

# The influence of Ti on the hot ductility of Nb containing steels

by

K.M.Banks<sup>+</sup>, A.Tuling<sup>+</sup>, C.Klinkenberg<sup>°</sup> and B.Mintz<sup>\*</sup>

<sup>+</sup> Industrial Metals and Minerals Research Inst.University of Pretoria, SA

<sup>°</sup> SMS Siemag.AG. Germany

<sup>\*</sup>City University, London, England

## Keywords

Hot ductility, low C steels, Ti, Nb and N additions, Under-cooling

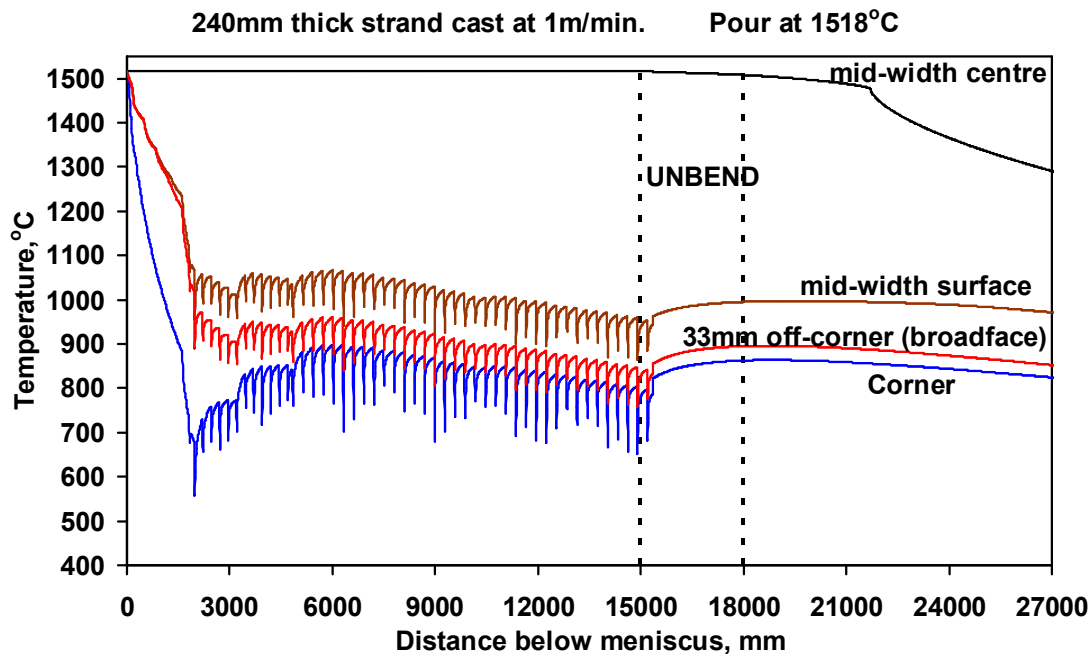
## Abstract

The influence of a low Ti addition, (~0.01%) on the hot ductility of Nb containing steels has been examined. For conventional cooling conditions in which an average cooling rate from the melting point to the test temperature was used, the ductility decreased markedly with the addition of Ti. However, when cooling conditions after melting were more in accord with the thermal heat treatment undergone by the strand during continuous casting, i.e. cooling is fast to begin with, reaches a minimum and then reheats, after which the temperature falls more slowly to the test temperature, the Ti addition was found to be beneficial.

## Introduction

The influence of a Ti addition to steel on hot ductility and how it affects transverse cracking has been the subject of much research in recent years [1]. Commercially, there is considerable evidence to indicate that a small Ti addition to steel improves surface quality and reduces transverse cracking [1]. Early laboratory hot ductility work also indicated Ti to be beneficial but a closer examination found this was due to grain refinement since the tensile samples were not melted but only heated to 1200-1300°C; these temperatures being insufficient to dissolve the TiN particles[2]. It was this grain refinement that gave rise to the better ductility [2] but such grain refinement is not present when a small Ti addition is made to cast steel. When Ti containing tensile specimens were melted and cooled to the test temperature, thus simulating the commercial continuous casting operation more accurately and then tested, hot ductility was in general much worse than for Ti free steels of otherwise similar composition. At best only a small improvement on adding Ti occurred [3,4]. Previous work has shown that the poor ductility was due to the precipitation of Ti rich fine particles [3,4]. This anomaly between the beneficial effect of Ti in commercial experience and the disappointing results from laboratory work has been a continual worry in using the laboratory results to predict the likelihood of Ti containing steels exhibiting transverse cracking during continuous casting.

It should be noted that tests in which solution treating has been followed by cooling at an average cooling rate from the melting point to the test temperature and straining to failure using a strain rate of  $\sim 10^{-2}$ - $10^{-3}$  s<sup>-1</sup> have been found to be adequate for C-Mn-Al, C-Mn-Nb-Al and C-Mn-V-Al steels and the results have fitted in well with the continuous casting experience [1]. For these steels it is not necessary to melt the samples but when melting has been used the hot ductility behaviour again reflects commercial experience.



**Fig.1. Predicted strand surface temperature during continuous casting of 240mm strand cast at 1m/min [6].**

However for Ti containing steels, work by Spradbery and Mintz [5] indicates that results can be very different if a slightly more complicated cooling pattern is carried out, more appropriate to the commercial process. In the commercial casting operation the primary cooling, underneath the mould is very rapid. The temperature at the foot-rolls reaches a minimum, rises again and then falls gradually during secondary cooling until the unbending temperature is reached. Additional temperature losses are also incurred when the strand passes over the guide rolls, as can be seen by the thermal oscillations at the surface from a 2-D strand temperature model [6] in Fig.1. The introduction of an under-cooling step of 100°C shown in Fig.2, as in Spradbery and Mintz's work[5] goes some way to representing the commercial cooling conditions more accurately and the results obtained were more encouraging.

Whereas for C-Mn-Nb-Al, Ti free steels, under-cooling gave rise to ductility deteriorating due to increased precipitation of NbCN, in the case of C-Mn-Al-Nb- Ti containing steels, under-cooling improved the ductility possibly because growth of the Ti rich particles had occurred. This under-cooling resulted in the 0.008% Ti containing steel having reduction of area (R of A) values slightly above the values given for a Ti free steel of similar composition as shown in Fig.3. However, at the 0.013% Ti level, although under-cooling gave improved hot ductility at temperatures  $\leq 1000^{\circ}\text{C}$ , ductility was still very much less than realised by the Ti free steel, Fig.3.

A more accurate simulation of the cooling conditions during continuous casting is that used by El Wazri et al [7] in which the cooling rate is fast at the start of the programme; the temperature reaches a minimum and then is allowed to heat up after which the cooling to the test temperature is much slower, as shown in Fig. 4.

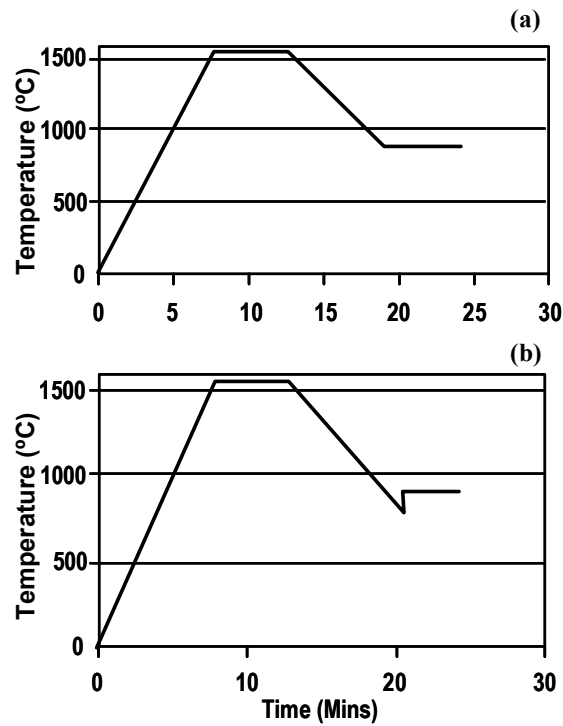


Fig. 2. Thermal schedules used by Spradbery and Mintz, (a) no under-cooling (b) under-cooling.[5]

