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Hot ductility of high Al TWIP steels containing Nb and Nb-V

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Abstract

The hot ductility of B-Ti-Nb-high Al (1.5%Al) containing TWIP steels having Ti/N ratios mainly in excess of 3.4/1 was obtained. After soaking at 1250°C, the tensile specimens were cooled at 12 or 60°C/min to the test temperature and then strained to failure at 3×10^{-3}/sec

Ductility was always good (reduction of area>40%), independent of Ti/N ratio or cooling rate. The good ductility is due to B segregation strengthening the grain boundaries and the low S level (0.005%S) limiting the volume fraction of MnS inclusions and restricting AlN precipitation to the matrix.

Increasing the cooling rate, higher N levels and Nb resulted in a small improvement in ductility. An addition of V to the Nb containing steels caused a slight deterioration in the hot ductility.

Key words

TWIP steel, hot ductility, B, Ti, Al, N, Nb, V, MnS.

Introduction

TWIP (Twin induced plasticity) steels offer themselves as very high strength steels with good ductility. They are used in the automotive industry for impact protection structures such as side impact bars, crumble zones and B-pillar members [1,2]. They depend on producing large number of twins on deformation and the elements Si and Al, alone or in combination are required to achieve these good properties. Al is particularly favoured because of its ability to delay fracture in deep drawn products [1,2]. However, these high Al, TWIP steels have been found difficult to continuous cast and considerable work has been carried out in defining the optimum composition for reducing

the likelihood of transverse cracking occurring during the straightening operation [3-8]. The work has shown that a low S and P content (preferably ~0.005%), by reducing the volume fraction of sulphides [5,7] and in the case of P preventing the low melting point iron phosphide phase forming, gives rise to better ductility [7]. More importantly, it is found that a small addition of B is needed so it can segregate to the boundaries and strengthen them [6]. In order for this to occur, the B must remain in solution and be protected by adding Ti to combine with all the N so that BN is prevented from forming. In addition the TiN particles that form need to be sufficiently coarse (>15nm) to no longer influence the hot ductility [9]. Ideally for this to occur, the cooling rate to the straightening temperature has to be slow ≤ 25°C/min [10,11]. Provided enough Ti is added to combine with all the N, high N levels (~0.01%N) can be readily accommodated, this becoming more essential with the increasing use of scrap in the melt and the use of the electric arc furnace for melting. The sulphides have also been found to be places where the B can diffuse rather than in solution at the grain boundaries where it is wanted [12]. Hence this is another reason for having a low S content for the steels examined.

In these high N (0.01%N) steels if the [Ti] x [N] product is increased, the precipitate will come out at higher temperatures and so will be coarser giving better ductility. Although there is more precipitation in the high N steels, provided the cooling rate is sufficiently slow, the particles will be too coarse to influence the hot ductility.

Previous work [8] has chosen a high Ti/N ratio of 6-7:1 so that typically the Ti level would need to be 0.06% in a 0.01%N steel. However, as long as the stoichiometric composition for TiN is attained (Ti/N ratio 3.4:1) all the N can be taken out of solution as TiN, enabling B to segregate un-impedingly to the boundaries. Such a high Ti level may therefore not be needed but one has to be aware that the stoichiometric composition often gives the finest precipitation in HSLA steels (high strength low alloy) leading to poor ductility [11]. Higher Ti levels might, nevertheless be needed to ensure that the precipitates come out at higher temperatures and are hence coarser and any excess Ti in solution will in addition encourage growth [11]. There is a need therefore to establish more clearly the optimum Ti/N ratio for good ductility.

The cooling rate to the test temperature is also important. The cooling rate in previous work [3,5,8] after reheating has generally been 60°C/min, which is higher than the recommended cooling rate of ≤25°C/min needed to coarsen the TiN particles to obtain the maximum ductility or to give the maximum segregation for B to strengthen the grain boundaries [13]. In this exercise two cooling rates, 12°C/min min and 60°C/min have been examined. Since 12°C/min is often the cooling rate for the secondary cooling stage in the continuous casting process, an average cooling rate of 12°C/min, may indeed, as has been shown from recent work [14] be the more suitable for simulating the industrial process.

Previous work [3,5,7] has concentrated on the simpler high Al, TWIP steels giving a room temperature yield strength of 800MPa. However, if a higher strength level is required ~1000MPa, then Nb needs to be added [8]. Nb additions have, unfortunately, been found to give rise to poor ductility in peritectic C, HSLA steels (~0.1-0.2%C) making it more difficult to avoid transverse cracking [15,16]. Adding V has on occasions enhanced the ductility in these HSLA steels because it delays precipitation [17,18]. However, when this was tried in the simpler high Al, TWIP steels, free of Ti or B, the Nb-V combination was found to be detrimental to hot ductility; presumably because it increases the amount of precipitation [4]. Nevertheless, a Nb-V TWIP steel has been included for examination.

The present exercise is concerned with examining the influence of cooling rate, Ti/N ratio, Nb and to a lesser extent Nb-V on the hot ductility of high Al, high N, TWIP steels containing B and Ti.

Experimental

Ideally, to simulate the continuous casting and straightening operation more closely "in situ melting" should be used and two cooling rates, a fast cooling rate for the primary cooling, followed by a slower cooling rate for secondary cooling should be incorporated [14]. However, in-situ melting to obtain a satisfactory tensile specimen, free of porosity and choosing silica tubing which doesn't react with the Ti present in the steel encounters serious practical difficulties, so before embarking on this melting route, the advantages of melting over "reheating," need to be weighed up carefully in advance.

The compositions of the steels examined (wt.per.cent) are given Table 1. In the present instance, except for one steel, Steel 1,the Ti/N ratio was either very close to stoichiometry (ST in Table 1) for TiN (steels 2 and 3) or greater than that of stoichiometry (>ST,Steels 4-7). Once there is sufficient Ti to combine with all the N, it is likely that very little N will go back into solution on re-heating to 1250°C so the condition for steels 2-7 will probably remain close to that present when melted. Reheating was therefore chosen rather than melting but this does put a limit on the applicability of the results to the continuous casting operation.

Table 1. Composition of steels chosen for examination. ,wt.per.cent

Steel	Ti /N ratio	C	Si	Mn	P	S	Al	Ti	Nb	V	B	N
Base 1	2.2	.60	.09	18.2	.009	.003	1.57	.019	.031	-	.0027	.009
ST 2	3.3	.59	.10	17.9	.009	.003	1.56	.022	.031	-	.0027	.007
ST 3	3.0	.60	.09	18.2	.009	.003	1.55	.030	.032	-	.0028	.010
4>ST	5.7	.60	.10	18.3	.010	.0045	1.51	.046	.026	-	.0029	.008
5>ST	6.8	.60	.10	18.0	.010	.006	1.50	.075	.032	-	.0028	.011
6>ST	7.7	.59	.10	18.2	.010	.004	1.51	.074	.033	-	.0028	.010
7,V/Nb ST	6.3	.59	.10	18.1	.010	.004	1.52	.075	.034	*	.0027	.012

*.04%V and ST is stoichiometric composition

The steels in Table 1 were cast as 50kg vacuum melt ingots and air cooled to room temperature. The base composition for all the TWIP steels was 0.6%C, 0.1%Si, 18%Mn, 0.01%N and 1.5%Al. P and S levels were low for all steels, ~0.01 and 0.005%, respectively. The boron level was the same as has been used previously ~ 0.002 to 0.003% [6,8].

Steel 1, Table 1, is the base composition with a Ti level of 0.019% and 0.009%N whose hot ductility curve was to be used for comparison purposes. The steel was the only steel with a less than stoichiometric Ti to N ratio (The Ti/N ratio for the stoichiometric composition for TiN being 3.4).

Steels 2 and 3 are steels made at approximately the stoichiometric composition for TiN. The remaining steels 4-6 were well in excess of the stoichiometric Ti/N ratio for TiN.

Steel 7 was similar to steels 5 and 6 but V had been added to see whether a Nb-V combination gives better ductility than a Nb only addition.

