input.It is claimed that excellent CTOD properties are one of the features of the TiO steel. The difference of CTOD properties between the TiO and TiN steels can be explained as follows. In the TiN steel, the remarkable local brittle zone still exists near the fusion line though it is very narrow as is apparent from Fig.44, while in the TiO steel it does not. Generally, the CTOD properties deterioate quite sensitively to LBZ, while Charpy impact properties are rather insensitive to LBZ. This is the reason why the TiO steel has excellent CTOD properties.

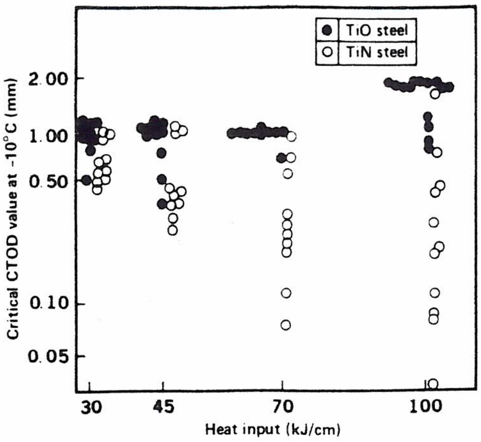


Fig.45 Critical CTOD values for various heat input levels of welding(21)

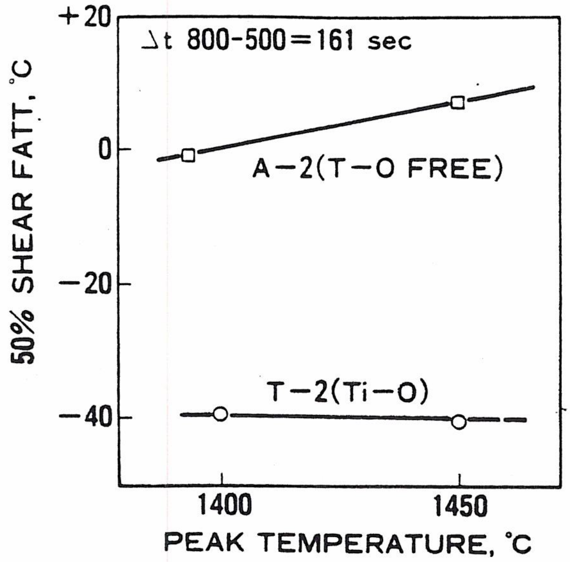


Fig.46 Results of impact tests on synthetic HAZs in hot-rolled submerged arc welds (heat (heat input: 10kJ/cm)(8)

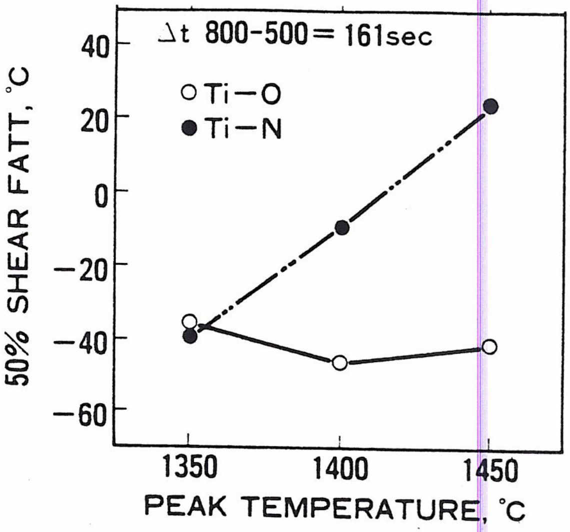


Fig.47 Results of impact test on sythetic HAZs in Ti-oxide-treated and TiN steels(8).

The same tendency was found by H. Homma et al(8). As shown in Fig.46, Ti-oxide containing steel indicated far better notch toughness as compared with Ti-oxide free steel. The results of impact tests performed in the synthetic HAZ simulation of TiN steel and Ti-O steel are shown in Fig.47. As can be seen from the Figure, notch toughness of TiN steel deteriorated considerably when the peak temperature increased. On the other hand, no toughness deterioration was found in the Ti-oxide-treated steel when the peak temperature was increased from 1350 °C to 1450 °C, indicating that the Ti-oxide treated steel is able to provide excellent notch toughness near the weld interface.

VI SUMMARY

This literature review can be summarized as follow:

1) Ti can form various types of particles. Among them, TiN and Ti-oxides are the most stable Ti particles even at temperature as high as 1350°C. That means that TiN and Ti-oxides can provide effective grain growth control during high heat input weld thermal cycle.
2) The stability of Ti particles can be affected by heating temperature, heat rate and the presence of other nitride formers such as Al, V and Nb. The presence of such an alloying elements may cause the formation of complex composition (Ti(V,Nb)(C,N)) particle and consequently, such a composition may lower the dissolution temperature of the Ti particles. If this occurs, an adverse effect on toughness can be expected.
3) Ti has been found to have a considerable influence on grain size and microstructures. Austenite grains can be effectively refined due to pinning effects of stable Ti particles on grain growth of austenite. Research also revealed that TiN additionally promotes the nucleation of ferrite (especially the polygonal ferrite) and bainite while TiO promotes the formation of acicular ferrite in weld metal, because they have very small disregistry with α-iron.
4) Also, Ti has a beneficial influence on CGHAZ notch toughness, if Ti particles are fine enough (smaller than about 0.5 µm) and dispersed uniformly in the matrix. The optimum Ti content is different from steel to steel. It is affected not only by Ti content and Ti/N ratio but also by the presence of some other microalloying elements. According to some research results, TiO steels have superior CGHAZ toughness properties compared to TiN steels. This is attributed to the more stable nature of the TiO particles.

However, having an improvement of CGHAZ toughness is not always so straight forward job. Steel producer should bear in mind that the correct amount of Ti, in connection with N and other alloying elements as well as optimum production and welding procedure should be combined.

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