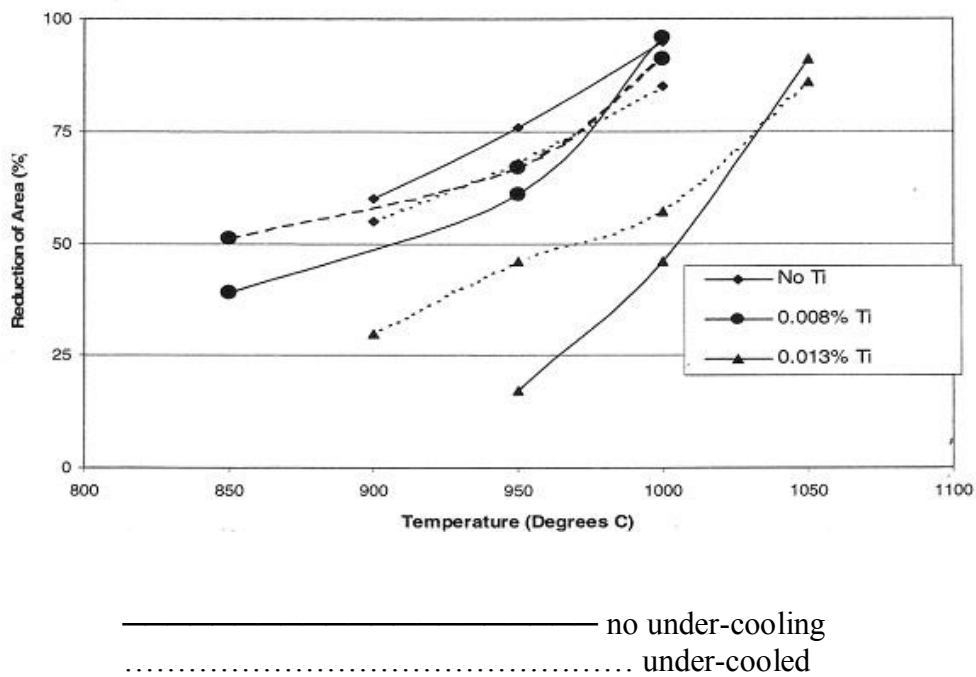
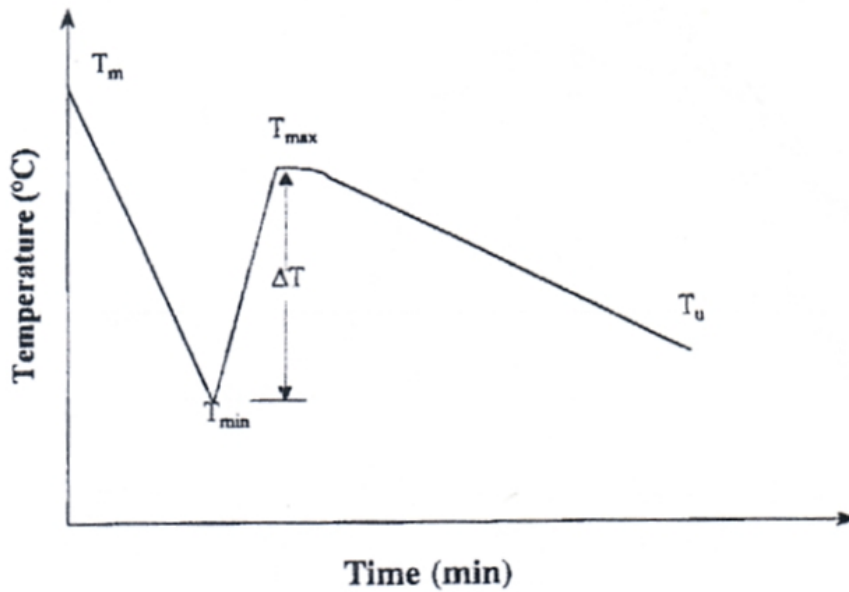


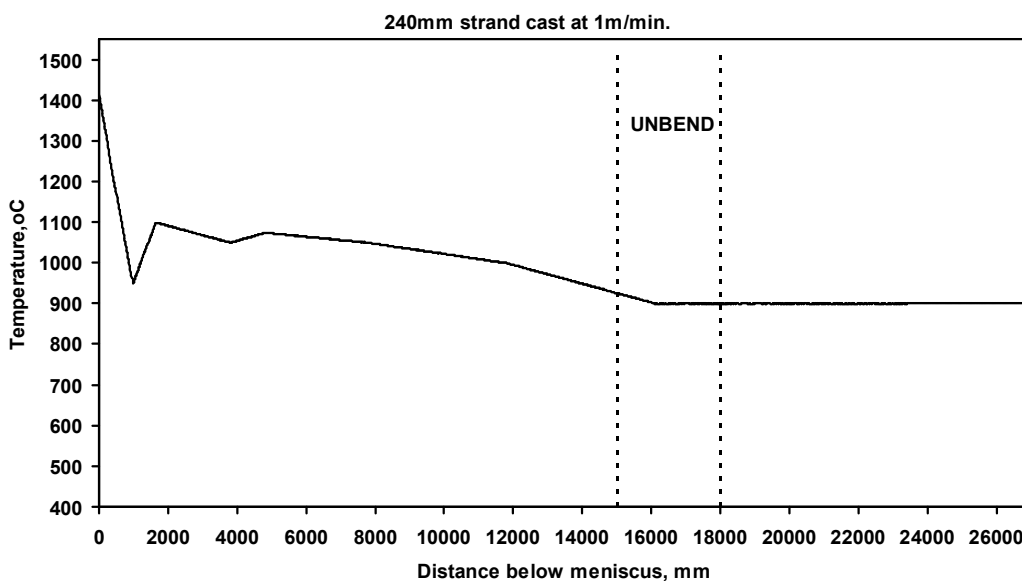
Fig.3. The effect of Ti on the hot ductility of C-Mn-Nb-Al steels with and without an under-cooling step [5]



**Fig.4. Thermal schedule used to generate the thermal condition of billet surface in the continuous casting process.  $T_m$  is the melting point,  $T_{min}$  and  $T_{max}$  are the lowest and highest temperatures, respectively and  $T_u$  is the temperature at the straightener[7].**

In this way by adjusting  $\Delta T$  and the cooling rate in the range from the melting point  $T_m$  to  $T_{min}$  at the foot-rolls and from  $T_{max}$  to the unbending point  $T_u$ , the primary and secondary cooling conditions during continuous casting, can be simulated more accurately in the hot tensile test.

The influence of Ti on the hot ductility of C-Mn-Nb-Al steels using such a thermal simulation has formed the basis of this paper.



**Fig.5 Typical Gleeble thermal cycle used to simulate continuous casting of a 240mm strand in this work**

## Experimental

The compositions of the steels examined, wt. per.cent. are given in Table1.

Table 1.  
Composition of steels examined, wt.per.cent

Steel	C	Mn	Nb	Ti	N	Ti/N	[Nb][N <sub>eff</sub> ] x10 <sup>-6*</sup>
1	.04	1.6	.030	-	.0045		135
2	.03	1.6	.030	.013	.0042	3.10	12
3	.04	1.6	.030	.012	.0077	1.56	105
4	.04	1.6	.016	-	.0062		99
5	.04	1.6	.013	.01	.0044	2.27	19
6	.05	1.6	.015	.01	.0081	1.23	78
7	.04	1.6	.059	-	.0032		189
8	.05	1.68	.033	-	.0082		271
9	.04	1.6	.055	-	.0066		363
10	.05	1.72	.044	.013	.0072	1.81	150
11	.04	1.6	.046	.036	.0048	7.50	0
12	.166	1.35	.020	.016	.0074	2.16	54
13	.150	1.50	.020	-	.0070		140

$$*N_{\text{eff}} = N_{\text{TOT}} - \text{Ti}/3.42$$

The low C steels, steel 1-11 in the table had very low Al levels  $\leq 0.01\%$  so that any detrimental influence of AlN precipitation on the hot ductility would be avoided. The casts were made as 5kgm vacuum casts and the tensile samples were machined from the castings and tested on a Gleeble using the thermo-cooling cycle used in Fig.5.

The cooling rate to the test temperature for all the tests in which an under-cooling step was not introduced was 300K/min. For the cycle used in Fig.5, the initial cooling rate was 600K/min and the cooling rate from T<sub>max</sub> to T<sub>u</sub> was 12 K/min. The path actually simulates the surface temperature at the mid-width position for 240mm thick strand quite closely, but overestimates the near corner temperatures somewhat (compare Figs 1 and 5)). The majority of this work, (steels 1-11) was carried out on low C, (0.04%C), 1.6%Mn steels having varying Nb levels (0.013-0.059%) and N levels (0.0032 to 0.0082%). Steels 1, 4, 7-9 were Ti free steels with the remaining steels having low Ti additions of 0.01 to 0.013% except for one steel, steel 11 which had a higher Ti addition of 0.036% and Ti/N ratio of 7.5/1. For the low Ti addition, the Ti/N ratio varied between 1.23 and 3.1 but most steels had Ti/N ratios well below 3.5/1, the ratio for the stoichiometric composition for TiN. The last two steels in the table, steels 12 and 13 were higher C steels, 0.15%C, 1.4%Mn, 0.02%Nb containing steels and were commercial casts, one being Ti free and the other having a Ti addition of 0.016%. These two steels had soluble Al levels of ~0.04%.

TEM (transmission electron microscopy) was carried out on carbon extraction replicas from steels 1, 2, 8 and 3, close to the point of fracture to compare the precipitation that had taken place in a Ti free and Ti containing steel after cooling directly to the test temperature( steels 1 and 2) and after under-cooling (steels 8 and 3).