Tensile specimens, 120mm in length and 10mm in diameter were machined from the as cast ingot and tested using a Gleeble. For each temperature, two tensile specimens were tested and the average value of reduction of area (RA) taken.

After casting, the ingot was stripped from its mould and air cooled. The position in the ingot where the tensile specimens were taken from and their dimensions are shown in Fig.1
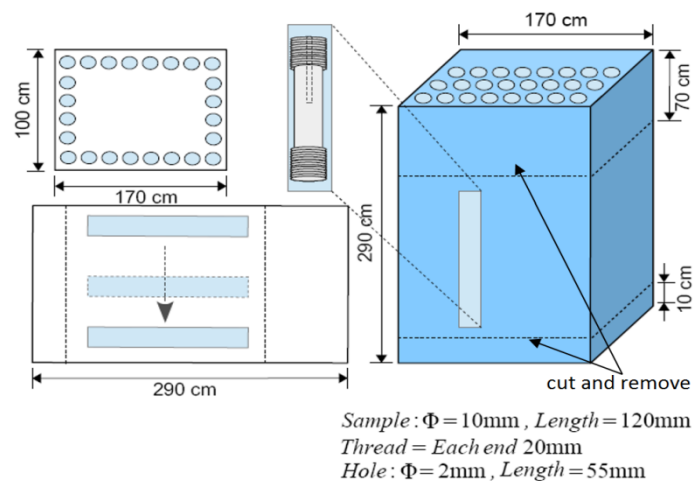

Sample: $\Phi = 10$mm , *Length* $= 120$mm
Thread $=$ *Each end* 20mm
Hole: $\Phi = 2$mm , *Length* $= 55$mm

Fig.1 Schematic diagram showing the dimensions and position that the tensile specimens where taken from in the ingot

The cooling rate to room temperature for the region in the ingot corresponding to where the tensile specimens were taken from is very slow ~1°C/min.

The tensile samples after machining were heated at 150°C min⁻¹ to 1250°C held 3 mins and cooled at 12°C/min down to the test temperatures in the range 1100 to 750°C. Three of the steels, 1, 3 and 5, were also cooled at 60°C/min. After holding for 30 secs, the tensile samples were strained to failure using a strain rate of $3X10^{-3}s^{-1}$. The temperature profile is shown in Fig.2
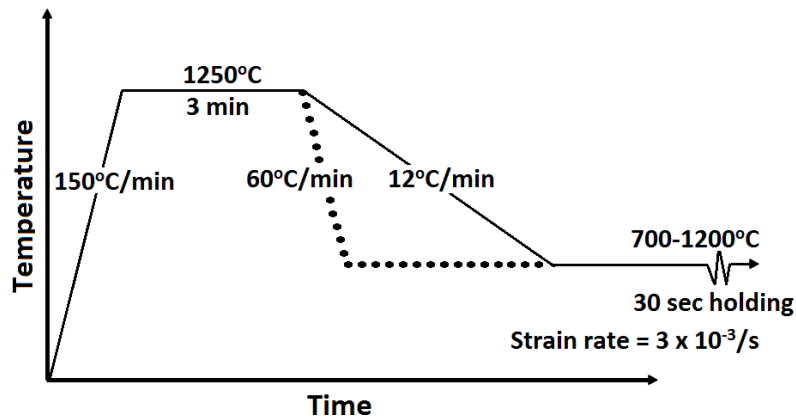

Fig.2 Schematic diagram of heating and cooling programme.

Once a tensile sample had failed it was immediately gas quenched with argon. The reduction of area was plotted against temperature and the hot ductility curves compared. Optical microscopy was carried out on longitudinal sections from the necked down region of the fractured tensile specimens. Scanning (SEM) and Transmission electron microscope (TEM) examinations were made on sections taken close to the point of fracture. For the TEM examination, the carbon extraction replicas were mounted on nickel grids.

Results

The hot ductility curves are shown in Fig. 3, for the steels, 1 to 7 given a cooling rate of 12°C/min from 1250°C. The hot ductility curves for the steels, 3, 5, and 1 cooled at 60°C/min are given in Figs 4, 5 and 6, together with the curves for the slower cooling rate. The points on all these curves are the average of two tests. (±5% scatter)
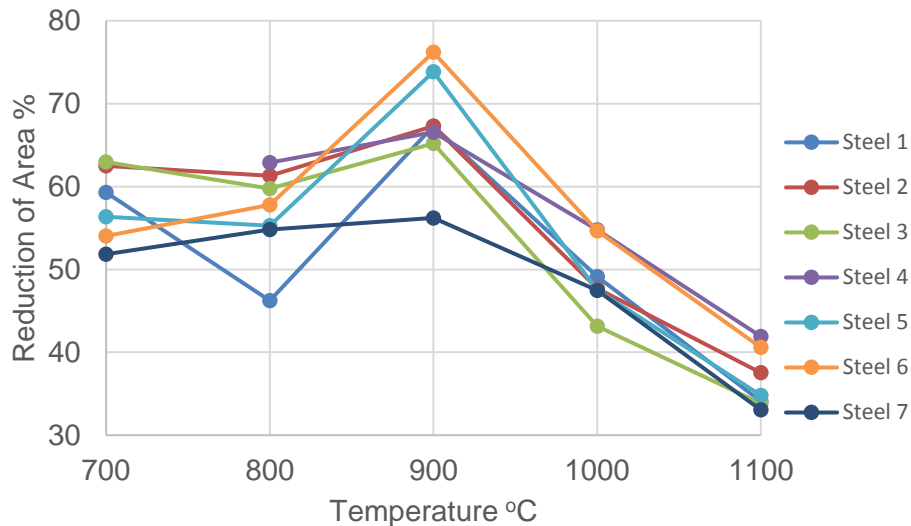
Fig.3 Hot ductility curves for steels in Table 1 cooled from 1250°C at 12°C/min

Hot ductility curves for tensile specimens cooled at 12°C/min

Except for steel 1 and steel 7, the latter containing V, the hot ductility curves for all the steels in Fig.3, cooled at 12°C/min are similar in shape, independent of the Ti/N ratio. In the temperature range 700-800°C the ductility was approximately constant (55%RA). As the temperature increased to 900°C, the ductility improved reached a peak (65-75%RA) and then fell and at a 1000°C was about 50%RA. The ductility for the Nb-V steel, steel 7, although being in excess of 40%RA (that generally needed to avoid transverse cracking) was the worst of all the steels and did not show a peak in ductility, remaining constant ~55% from 700 to 900°C and then decreased with further increase in temperature. Steel 1 in contrast to the other steels showed a minimum RA at 800°C of 46% RA.

Hot ductility curves for tensile specimens cooled at 60°C/min

At the faster cooling rate, 60°C/min the hot ductility curves, Figs 4, 5, 6 all behaved in a similar manner giving surprisingly higher RA values than at the slower cooling rate, about on average, 10% higher for steels 3 and 5, respectively. Whereas at the slower cooling rate, there is a tendency for the hot ductility curves to dip at 800°C, Fig. 3, this being most marked for steel 1, this behaviour was absent at the faster cooling rate, Fig.6.
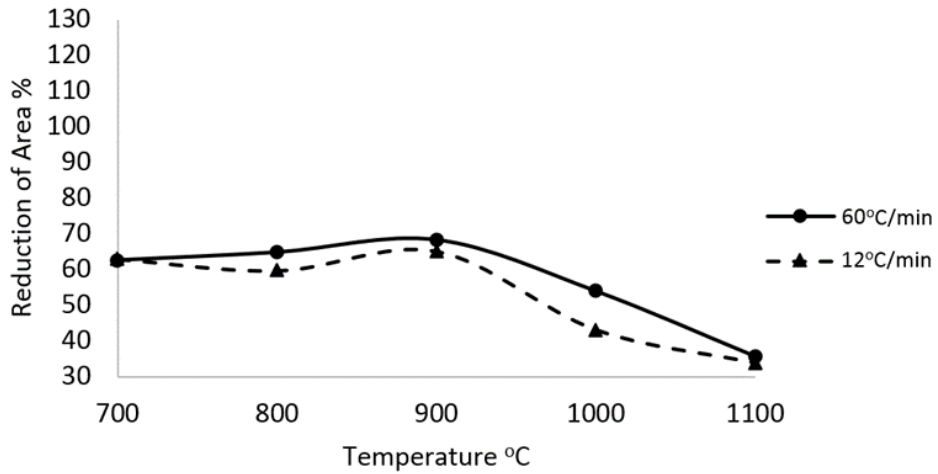
Fig. 4 Hot ductility curves for steel 3 for cooling rates of 12 and 60°C/min., after reheating to 1250°C, ductility being slightly better for the faster cooling rate.
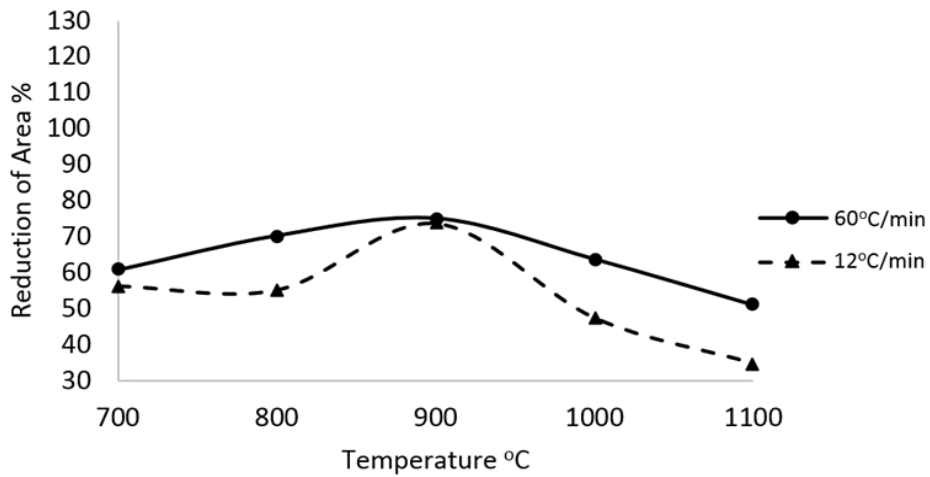

Fig.5. Hot ductility curves for steel 5 for the cooling rates 12 and 60°C/min, after reheating to 1250°C.
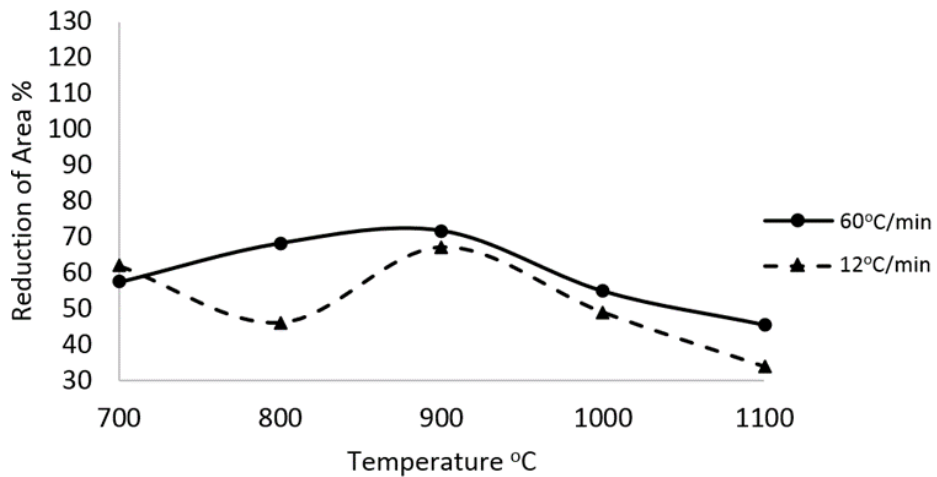

Fig.6 Hot ductility curves for steel 1, cooled at the two cooling rates, 12 and 60°C/min.

Nevertheless, because of the general similarity in the hot ductility curves of the Nb containing steels, steels 2-6, at both cooling rates, only one steel, steel 6 (similar to steel 5 in composition) was chosen for more detailed microscopic examination and only one cooling rate, 12°C/min was examined. Two steels, therefore, Steel 1, which had shown significantly different hot ductility behaviour to the rest of the steels and steel 6, which gave representative behaviour for the remaining steels were selected for examination.

Optical Microscopy

The optical micrographs are shown in Figs 7a-e for steels 1 and 6 in Table 1, cooled at 12°C/min.

Three test temperatures were examined 800, 900 and 1000°C. The austenite grain size can be seen to be coarse and similar for both steels 1 and 6, approximately 600μm and did not change with the test temperature. Inter-granular cracks are visible close to the point of necking, Figs.7a-c. Dynamic recrystallisation was found to occur only close to fracture in regions where the deformation was high, Figs, 7 b, d and e but was present even at as low a temperature as 800°C, Fig 7b.

Particles were seen at the grain boundaries, Figs 7a and 7b, these being identified subsequently, as generally MnS inclusions.
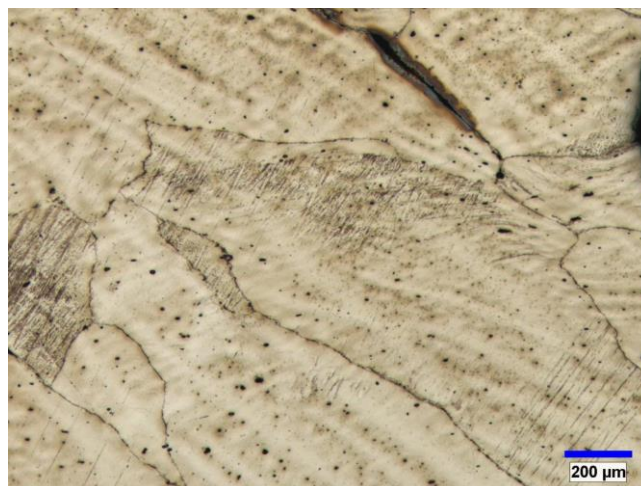

Fig.7a. Lower Ti steel 1, tested at 800°C showing on this occasion no dynamic recrystallisation and some precipitates at the boundaries, probably MnS
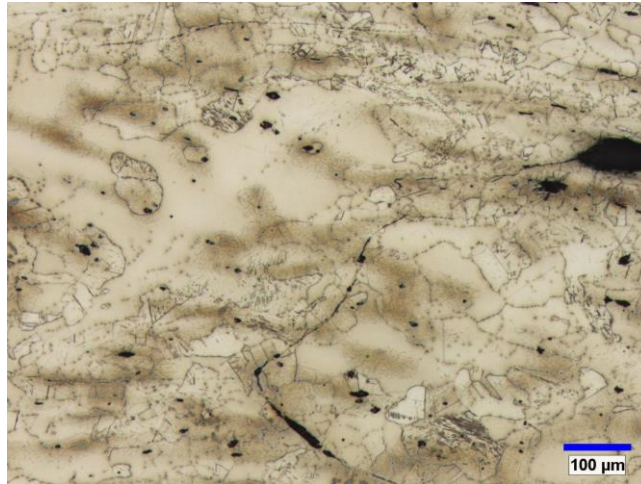
Fig. 7b. Steel 1 showing dynamic recrystallisation at the austenite grain boundaries in heavily deformed regions close to the neck in the fractured tensile specimen at as low a temperature as 800ºC.
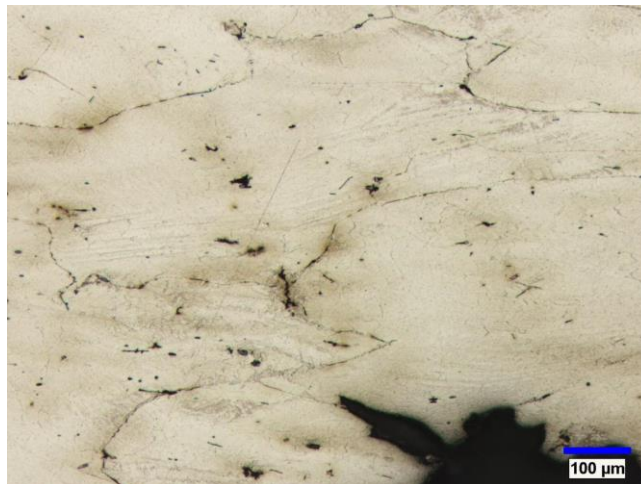