## Results.

### 1) Influence of Nb and N on the hot ductility of Ti free steels without under-cooling.

It can be seen from Fig.6, that for steels having N contents in the range 0.006 to 0.008%, solid line curves, increasing the Nb level from 0.016 to 0.055% causes the ductility to worsen, both the depth and width of the trough increasing. It is also apparent from Fig.6 that increasing the N level in these low C steels from the range 0.003-0.004%(dashed line curves) to the range 0.006-0.008% (solid line curves) also results in a deterioration in the ductility and this is shown by the increasing [Nb][N<sub>eff</sub>] product (Table I) and Fig.6 indicate an increase in the precipitate volume fraction.

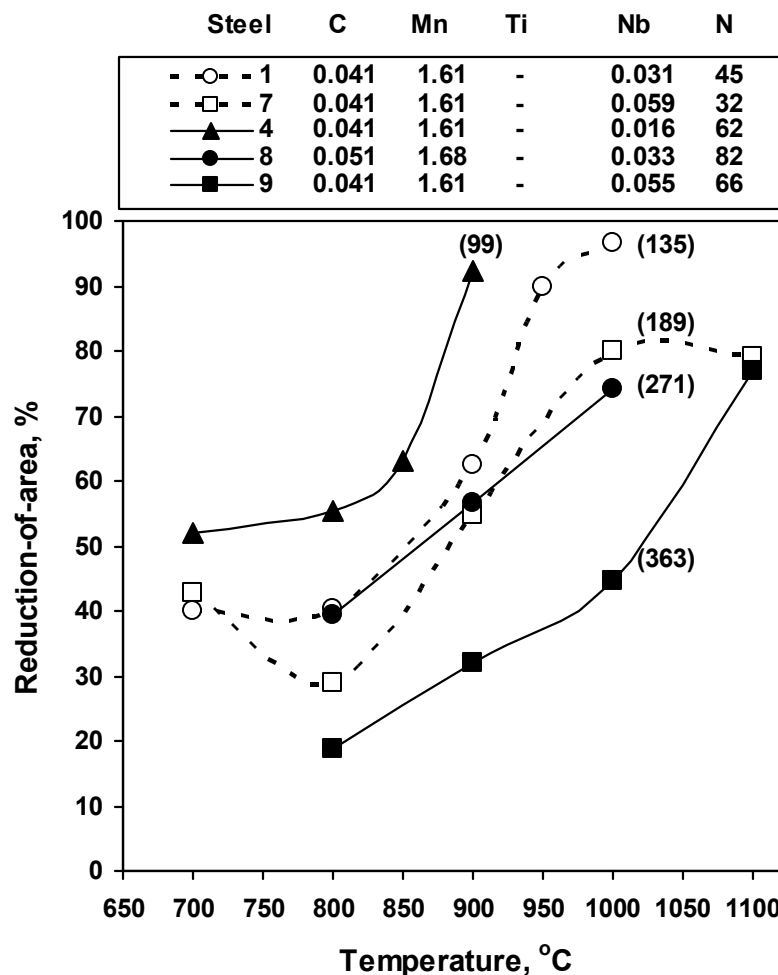


Fig.6. Influence of Nb and N on the hot ductility of a low C, 0.04%C, 1.6%Mn, Ti free steel. The cooling rate that was used was 300K/min. Values in parentheses are the [Nb][N<sub>eff</sub>] x 10<sup>-6</sup>.

## 2). Influence of Ti on the hot ductility of Nb containing steels without under-cooling.

The effect of adding Ti to these Nb containing steels is to make the ductility even worse as shown in Figs.7, 8 and 9 for steels having Nb contents of 0.015, 0.03 and ~0.05%Nb, respectively. Increasing the N level led to worse the ductility as might be expected from the greater volume fraction of precipitates which will be present. When Ti is present, increasing the Nb level seems to make little difference to ductility in the temperature range 700-950°C but above this range there is some indication of ductility actually improving with increase in Nb level, Fig.9.

It is interesting to note that the effect of N in decreasing the R of A values is very marked in the highest Nb containing Ti free steels, Figs.6 and 9. Ductility recovery at the high temperature side of the trough  $\geq 900^\circ\text{C}$  also takes place more rapidly in the low Ti (0.013%), high Nb containing steel, Fig.9. Even the Ti steel with the highest Ti/N ratio of 7.5, steel 11 does not show any improvement in ductility over the Ti free steel 10 of otherwise similar composition, Fig.9. It was also observed that in Ti containing steels, Ti precipitation dominates the hot ductility behaviour and the  $[\text{Nb}][\text{N}_{\text{eff}}]$  product has little influence on the R of A (see bracketed values in Figs 7-9).

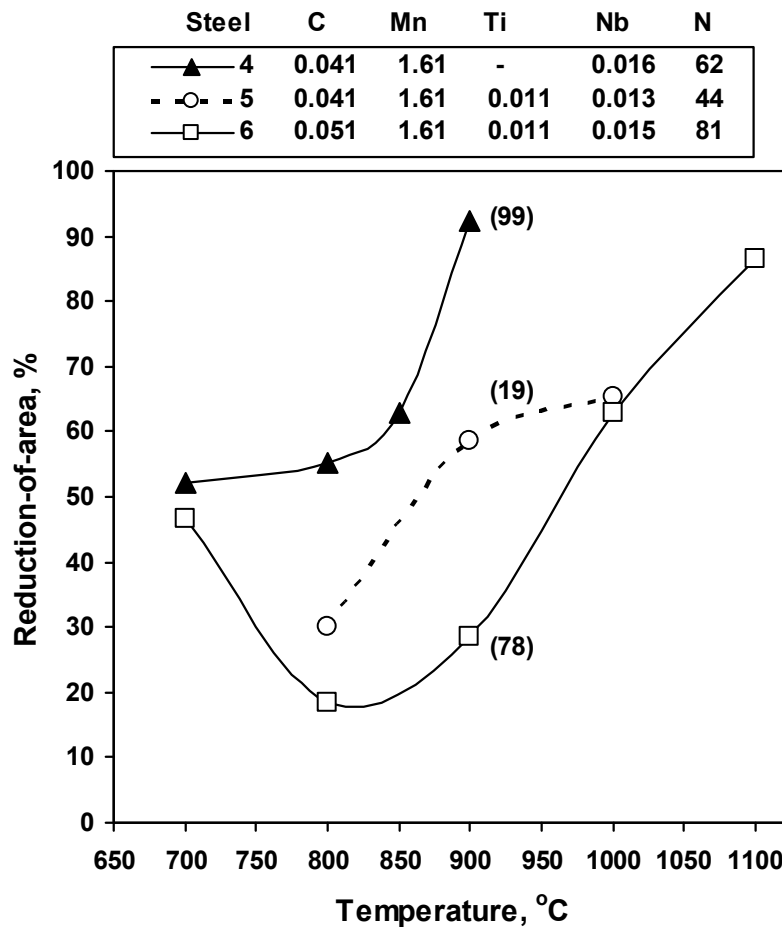
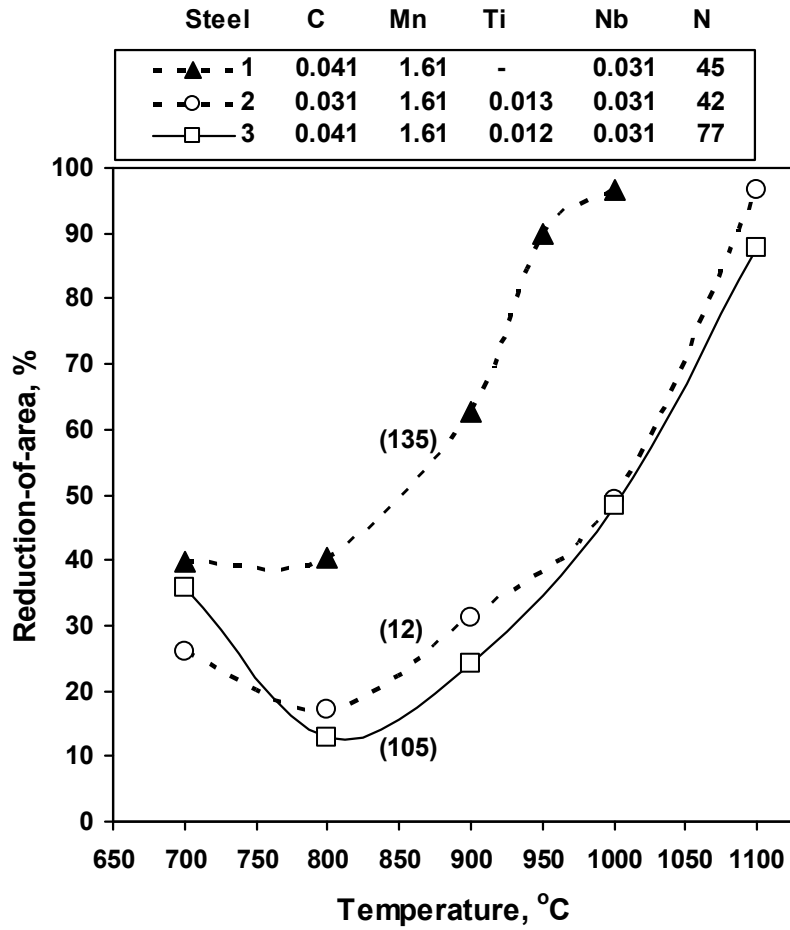
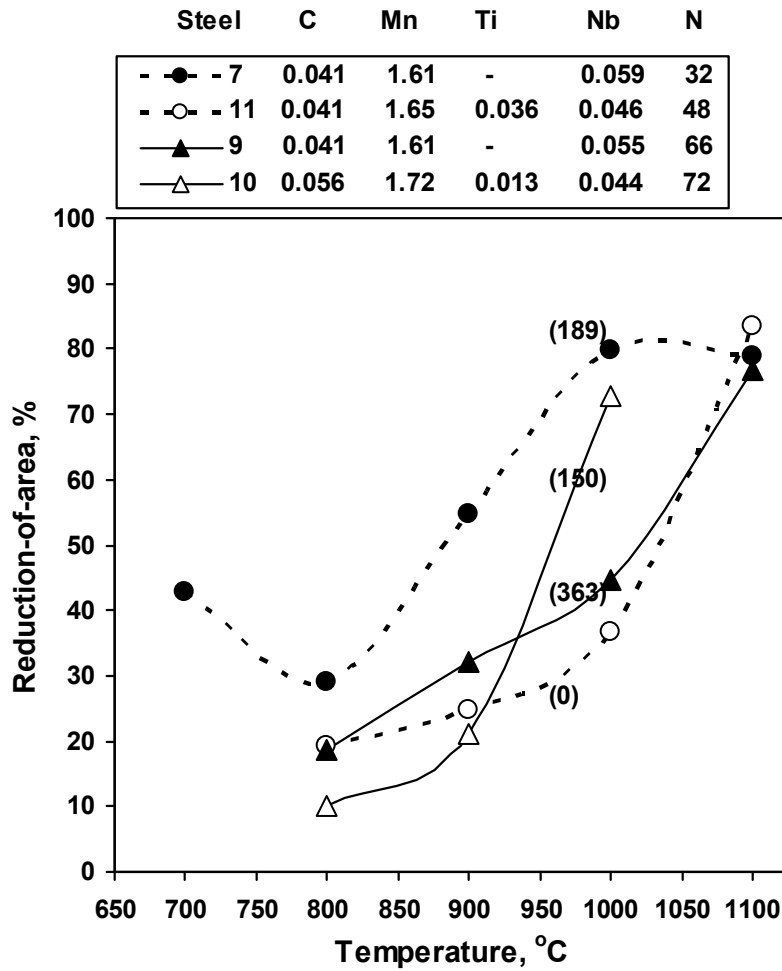