Fig. 7c Higher Ti steel, 6 tested at 800ºC, in an area tested, in which no dynamic recrystallisation is seen around the grain boundaries,
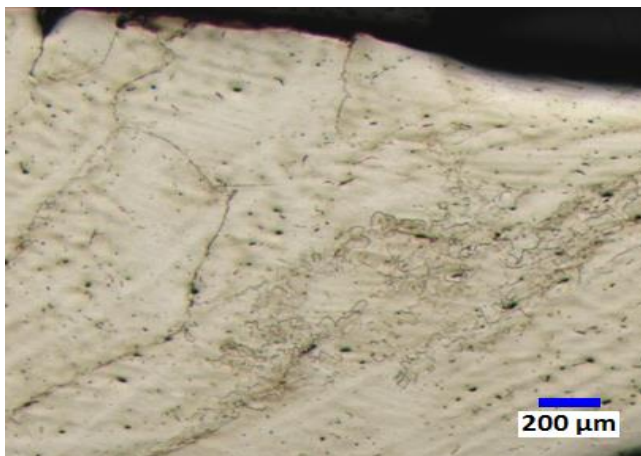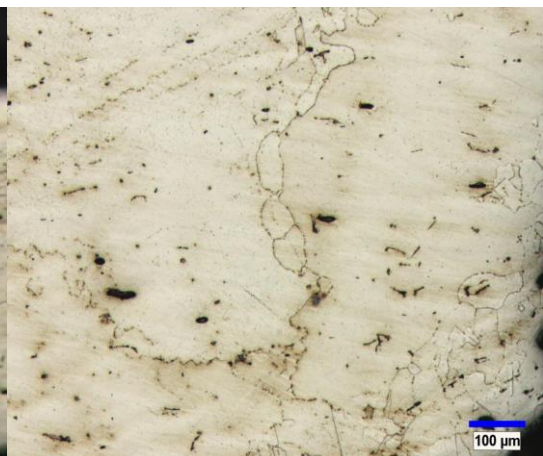

Fig.7 d

Fig.7 e

Fig. 7d and e High Ti, Steel 6 showing dynamic recrystallisation at boundary region when tested at 900°C Fig.7d and 1000°C, Fig.7e. The higher test temperature results in coarser recrystallised grains

<u>SEM examination</u>.

Typical SEM photographs for the Steel 1 after reheating and cooling at 12°C/min to test temperatures are shown for steel 6 in Figs 8 a, b and c.

The results of a study on the size of all precipitates and inclusions for both SEM and TEM work is on-going and will be reported in detail later and only analysis of the particles is discussed in detail here. It should be noted that the presence of Se in some of the analysis spectrum, Figs. 8a,b and c is due to having to add pure Mn produced via electrolysis which uses a Se compound as the electrolyte to help in attaining the required Mn level on casting. The Au peak in the spectrums is due to the gold coating used to supply conductivity to the sample for the SEM work.

Using the SEM, the larger (1-10um) particles (nitrides and inclusions) can be analysed. As such they are generally MnS particles but there are important differences between the two steels, 1 and 6. For the lower Ti steel, steel 1, most of the coarser particles were MnS inclusions which generally seemed to be attached to AlN precipitates, Fig 8a and these were located in the matrix. AlN is very sluggish in precipitating out [19] after melting and cooling to room temperature and previous work has shown that MnS particles provide good nucleation sites for the AlN [5]. When the S level is low, as in the present work, AlN precipitation is restricted because of the lack of MnS nucleation sites and seems then to be mainly in the matrix. Very coarse Ti rich particles were also found in this steel.