Fig.7. Influence of Ti on steels with ~0.015%Nb. Constant cooling rate at 300K/min. Values in parentheses are the  $[\text{Nb}][\text{N}_{\text{eff}}] \times 10^{-6}$ .



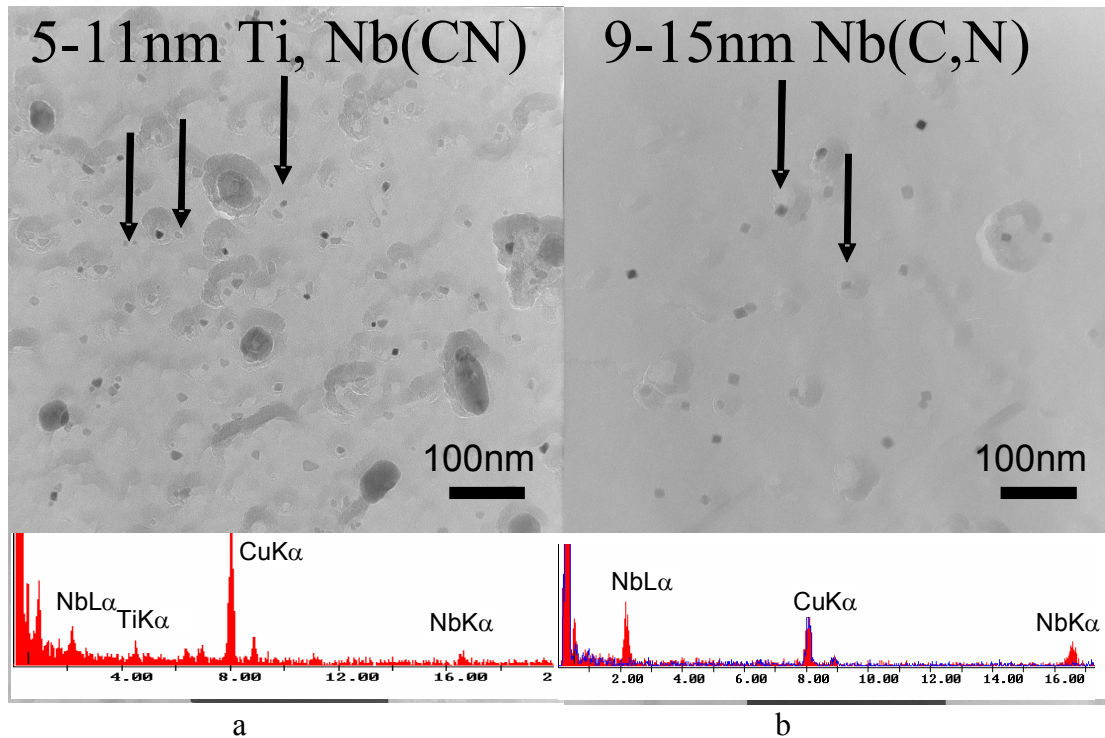
**Fig.8. Influence of Ti on steels with 0.03%Nb. Constant cooling rate at 300K/min. Values in parentheses are the  $[Nb][N_{eff}] \times 10^{-6}$ .**





**Fig.9. Influence of Ti on steels with 0.044 to 0.059%Nb. Constant cooling rate at 300K/min. Values in parentheses are the  $[Nb][N_{eff}] \times 10^{-6}$ .**

A TEM examination was carried out at this stage to see whether the worse ductility shown by the Ti containing steel could be ascribed to changes in the mode of precipitation.



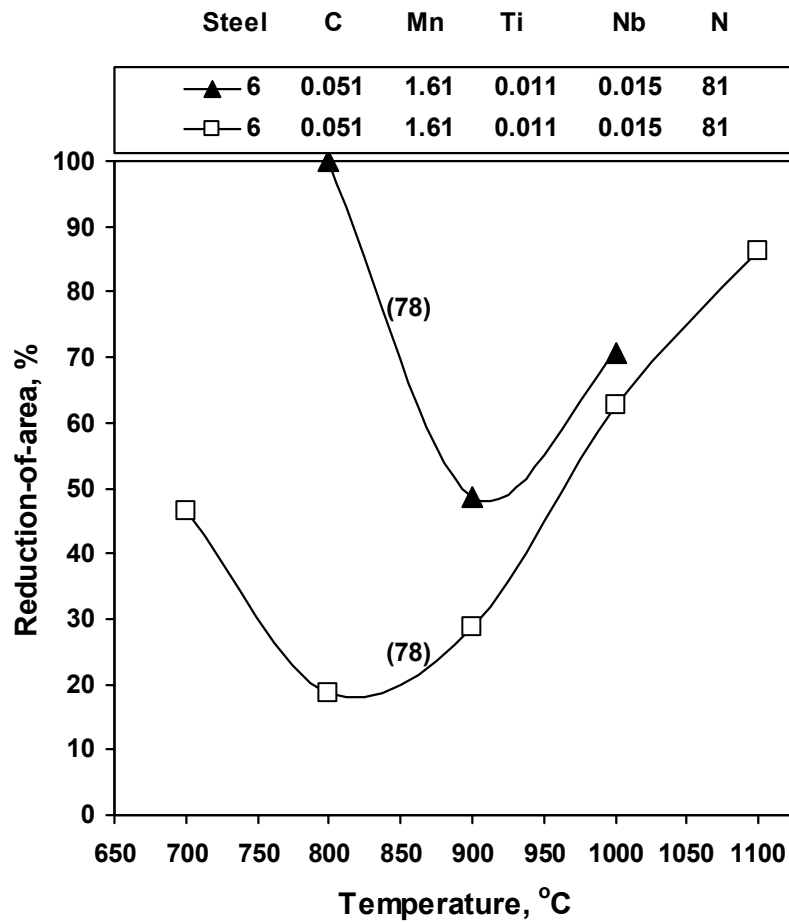
**Fig.10. Precipitation present in a) Ti containing and b) Ti free steels 1 and 2, respectively. The tensile sample was tested at 900°C.**

It can be seen from Fig.10 that adding Ti has resulted in a finer average precipitation size and a greater number of precipitates. For steel 1, the precipitates were Ti Nb(CN) with a size range of 5-11nm and for steel 2, the precipitates were Nb(CN) with a coarser particle size range of 9-15nm.