In contrast, the high Ti steel, 6, showed little evidence for AlN precipitation but coarse "TiN" particles with a small amount of Nb were often present, Fig.8c. This suggests that TiN will form before AlN can precipitate out.
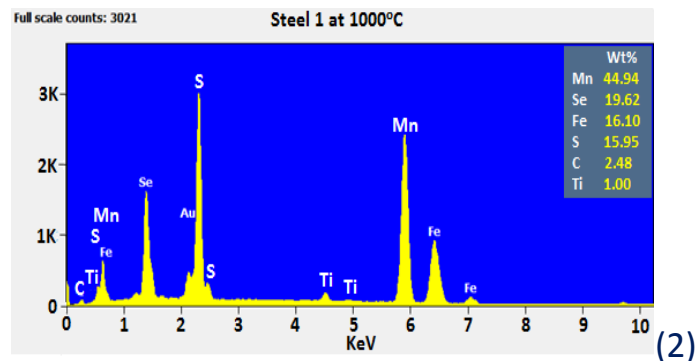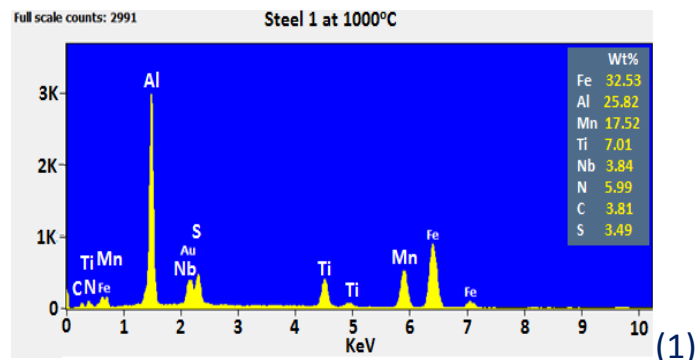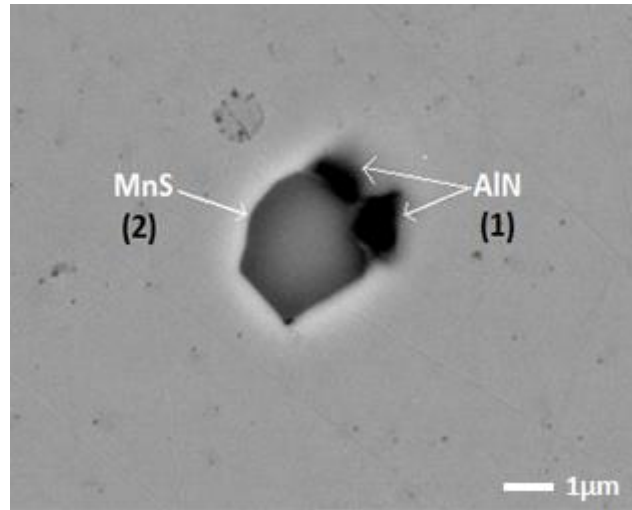
Fig.8a. Lower Ti steel 1, showing the likely presence of AlN on MnS inclusions. (AlN shows up as black in the photo and MnS as grey).The analysis spectrums show particle (1) AlN with Ti rich nitride. Particle (2) MnS with a Ti containing particle.
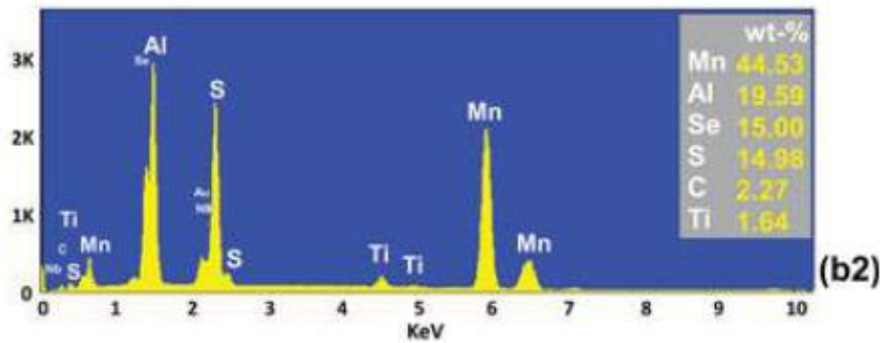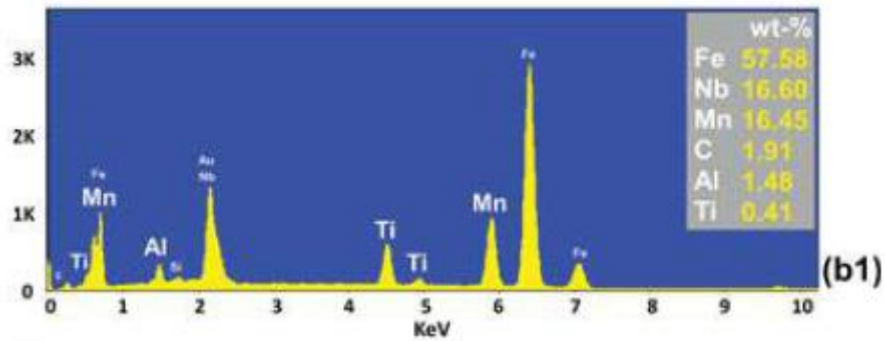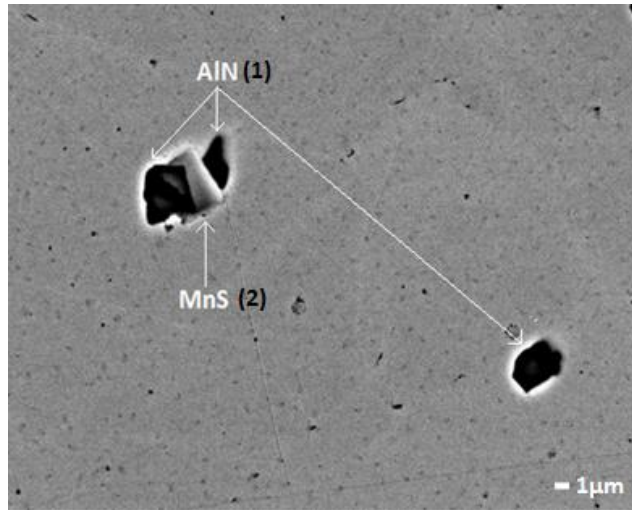
Fig. 8b. Steel 1, tested at 1000°C. Particles (1) AlN with Ti-Nb Nitrides and MnS. Particle (2), MnS with probably AlN and some TiN.
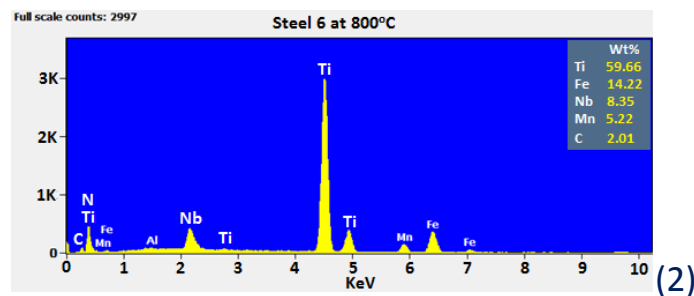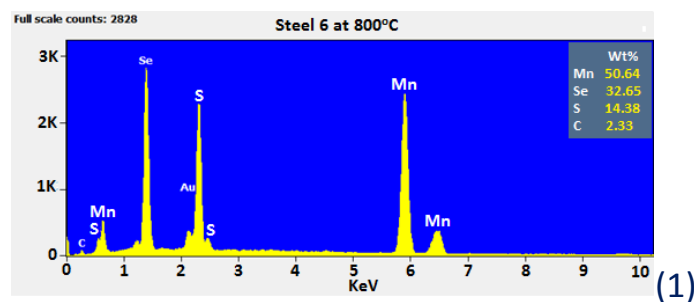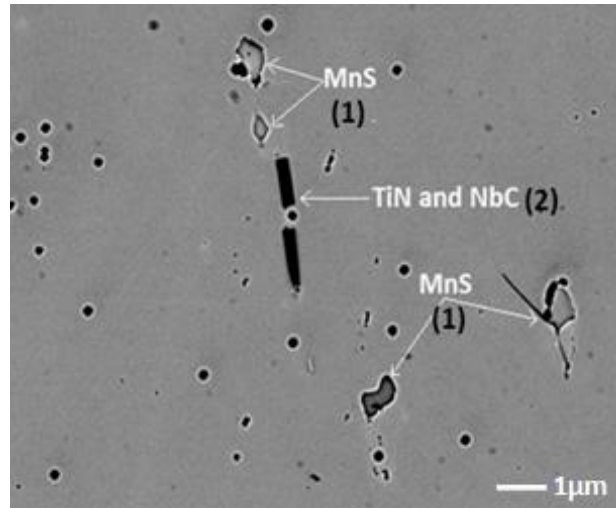
Fig. 8c. Higher Ti steel 6 tested at 800°C. Particles (1) are MnS. Particle (2) is a Ti-Nb nitride.

<u>TEM examination</u>

Again steels 1 and 6 were examined after cooling at 12°C/min from 1250°C and representative areas showing these finer particles using the TEM are given in Fig.9a

Particles in steel 1, Fig 9b were mainly Nb-Ti "nitrides", the niobium wt.per.cent content being 50% higher than the Ti content.

	Wt%	σ
Ni	28.6	0.2
Nb	26.8	0.3
C	25.3	0.3
Ti	17.3	0.2
Fe	1.0	0.1
Si	0.7	0.0
Mn	0.2	0.0
Cr	0.1	0.0
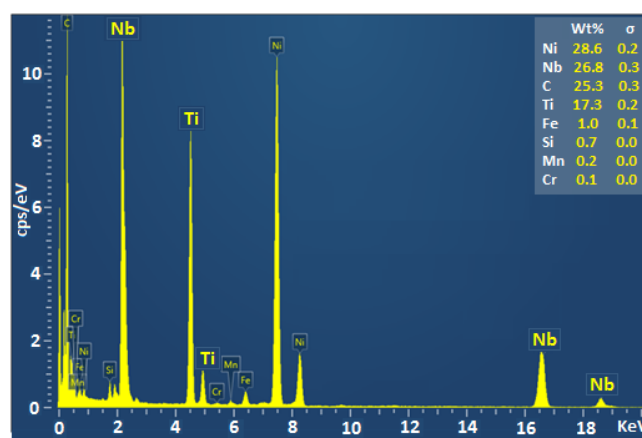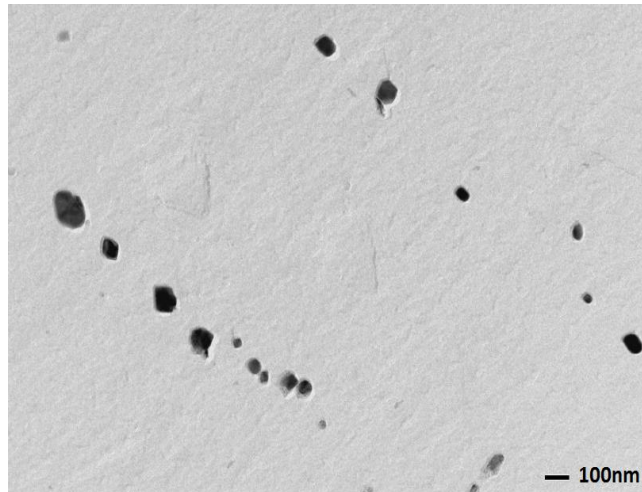
Fig 9a Nb-Ti carbonitrides found in steel 1 tested at 800°C. The precipitates varied considerably in size (~80nm in average size) but always gave similar composition.

For the higher Ti steel, 6, the Ti rich precipitates were far more numerous due to the higher Ti level. The Ti level in the precipitate is now enhanced so the Ti level is greater than the Nb level, ~100% higher. The size of particles was very variable as can be seen from Fig.9 b with the average size being ~80nm
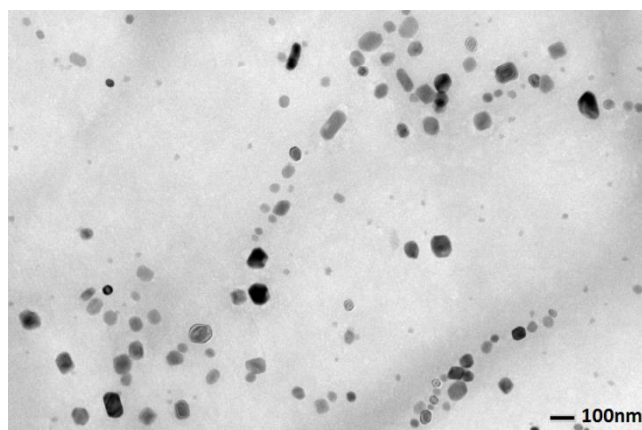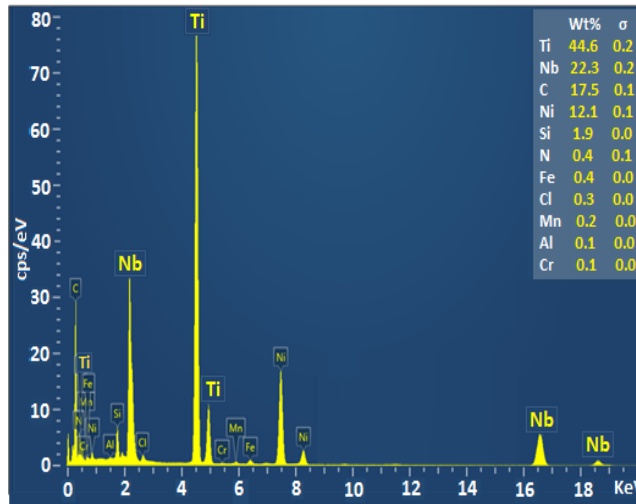
Fig.9b Ti-Nb carbonitrides found in steel 6 tested at 1000°C.

Generally, particle sizes were similar for steels, 1 and 6.

The Ni peaks in the TEM analysis spectrum, Figs. 9a and b are derived from the Ni grids needed to support the replicas. A carbon peak can also be derived from the replica and because N and B are light elements they are not always detected on the SEM and TEM spectrums and at times have to be assumed.

Discussion

Role of alloying elements

Having a high-Al addition and an addition of Nb in a HSLA steel would from previous work often [9] make casting difficult. AlN normally precipitates preferentially at the austenite grain boundaries and so encourages inter-granular failure. High Al containing and Nb free, TWIP steels also show poor ductility when the S level exceeds ¬ 0.005% because AlN then precipitates similarly at the boundaries giving "rock candy" type failures [5]. Nb additions result in dynamic precipitation of Nb(CN) which is particularly detrimental to the hot ductility of HSLA steels. To make it possible to cast **wit**hout cracks forming on straightening, Ti has been added commercially to remove all the N from solution as a Ti rich nitride. Provided the cooling rate is sufficiently slow <25°C/min as after ingot casting, the Ti rich nitrides will be coarse and so not significantly influence ductility [11].

Turkdogan [20] has suggested that the addition of Ti to the melt reduces transverse cracking by providing nucleation sites for Nb and V precipitation, thus, coarsening the precipitates of Nb and V so improving ductility. During the

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later stages of solidification, most of the N would be expected to precipitate in a relatively coarse form as TiN in the inter-dendritic boundaries. These coarse particles then serve as nucleation sites for equilibrium precipitation of NbC at higher temperatures. Turkdogan [20] calculated by the time the temperature reached 1200°C during solidification most of the Nb would be precipitated as NbC on the coarse TiN particles so that the detrimental fine strained induced Nb(CN) would not occur at lower temperatures in the temperature range of the straightening operation. Turkdogan [20] also noted that alumina inclusions would also act as nucleation sites for high temperature precipitation of nitrides and carbo-nitrides. His predictions appear to be borne out by the present steels and in accord with this, Subramanian et al [21] have also shown that increasing the Nb content in a steel with 0.008%N and 0.01%Ti increases the temperature for the start of precipitation of Nb(CN) and hence gives coarser particles. In addition, Kirkwood has found that Al additions to Ti-containing steels result in coarser TiN particles [22].

Although Nb additions do make it more difficult to avoid transverse cracking during the straightening operation, particularly for peritectic C, HSLA steels, (~ 0.1 to 0.2%C), the research work that has been carried out on these steels has enabled them to be continuous cast successfully. For Ti-containing steels, on casting, the Nb precipitates on the coarse TiN particles at high temperatures so that no grain refinement or precipitation hardening occurs. However, reheating to 1250°C prior to rolling will cause the Nb to go back in solution and as the rolling operation provides new nucleation sites for the re-precipitation of a fine precipitation of Nb(CN) onto the dislocations, the benefits required of grain refinement and precipitation hardening are restored in the final product. The hot ductility work that has been carried out on Nb containing steels has gone a long way into alleviating the problem of transverse cracking but not eliminating it and considerable scarfing is often required to remove the surface cracks and in many companies the slabs have to be rolled wide and the edges trimmed to remove the edge cracks. Thus, although these steels can be continuous cast, the scrap allowance is greater than with plain C-Mn steels.

Having Ti, B, Al and Nb present, means there is great competition for the nitrogen but of all the nitride formers Ti will always combine preferentially

with N. It should be noted that TiN and Nb(CN) are mutually soluble so that mixed carbo-nitrides are formed in as-cast material, often rich in Nb rather than Ti and this will account for the analysis spectrums shown in Fig.9a and 9b. [11]

Nevertheless, even when Ti, Nb and Al are present together, good ductility has only been achieved in these TWIP steels on adding boron which can segregate to the boundaries and strengthen them; the Al and Ti forming nitrides in preference to BN. Indeed, boron in solution has been found to be an excellent addition to improve ductility in steels even when no nitride formers are present provided conditions are suitable [13].

Analysis of Results

On examining the hot ductility curves in Fig.3 and the micrographs in Figs 7a-e, the improvement in ductility when the test temperature changes from 700-900°C is most likely due to the onset of dynamic recrystallisation. Dynamic recrystallisation in these steels is most readily seen in the region of the tensile specimen which has necked down to failure and occurs at temperatures as low as 800°C, Fig. 7b and c.

The absence of a peak at a test temperature of 900°C in the hot ductility curve for the Nb-V steel, Fig.3 may be due to the extra precipitation from having V present delaying the onset of dynamic recrystallisation. Further work is needed to clarify this.

The fall in ductility on increasing the test temperature above 900°C, Fig.3 is from previous work, most likely to be in part due to a reduction in the degree of B segregation [8].

A recent SIM study l8] has shown that B segregation to the boundaries in these steels takes place throughout the temperature range of 700-1200°C. It is most intense in the temperature range 700-800°C. Although at higher temperatures >800°C, the intensity of B segregation is less, B segregation nevertheless takes place even at as high a temperature as 1200°C [8]. Thus a decreased B segregation combined with an increase in grain boundary sliding from the higher temperature and a coarser recrystallised grain size probably accounts for the marked fall in ductility at temperatures >900°C. It also must be

appreciated that full solidification from the melt under equilibrium conditions does not take place until as low a temperature as 1270°C so that ductility may at the higher temperatures also be reduced by liquid films at the austenite grain boundaries [23]. Unfortunately, the cause of the decrease in ductility at 800°C, shown in Fig.3 for steel 1 when the cooling rate is 12°C/min, is not presently known.