## **2) Influence of Ti additions on the hot ductility of Nb containing steels with an under-cooling step**

The inclusion of an under-cooling step in the thermal programme for the Ti containing steels as in Fig.5 results in the ductility improving and this can be quite marked as shown in Figs.11, 12 and 13 for steels with 0.015, 0.03 and 0.045-0.055%Nb, respectively. At the lowest Nb level, Fig.11, the improvement in ductility on adding Ti is very marked, and the R of A values always exceeds 45% for the temperature range 750-950°C and the trough is narrow. For the Ti free, 0.03%Nb containing steel, steel 8, Fig.12, under-cooling causes the ductility to deteriorate for temperatures  $\leq 950^{\circ}\text{C}$  but for the Ti containing steels, ductility improves a small amount on under-cooling. However, it should be noted that for these low Ti containing steels, Fig 12 even with the marked improvements that occur on under-cooling, the ductility is still only slightly better than for the Ti free steel and then only in the temperature range 800-900°C. At the 0.036%Ti level, steel 11, (Ti/N ratio of

7.5), Fig.13, the improvement is much more, the R of A value being 60% for temperatures in excess of 800°C. This steel also shows a marked improvement in ductility over a Ti free steel of otherwise similar composition, Fig.13. The hot ductility curves for the higher Nb containing steels ( $\geq 0.03\%Nb$ ) are summarised in Fig.14 and it can be seen that by adding Ti, the R of A values comfortably exceed the 40% R of A value required to avoid transverse cracking.. It is noticeable that for these steels increasing the  $[Nb][N_{eff}]$  product again leads to worse ductility, Fig.14.



**Fig.11. Influence of under-cooling on the hot ductility of 0.015%Nb containing steels. Values in parentheses are the  $[Nb][N_{eff}] \times 10^{-6}$ .**

Closed: industrial cycle, Open; constant cooling rate of 300K/min

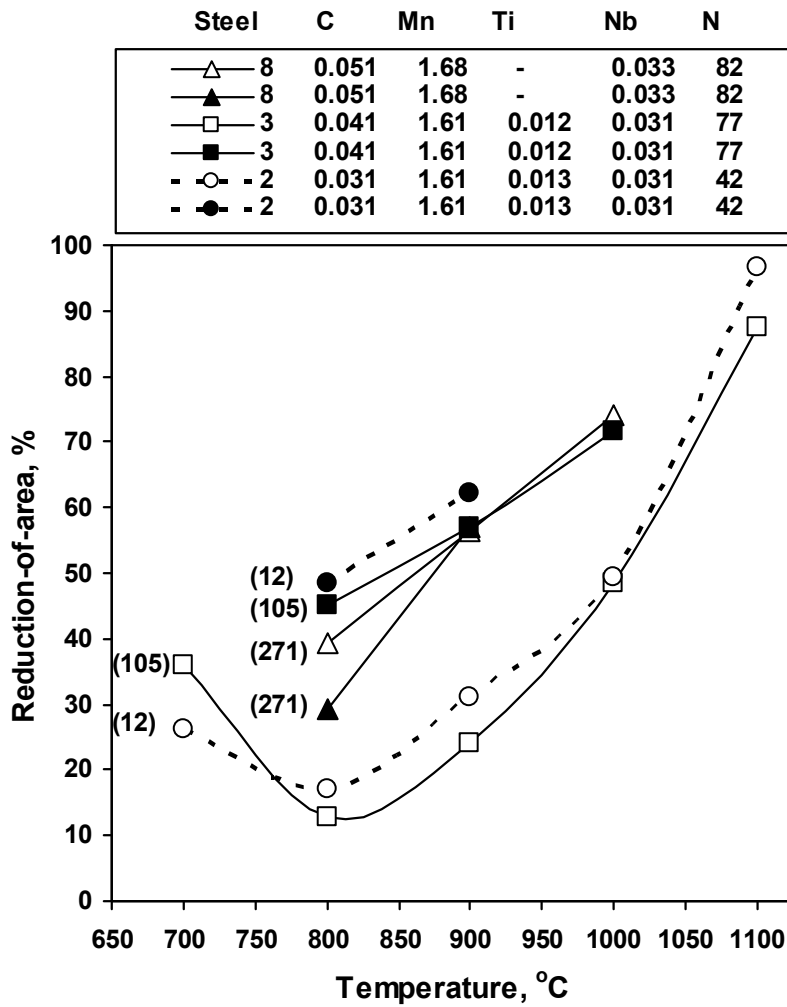
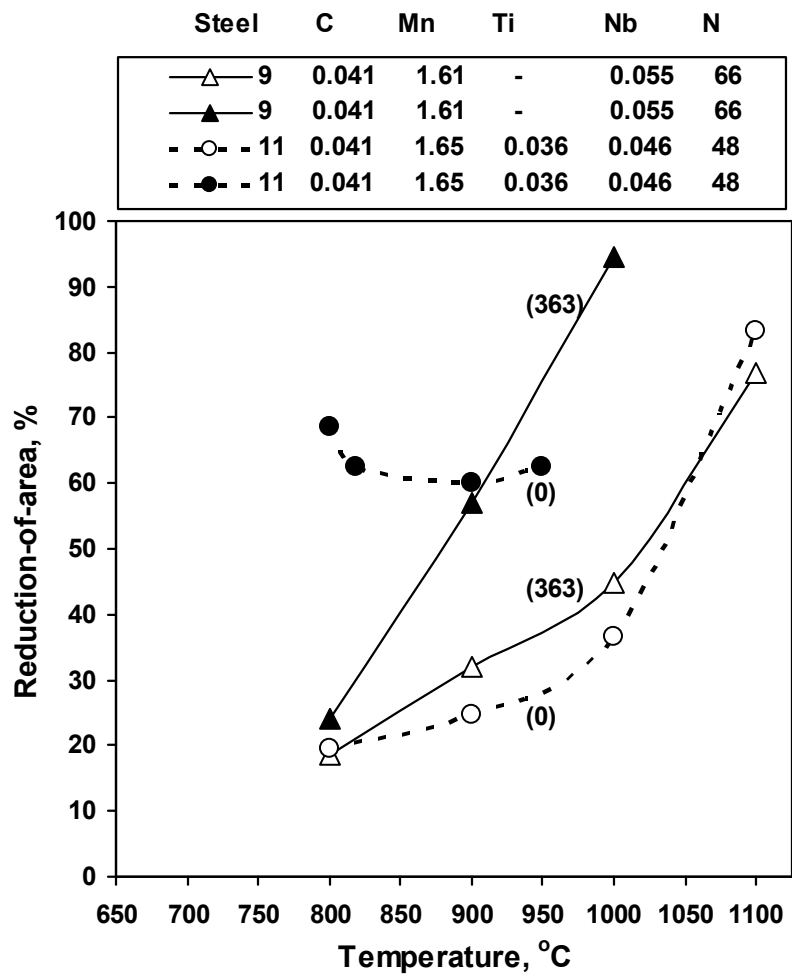
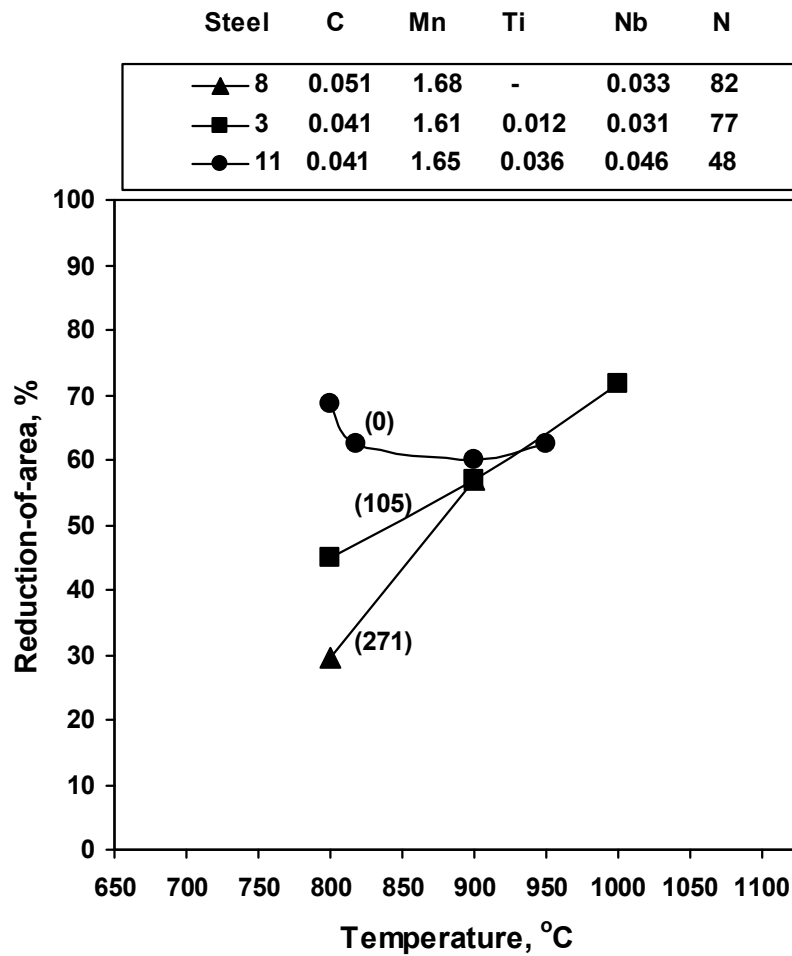


Fig.12. Influence of an under-cooling cycle on the hot ductility of 0.03%Nb containing steels with and without a Ti addition. Values in parentheses are the  $[Nb][N_{eff}] \times 10^{-6}$ . Closed: industrial cycle, Open: constant cooling rate of 300K/min



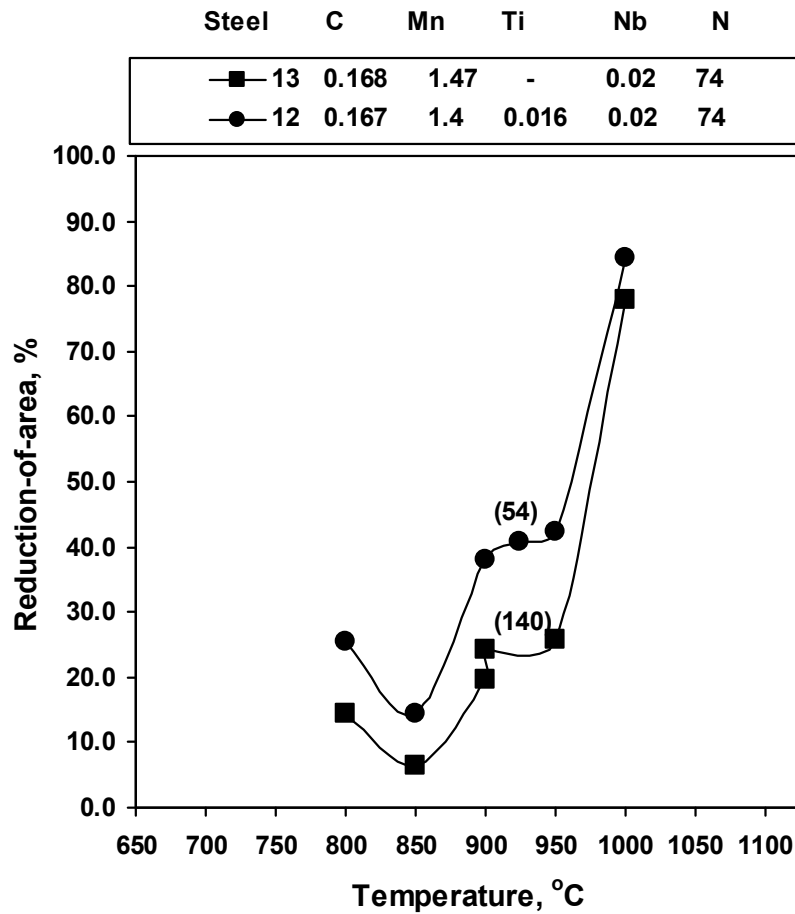
**Fig.13. Influence of under-cooling on the hot ductility of high Nb containing steels (0.046-0.055%Nb). Values in parentheses are the  $[Nb][N_{eff}] \times 10^{-6}$ . Closed: industrial cycle, Open: constant cooling rate of 300K/min.**



**Fig.14. Improvement in hot ductility when a commercial cycling treatment is introduced on cooling after melting for Ti-Nb containing steels. The steels were low C, 0.04%C, 1.6%Mn steels having Nb levels of 0.03 to 0.046%. Industrial cycles. Values in parentheses are the  $[Nb][N_{eff}] \times 10^{-6}$ .**

**3) Influence of Ti on the hot ductility of a higher C, Nb containing steel, (0.16%C) in the peritectic C range given an under-cooling step.**

The results of most interest in the present work are shown in Fig.15. Here the hot ductility of an ~0.15%C, 1.4%Mn, 0.02%Nb containing steel which is notoriously difficult to cast without transverse cracking occurring is given in association with a similar steel having a small Ti addition of 0.016%. It can be seen that the hot ductility of the Ti containing steel is better than the Ti free steel throughout the temperature range 800-950°C. More importantly, in the temperature range  $\geq 900^\circ\text{C}$ , the R of A values are ~ 40% which is the value required to avoid the transverse cracking problem [1]. The influence of Ti and V in peritectic Nb containing steels will be the subject of a later paper.



**Fig.15. Influence of a commercial cycling treatment on the hot ductility of C-Mn-Nb, Ti containing steel of peritectic C content after melting showing that a Ti addition is now beneficial to ductility. Values in parentheses are the  $[Nb][N_{eff}] \times 10^{-6}$ .**

## Discussion

### Nb containing Ti free steels tested conventionally with no under-cooling

Dynamic precipitation is very rapid in Nb containing steels and their poor ductility is ascribed to a combination of extensive matrix and  $\gamma$  grain boundary precipitation and the tendency to form precipitate free zones which lead to strain concentration at the boundaries [1]. Nb also has a powerful influence in decreasing the  $A_{r3}$  so widening the trough at the low temperature end [1].

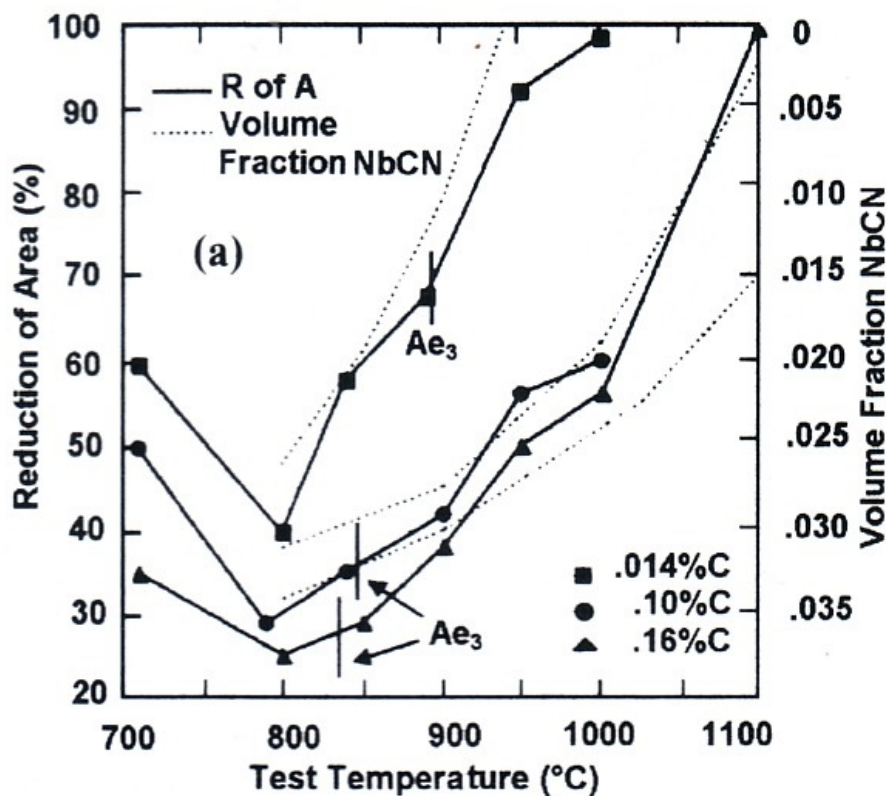
Static precipitation of NbCN in a 0.16%C steel starts after 1s at 950°C [8] and Jonas and Weiss [9] have shown that dynamic precipitation can be complete in about 100s at 900°C, the temperature corresponding to that for the maximum rate of precipitation. Nb is of course added for its ability to refine the  $\gamma$  grain size and provide precipitation hardening so that high strength and toughness can be achieved in the final product but the same precipitation of Nb(CN) which causes these desirable qualities also make it

difficult to cast these steels. Previous work [3 and 4] has concentrated on Nb additions in the range 0.015 to 0.03% but higher strength steels which can be control rolled to replace the conventional quenched and tempered route are now being produced which have lower C contents and require greater amounts of Nb and hence the hot ductility behaviour of such steels is needed to define the conditions which will give freedom from transverse cracking.

### Influence of C and N on Nb containing Ti free steels

The present work has concentrated on the influence of Nb and Ti on low C steels. Although there has been considerable work on the influence of these elements on steels with C contents in the range 0.10 to 0.16% (the peritectic range) there has been limited work on steels with low C levels.

Ouchi and Matsumoto [10] have shown that for Nb containing Ti free steels, having 0.03% Nb and N levels of ~0.005%, decreasing the carbon level improves the ductility as it controls the volume fraction of the detrimental NbCN precipitation. However, above the 0.1%C level, Nb only has a further small detrimental influence on hot ductility.



**Fig.16.** Hot ductility curves for C-Mn-Nb –Al steels(solid lines) and calculated curves of the volume fraction of Nb(CN) precipitated as a function of the test temperature assuming equilibrium is achieved (dotted lines) [11].