In order to discuss the results, it is necessary to compare the present work with past work on B treated Nb free TWIP steels of otherwise similar composition. Previous work [5-8] on steels reheated to 1250°C after melting have mainly been carried out using a cooling rate of 60°C/min whereas this work has concentrated on a slower cooling rate of 12°C/min. Nevertheless, three of the steels in the present exercise (1, 3 and 5) were also cooled at 60°C/min and are listed in Table 2 together with three (8,9 and 10) steels from earlier work on Nb free TWIP steels [7]. Also included in the table are the Ti/N ratio and the product of [Ti][N].

Table 2. Compositions examined (wt.per.cent) for Nb free[7] and containing TWIP steels cooled at 60°C/min

	C	Si	Mn	P	S	Al	Nb	Ti	B	N	Ti/N ratio	[Ti][N
5	.60	.10	18.0	.010	.006	1.50	.033	.075	.0028	.011	6.8	8.25
3	.60	.09	18.2	.009	.003	1.55	.032	.030	.0028	.010	3.0	3.00
1	.60	.09	18.2	.009	.003	1.57	.031	,019	.0027	.009	2.2	1.71
8	.55	.07	17.6	.019	.0014	1.44	-	.098	.0017	.009	10.9	8.8
9	.62	.30	18.2	.007	.006	1.50	-	.105	.0026	.0073	14.4	7.7
10	.60	.30	18.2	.019	.005	1.50	-	.100	.0027	.0068	14.7	6.8

The hot ductility curves for these steels given the same cooling rate of 60°C/min and processing conditions are given in Fig.10 and show that after reheating to 1250°C, higher nitrogen contents and higher [Ti][N] products as well as adding Nb all lead to better ductility.
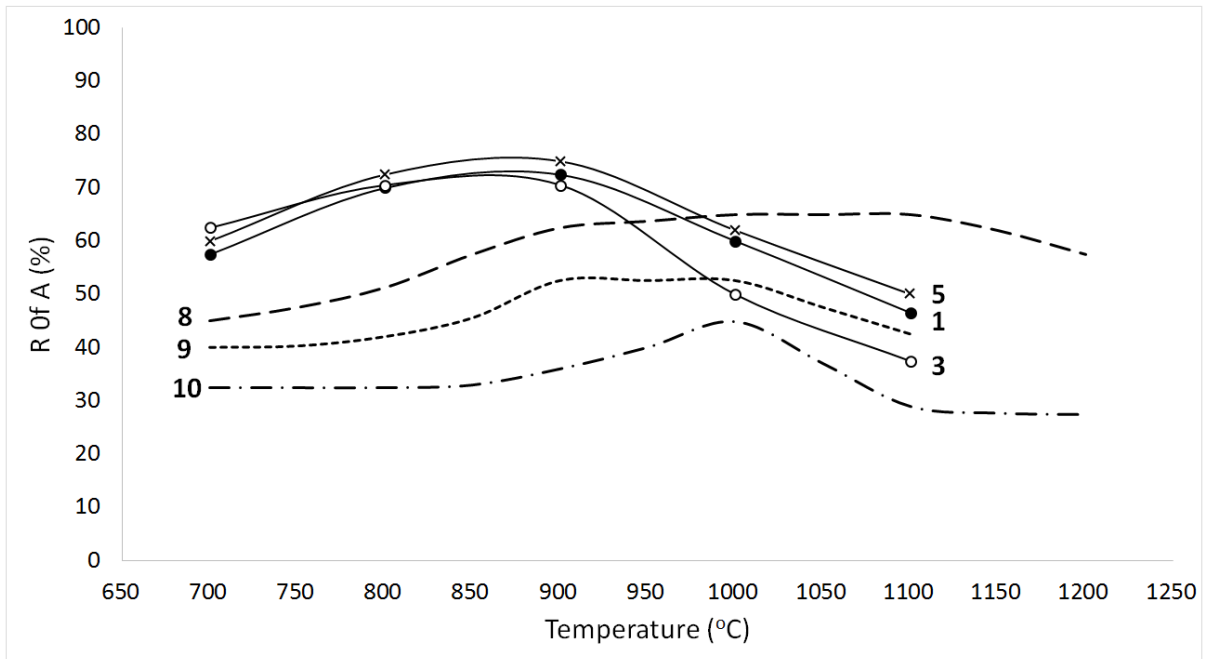
Fig.10. Hot ductility curves for Nb and Nb free TWIP steels, cooled at 60°C/min.

Examination of the curves in Fig.10 and Table 2 shows the [Ti][N] product gives a better measure of the ductility than the Ti/N ratio. For the Nb containing steels, differences in hot ductility in the temperature range of most interest for the straightening operation in continuous casting, 800-900°C are small and in keeping with what might be expected from the present experimental scatter band of ± 5%RA . The higher Ti-N steel 5 does however, give the best ductility.

 For the Nb free TWIP steels, the hot ductility curves for steels, 8, 9 and 10 are well separated making it possible to identify differences. As the product [Ti][N] increases from 2.5 to 7,7 to 8,1 x 10^{-4}, respectively the ductility improves, Fig.10.

In contrast for steels 8, 9 and 10 having Ti/N ratios of 8.7, 14.4, 14.7, the ductility improves as the Ti/N ratio decreases.

Increasing the [Ti][N] product would normally by encouraging precipitation at higher temperatures be expected to coarsen the precipitates so improving the ductility and preventing inter-granular failure.

It should be understood that the main interest in the paper has been in examining the hot ductility in the temperature range 800-1000°C, this being the temperature range for straightening during continuous casting, when

transverse cracks form. Although, steel 8 gives the best hot ductility above 1000°C this is not the case for the range of interest and again the reason for this is not as yet clear.

In the present work, it is interesting that even with the lowest Ti/N ratio steel, steel 1, (<stoichiometric) the N remaining in solution does not precipitate out as the coarse very detrimental to ductility AlN particles concentrated at or close to the boundaries, as has been found in the higher S, TWIP steels[5]. AlN does nevertheless precipitate out but then mainly in the matrix and so has no detrimental effect on "inter-granular" ductility. Although there is a greater volume fraction of precipitate present at higher N levels, there is also a coarsening of particles; the former decreasing the ductility while the latter improving "inter-granular" ductility, the latter having the greatest effect.

 At the same Ti level, 0.1%, (Table 2 and Fig.10) steels with the higher N levels give better ductility. This again is related to an increase in the [Ti] [N] product which will cause precipitation to occur at higher temperatures and so be coarser.

Finally, very surprisingly the Nb containing steels do better than the Nb free steels. Presumably, the NbC precipitates out onto the Ti rich particles at higher temperatures. This will coarsen the NbC precipitates as well as the TiN particles in addition to preventing Nb precipitating out in a fine form during deformation, so that ductility can improve.

<u>Difference between inter-granular and trans-granular failure</u>

Hot ductility in the austenite is very dependent on the ease of cracks forming and linking up along the austenite grain boundaries. However, inter-granular failure although very common in HSLA steels in the temperature range 700-950°C often giving a wide and deep ductility trough [9] but in these boron containing TWIP steels because the ductility is so good, the failure is mainly trans-granular.

With inter-granular failure and this occurs when the RA values are <40%, the closer the particles are together along the boundary the easier it is to propagate a crack along the boundary from one particle to the next. In addition, finer particle distribution at the boundary can pin or delay grain

boundary movement encouraging grain boundary sliding. Furthermore, the finer the particles are in the matrix, the greater will be the stress activating grain boundary sliding making inter-granular failure more likely [9]. This is very different to the fracture mode for trans-granular failure which is more related to void nucleation, as with ductility at room temperature.

As far as normal ductile behaviour is concerned finer inclusion distributions in the matrix will give higher RA than coarser, as void nucleation is easier with coarser particles [24]; the much deeper cavities around coarse particles making it easier to join up to give trans-granular failure.