The hot ductility curves from previous work [11] for a series of steels with 0.03%Nb at three carbon levels which were solution treated at 1330°C and cooled at 60K/min to the test temperature are shown in Fig.16 and it is interesting to note that as in the



present investigation, the minimum ductility occurs at 800°C which is below the temperature for the maximum rate of precipitation (900°C). It was suggested in this previous work[11] that not only was precipitation of Nb(CN) reducing the ductility but the presence of a thin film of ferrite at the  $\gamma$  grain boundaries was also contributing to the poor ductility. Included in this figure is the calculated volume fraction of NbC assuming equilibrium conditions are achieved during the tensile test and the shape of these curves can be seen to follow closely the shapes of the hot ductility curves. The benefit of working at a low C level is clearly shown. However, in the present work, it can be seen from Fig.6 that a lot of this benefit is lost when the nitrogen level is raised particularly for the very high Nb containing steel, steel 9.

Ouchi and Matsumoto have suggested that of the two precipitates NbCN and NbC, the former is the most detrimental to hot ductility as it precipitates high up in the  $\gamma$  whereas NbC precipitates at lower temperatures and although detrimental, precipitates at temperatures which are below that used normally for straightening. Increasing the N would favour precipitation of NbCN and it is interesting to note that it is the higher end of the ductility trough which is most affected when the N level is increased, Fig.6. For the Ti free (0.04%C) steels ductility is seen to deteriorate as the  $[Nb][N_{eff}]$  product increases, Fig.6 and more precipitation of the fine detrimental NbCN then takes place.

#### . C-Mn-Nb-Al-Ti steels given no under-cooling

The  $[Nb][N_{eff}]$  product is very significant in the absence of Ti but less important in Ti bearing steels, Figs7-9. Presumably increasing the Ti level decreases the product of  $[Nb][N_{eff}]$  favouring less precipitation of the finer more detrimental CN precipitation but the improvement in ductility from this source is balanced by the detrimental influence of having the finer more densely populated precipitation that occurs on adding Ti, Fig.10.

The Ti and N levels which are believed to reduce cracking in the higher C-Mn-Nb-Al-Ti steels taken from the previous work based on tensile tests in which there was no under-cooling[3,4] can be summarised as follows:

- 1) The stoichiometric composition for TiN should in general be avoided as this corresponds to both the greatest volume fraction of TiN but also the finest particle size. It is generally found that the coarser the precipitation the better the ductility [1].
- 2) For low N steels (0.005%) where the particle volume fraction is limited, high Ti/N ratios such as 6/1 should be aimed at so as to remove the N as TiN and more importantly give coarse particles.
- 3) For high N steels (0.01%) a small addition of Ti, (0.015%) should be made so as to limit the volume fraction of precipitates. The high  $[Ti][N]$  will favour precipitation at higher temperatures leading to coarse precipitation.
- 4) For Nb free C-Mn-Al-Ti steels, the Al level should be kept as low as possible for steels having less than the stoichiometric value so as to limit the detrimental precipitation of AlN (AlN has been found to be more detrimental to ductility than TiN because it precipitates preferentially at the  $\gamma$  grain boundaries). However, no influence of Al level could be found for the C-Mn-Nb-Al steels with 0.1%C and 0.03%Nb.
- 5) Cooling rates should be as slow as possible to help coarsen the precipitates.

- 6) Precipitates coarsen as the test temperature increases so that straightening should be carried out at the highest possible temperature.

For Ti to improve the ductility of Nb containing steels it is not sufficient to remove all the N in a coarse form as TiN, since the detrimental influence of Nb has also to be assuaged. Turkdogan [12] has suggested that the way to achieve this is to ensure coarse TiN particles are produced which can act as nucleation sites for the precipitation of Nb. There is also the possibility that if all the N is combined in Ti rich compounds prior to deformation then precipitation of Nb can only take place as the carbide and this doesn't take place until low temperatures, below that used for normal straightening.

Although these recommendations for reducing cracking could be made on the basis of this past work in which no under-cooling had been used, it should be noted that Ti additions were generally found to be very detrimental to ductility [4] and on the basis of the un-cycled results could not be recommended.

Similar results have been found in more recent work by Luo et al [13] who examined the influence of Ti/N ratio on the hot ductility of a 0.15%C, 1.4%Mn, 0.03%Nb, low N (0.005%) steel having Ti/N ratios of 0, 2.6 and 6.4. Hot tensile testing of in situ melted samples, led to a large volume fraction of fine strain induced precipitates at temperatures as high as 1000°C seriously impairing ductility. An increase in the Ti level led to even worse ductility. Two cooling rates, 24K/min and 240K/min were examined. The slower cooling rate improved ductility due to the coarser precipitation but ductility was still worse than that shown by a Ti free steel of otherwise similar composition. In the earlier work of Comineli et al [4] in which no under-cooling was used a large number of similar steels having a wide range of Ti/N ratios were examined and only three Ti containing, Nb steels gave better ductility than the Ti free Nb containing steels of similar composition. These were 1) a low N steel (0.004%N) with 0.02% Ti which had surprisingly the stoichiometric Ti/N ratio (3.5/1). This gave good ductility presumably because of the relatively low volume fraction of precipitates from the low N level and the use of a slow cooling rate of 25K/min, 2). A higher N steel, 0.008% with 0.02%Ti (Ti/N ratio of 2.5) whose higher [Ti][N] product would favour precipitation at high temperatures combined with again a slow cooling rate of 25K/min to encourage coarse precipitation. 3) Finally a steel with a high Ti/N ratio of 8/1 (0.045%Ti, 0.0056%N) which gave slightly better ductility than the Ti free steel, even at the faster cooling rate of 200K/min.

The present results on lower C steels in which the under-cooling step is absent again fits in with the past work in that a Ti addition could not be recommended to improve ductility. The ductility was indeed always seriously impaired. Even at the high Ti/N ratio of 7.5, ductility was very poor on adding a Ti addition, Fig.9. The cooling rate in the present work is such that the particles are always sufficiently fine to have a powerful detrimental influence on ductility, Fig.10a.

### **C-Mn-Nb-Ti steels given an under-cooling step**

The present work has clearly shown that for Ti containing steels when a cooling procedure closer to that being used in the continuous casting operation is applied, substantial improvements in ductility occur, Figs.11-13. Nevertheless, in the case of the 0.01%Ti addition only a very small overall improvement in ductility occurs over that given by a Ti free steel. However, for the steel with a high Ti/N ratio, 7.5/1, a

substantial improvement in ductility occurred in the temperature range 800-900°C with the R of A value being ~60%, Fig.13.

To explain these results it should be noted that there were no apparent differences in the grain sizes between the Ti and Ti free steels, whether in the under-cooled or directly cooled rate tests. Thus, of the factors that can influence ductility (grain size, precipitate size and volume fraction), grain size is not responsible for the difference in the ductility. Preliminary TEM work (this work is to be published more fully in another paper) has shown that under-cooling coarsens the precipitates (25-35nm) both for Ti free and Ti containing steels even at as low a test temperature as 800°C and this would account for the generally beneficial effect of under-cooling in this work. This was found to be so also in Luo et al's work [13] although surprisingly this did not result in any improvement in ductility. Koethe [15] has also shown there is a marked influence on the holding time at 900°C before deformation on the precipitate size of TiN particles in pure iron; particles growing in size from ~10nm after 5s to 20nm after 30s.

However, to account for the benefit of adding Ti, the present work strongly suggests that the improvement in ductility shown by the Ti containing steels on under-cooling is due to two causes: 1) the slow secondary cooling rate (12K/min) allowing the precipitates to coarsen so that the Ti(Nb)CN precipitates reach a size  $\geq 20\text{nm}$ , a size which has been shown to be so coarse as to no longer have any influence on the hot ductility [1]. 2) however, the remaining N in solution ( $N_{\text{eff}}$ ) can then precipitate under deformation as a fine detrimental precipitate. The higher the value of  $[N_{\text{eff}}]$  the worse will be the ductility. When there is no Ti, all the N is available to precipitate out in this fine form on deformation and so the ductility is poor. As the Ti/N ratio increases the amount of fine precipitation decreases and ductility improves. This can be seen from Fig.14, the ductility below 900°C decreasing with increasing  $[\text{Nb}][N_{\text{eff}}]$  product and decreasing Ti content in the following order; steels 11,3 and 8, while the corresponding  $[\text{Nb}][N_{\text{eff}}]$  product increases from 0,  $105 \times 10^{-6}$  and  $270 \times 10^{-6}$ .

Clearly more electron microscope work is required to confirm this theory but if the theory is correct, then when the secondary cooling conditions are slow so that coarse precipitates are formed as in the present instance, the optimum ductility would be achieved when the stoichiometric ratio for TiN is reached and all the N is combined with the Ti.

The application of this under-cooling step to the only higher C steel (0.15%C) examined, Fig.14, has given even more encouraging results indicating that a Ti addition of 0.016% is very beneficial giving rise to improved ductility over the Ti free steel, lifting the ductility in the temperature range 900-950°C to give an R of A value of ~40%, the value needed to avoid transverse cracking [1]. Clearly more work is required on these steels to obtain the optimum Ti/N ratios and it is likely the previous recommendations based on direct cooling to the test temperature will have to be revised. Previous work [5] on introducing an under-cooling step as in Fig.2 has not been found to give such promising results. In Spradbery and Mintz's work on higher C (0.1%C), Nb containing steels, under-cooling was again found to be very beneficial as in the present work, Fig.3 for Ti additions in the range 0.008 to 0.013% but only the steel with 0.008%Ti gave a marginal improvement in ductility over the Ti free steel and then only in the temperature range 800-900°C. Higher Ti/N ratios were not examined so on the available data the agreement between their work and the present is reasonably close. It might be expected that if the cooling programme did not include a separate secondary cooling stage so that the cooling rate was 100K/min rather than

the 12K/min as in Fig.5, precipitates would not be able to coarsen leading to worse ductility.

This is shown in Luo et als work [13], in which an under-cooling step was introduced. Introducing an under-cooling step to their 0.1%C, 1.4%Mn steels having Ti/N ratios of 0, 2.6 and 6.4 resulted in little difference in ductility behaviour even surprisingly in the steel with the highest Ti/N ratio. Their cooling regime was similar to that used by Spradbery and Mintz in Fig.2 and not the cooling regime in which two different cooling rates, a fast rate to represent primary and a slow rate for the secondary cooling as used in the present exercise, Fig.4. However, a relatively high cooling rate of 240K/min was used compared to the 100K/min used in Spradbery and Mintzs' work. On the basis of their results Luo et al concluded that Ti additions would only be beneficial when added to electric arc steel at a low Ti level so that the volume fraction of precipitates would be limited and the high Ti/N ratio would encourage coarse precipitation at higher temperatures.

It is likely that cycling coarsens the precipitates so improving ductility. However, the notion of Ti additions being of benefit only to electric arc steel, although a reasonable conclusion to make from Luo et als' work [13], goes against the substantial commercial evidence and the present results which indicate Ti is a good element to add to prevent transverse cracking even in low N steels.

### **Importance of Al**

When Ti additions are in excess of the stoichiometric composition for TiN (3.5/1), all the N is combined in the form of Ti rich nitrides. Ti always combines preferentially with N and further cycling does not lead to any more precipitation. Indeed, the evidence is that cycling leads to the growth of TiN and Ti/Nb particles improving the ductility even more, so that under appropriate conditions Ti additions can be beneficial. In Nb free steels, when there is insufficient Ti to combine with all the N, the remaining free N combines with the Al. AlN precipitates sluggishly and at lower temperatures and is finer. More importantly, AlN precipitates preferentially at the  $\gamma$  grain boundaries, which is more detrimental to ductility. Further precipitation occurs on cycling making the ductility even worse. Some caution should therefore be used in generally applying the present results to commercial practice as the low C steels all contained a very low Al addition. Nevertheless, in Comineli et als work[3,4] it was found that for Ti containing steels both increasing the Al and the Nb contents appeared to have little influence on the hot ductility. This is in contrast with the present work which clearly shows that Nb additions to a Ti containing steel leads to worse ductility. The reason for this difference in behaviour may be related to the lower C level (0.04) in this exercise compared to 0.1%C in Comineli's work). It was also found that on adding Nb to a Ti containing steel, the NbCN particles were coarser than in a Ti-free steel. Thus the expected deterioration in ductility from an increased volume fraction of precipitates from having both Nb and Ti present was balanced by Nb causing the precipitation to occur at higher temperatures [4] and hence be coarser. Similar reasoning may also apply to Al when present with Nb [14,15]. In the present work the steels had only a very low Al addition which would be unlikely to influence the results but the higher C steel did have Al present and there is no indication that it is having any influence on the hot ductility of the Nb-Ti containing steel. Nevertheless, the low Al addition made to the low C steels may be influencing the results and

further work is required into establishing the influence of Al on these C-Mn-Nb-Ti containing steels.

## Summary

Obviously the actual R of A value obtained will depend very much on the cooling rates that have been chosen and increasing the secondary cooling conditions would be expected to reduce the ductility and may not lead to a sufficient coarsening of the precipitates to give a chance for the Ti addition to improve ductility. The thermal programme chosen has been based on one particular continuous casting simulation. Nevertheless, the results indicates that to obtain meaningful results that can be used commercially for Ti containing steels to avoid transverse cracking a thermal programme of the type shown in Fig 5, needs to be applied. Even this is of course is an approximation of the real cooling conditions that the strand undergoes and the temperature cycling that occurs as the strand enters and exits the rolls should ideally also be incorporated in the thermal programme but this is difficult to practically simulate in the laboratory.

The present work has shown that when a cooling programme is chosen which is closer to the continuous casting situation, then Ti additions can indeed improve the ductility.

## Conclusions

1. In low C, 0.03-0.05%C steels, increasing the Nb or N level leads to a deterioration in ductility as increasing the product of  $[Nb][N_{eff}]$  results in more fine precipitation taking place.
2. The ductility of Ti containing steels when melted and cooled to the test temperature without an under-cooling step is generally very poor due to the finer and more numerous precipitation, that occurs in the presence of Ti.
3. Introducing an under-cooling step and cooling regime similar to that undergone by the strand during continuous casting has been shown for low C low Ti containing, C-Mn-Nb steels to always give rise to an improvement in hot ductility below 900°C which is typical of off-corner temperatures during unbending.
4. In the case of an 0.01%Ti addition this improvement although marked only led to a small improvement in ductility over that for a Ti free steel and then only for the temperature range 800 to 900°C.
5. In a high Nb containing steel increasing the Ti to 0.036% so that the Ti/N ratio was high, 7.5/1, led to much better ductility in the temperature range 800-900°C, the R of A value being 60%. The ductility was considerably better than that of a Ti free steel of otherwise similar composition.
6. For the two higher C, Nb containing steels examined, (0.15%C, 1.5%Mn, 0.02%Nb) a significant improvement in ductility occurred in the Ti bearing steel at 900-950°C; the R of A value being ~40%, the level needed to avoid transverse cracking.
7. This closer simulation of the cooling conditions pertaining to the continuous casting operation has shown that Ti additions can be of benefit in improving the hot ductility at typical off-corner unbending temperatures. However, there

is a need to establish the compositional (Ti/N ratios) and thermal cycles which can give the optimum R of A values.

8. More carbon extraction replica work is also required to fully establish the cause of this improved ductility on under-cooling.
9. In the present work the Al levels were very low which may have led to better than expected ductility for steels with Ti/N ratios less than the stoichiometric for TiN and this also needs to be explored.

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List of figure captions:

Fig.1. Predicted strand surface temperature during continuous casting of 240mm strand cast at 1m/min[6].

Fig.2. Thermal schedules used by Spradbery and Mintz, (a) no under-cooling (b) under-cooling.[5].

Fig.3. The effect of Ti on the hot ductility of C-Mn-Nb-Al steels with and without an under-cooling step [5].

Fig.4. Thermal schedule used to generate the thermal condition of billet surface in the continuous casting process.  $T_m$  is the melting point,  $T_{min}$  and  $T_{max}$  are the lowest and highest temperatures, respectively and  $T_u$  is the temperature at the straightener [7].

Fig.5. Typical Gleeble thermal cycle used to simulate continuous casting of a 240mm strand in this work.

Fig.6. Influence of Nb and N on the hot ductility of a low C, 0.04%C, 1.6%Mn, Ti free steel. The cooling rate that was used was 300K/min. Figures in brackets are the  $[Nb][N_{eff}] \times 10^{-6}$  values.

Fig.7. Influence of Ti on steels with  $\sim 0.015\%$ Nb. Constant cooling rate at 300K/min. Figures in brackets are the  $[Nb][N_{eff}] \times 10^{-6}$  values.

Fig.8. Influence of Ti on steels with 0.03%Nb. Constant cooling rate at 300K/min. Figures in brackets are the  $[Nb][N_{eff}] \times 10^{-6}$  values.

Fig.9. Influence of Ti on steels with 0.044 to 0.059%Nb. Constant cooling rate at 300K/min..

Fig10. Precipitation present in a) Ti containing and b) Ti free steels. The precipitation is finer in the Ti containing steel. The tensile samples were directly cooled to 900°C and strained to failure.

Fig.11. Influence of under-cooling on the hot ductility of a steel with 0.015%Nb containing steels. Closed: industrial cycle, Open; constant cooling rate of 300K/min

Fig.12. Influence of an under-cooling cycle on the hot ductility of 0.03%Nb containing steels with and without a Ti addition. Closed: industrial cycle; Open: constant cooling rate of 300K/min.

Fig.13. Influence of an under-cooling cycle on the hot ductility of high Nb containing steels (0.046-0.055%Nb). Closed: industrial cycle, Open: constant cooling rate of 300K/min.

Fig.14. Improvements in hot ductility when a commercial cycling treatment is introduced on cooling after melting for Ti-Nb containing steels. The steels were low C, 0.04%C, 1.6%Mn steels having Nb levels of 0.03 to 0.046%.

Fig.15. Influence of a commercial cycling treatment on the hot ductility of C-Mn-Nb, Ti containing steel of peritectic C content after melting showing that a Ti addition is now beneficial to ductility.

Fig.16. Hot ductility curves for C-Mn-Nb-Al steels, (solid lines) and calculated curves of the volume fraction of Nb(CN) precipitated as a function of the test temperature assuming equilibrium is achieved (dotted lines) [11].