Trans-granular failure becomes important above 40%RA. For the present steels because B improves ductility by strengthening the boundaries, trans-granular fracture plays a more important role in the fracture process. At these high temperatures, creep behaviour will always be present so that cracks will usually originate as grain boundary cracks whose development before they lead to fracture can be stopped by dynamic recrystallisation and the appearance of finer recrystallised grains. Much of the deformation can then be dependent on the cracks linking up in a trans-granular manner. In the present case, grain boundary cracks develop but are stunted by dynamic recrystallisation, Fig.7b. These cracks can then elongate into cavities which are able to link up with the microvoids formed around the inclusions in the matrix and give a mixed inter-granular and trans-granular failure. Wang et al [25] have also shown similar behaviour in the high Al (2%) TWIP steel they examined.

The two types of fracture are subject to entirely different mechanisms. For example from previous work, when comparing the hot ductility of fully austenitic with fully ferritic structures in the temperature range under examination [26], the former was mainly inter-granular having in this case precipitates at the boundaries and the latter trans-granular. Austenite recrystallises when deformed at elevated temperatures, so that the amount of grain boundary sliding and dynamic recrystallisation control the fracture process. In ferritic steels only recovery is possible and the trans-granular failure depends very much on the ductility of the matrix which is controlled as is normal room temperature ductile failure by microvoid coalescence around the inclusions in the matrix. For example, increasing the strain rate when grain boundary sliding is the major source of failure is beneficial because it reduces

the time available for sliding and hence reduces the size of the inter-granular cracks improving ductility. In contrast for trans-granular failure increasing the strain rate makes ductility worse as it causes work hardening, giving no time available for recovery. The presently examined TWIP steels because of their good ductility, >40% although austenitic will have a large contribution to fracture from trans-granular failure and this can result in mixed fracture behaviour.

When inter-granular separation has been stunted, in contrast to trans-granular failure, finer particle distributions are better for ductility than coarser. Grain boundary sliding is still, however, the most critical operation that controls crack development, the greater it is, the longer are the cracks and the worse is the ductility.

Cracks start along the grain boundary so inter-granular failure will always play a major role in failure. Coarse precipitation is then beneficial because it prevents the cracks from joining up along the boundaries and also allows dynamic recrystallisation to occur more readily. Once inter-granular failure is prevented from developing, trans-granular failure takes over and having finer distributions can then give some further small improvement in ductility.

There is always a balancing act on the hot ductility behaviour even when inter-granular failure is the fracture mode as coarsening the TiN precipitates by for example increasing the N level will also increase their volume fraction, the coarsening being beneficial and the latter detrimental to the hot ductility. Comineli et al. [27] have found for example that the addition of Nb to a Ti containing steel coarsened the particle size but resulted in no change in ductility, as the benefits to ductility from the coarsening were offset by the greater volume fraction of precipitation.

Influence of cooling rate

 Although changes in hot ductility behaviour on altering the cooling rate are small, Fig.3,4 and 5, there is a definite but small improvement on fast cooling. Faster cooling rates will restrict growth. For inter-granular failure this would lead to early failure and poor ductility. However, when trans-granular failure takes over from inter-granular, a finer distribution will be beneficial to ductility

The TiN particles need to be coarse enough to avoid influencing significantly the hot ductility. The present work where reheating is used does not give any information on this but previous work on melted samples [10] has shown for HSLA steels where prevention of inter-granular failure is critical that again the ductility of Ti containing steels improves when the cooling rate is reduced from 60°C/min to 12°C/min and particles coarsen.

Influence of reheating at 1250°C

The effect of reheating at 1250°C after melting must also be discussed to interpret the results in relation to the continuous cast process. Reheating to 1250°C assuming TiN is the major precipitate, does even at the stoichiometric composition for TiN take some N back into solution when equilibrium is achieved (0.003 to 0.004%N). Table 3 gives the amount of N that goes into solution at 1250°C using the solubility equation derived by Wada and Pehlke [28].

Log (wt.%Ti)(wt.%N)$_{total}$ = -14400/T + 4.94 where T is in K.

The solubility equation of Leslie et al [29] for steels with 1.5% Al free of Ti , also shows that no N goes back into solution at 1250°C from the AlN precipitates. It is therefore unlikely having both Ti and Al together that any N will go back into solution on reheating so that the precipitate pattern will not change on reheating to 1250°C although there may be some further growth.

 Also from the solubility equation for MnS. log [Mn][S]= -14855/T +6.82.

 no sulphur will go back into solution at 1250°C [30].

NbC can go back into solution but with coarse Ti rich precipitates it is likely to precipitate at higher temperatures as before.

Furthermore, since the steel is fully austenitic, no phase change is involved on reheating so it is likely the grain size will remain that of the as-cast condition.

Table 3

Nitrogen in solution at 1250°C from solubility equations for TiN.(wt.per.cent)

Steel	N_2 in solution	Ti/N ratio	Ti	Total N
1	.0052	2.2	.019	.009
2	.0033	3.3	.022	.007
3	.0037	3.0	.030	.010
4	.0013	5.7	.046	.008
5	.0008	6.8	.075	.011
6	.0007	7.7	.074	.010
7	.0008	6.3	.075	.012

When there is insufficient Ti present to combine with all the N, "TiN" forms and the remaining free N combines with the Al. This is shown in the electron microscope TEM results for steels 1, Figs.8a and 8b For steel 1 with a Ti/N ratio of 2,(less than stoichiometry) there are AlN and Nb-Ti "nitride" precipitates present. However, for a steel with composition more than the stoichiometric for TiN, steel 6, Fig.8c, Ti-Nb rich particles are only observed and no AlN is present. It seems therefore in these steels that Ti, first combines with the N and any N remaining in solution, as for steel 1, ends up combined with the Al .

For these Nb containing TWIP steels, ductility is good >40% R of A, which is above the value that is needed to avoid cracking on continuous casting. This similarity in hot ductility behaviour for all the steels is in most cases not too unsurprising since there is no change in grain size. Furthermore, on solidification (melting point ~1420°C and solidus~1270°C from the FactSage programme [23], austenite forms and cooling to the straightening temperature does not change the crystal structure. Except for steel 1 all the N will be combined with the Ti and very little will go back into solution at 1250°C, although there is the possibility that some growth of the precipitates after melting might occur. Nevertheless, the precipitation on cooling from 1250°C will probably only change slightly from that which was present after melting and cooling to room temperature, in agreement with the only small changes that take place in ductility

Importance of low S for good ductility

The role of S in influencing the hot ductility of these steels cannot be underestimated. S segregation to the ϒ grain boundaries has been found to result in poor ductility [31]. Indeed, Osinkolu and Kobylanski [32] have shown that in low Mn, ultra-high purity steels, heated directly to the test temperature, AlN reduces the hot ductility indirectly by pinning the boundaries allowing the S to segregate to them. When S levels were very low (<0.005%S) the hot ductility was excellent even when high volumes of AlN were present both at the ϒ boundaries and within the matrix. A recent paper by Wang et al [25] has shown that a "plain" high Al containing TWIP steel with a very low S level, (0.0005%) and given a very similar processing route to the one used in the present work, gives high ductility throughout the normal straightening temperature range (700-1000°C) of continuous casting. Presumably because of the low S level, there are few sites available for AlN to precipitate out at and precipitation occurs within the matrix rather than detrimentally at the boundaries [5]. However, Wang et al [25] in their ultra-low S steel did not find MnS particles attached to the AlN particles.

Nevertheless, because of the very high Mn content again as with nitrogen, no sulphur will go back into solution at 1250°C.

Furthermore, low sulphur in a steel with a high Mn level [33] has been shown to encourage precipitation in the matrix rather than the boundary so that reducing the S content in addition to reducing the volume fraction of MnS precipitated at the γ grain boundaries will with a high Mn content, encourage precipitation of MnS in the matrix than more detrimentally at the ϒ grain boundaries.

Commercial Relevance

Much of the hot ductility behaviour discussed in this paper has been concerned with the role of dynamic recrystallisation in improving ductility and as such, although relevant to the high strains to fracture from the tensile test, this is not relevant to the straightening operation on continuous casting where the strain is only ~ 3%. No dynamic recrystallisation occurs on straightening the strand in continuous casting.

Although reheating at 1250°C followed by testing is a very approximate simulation of the as-cast state, the work does illustrate that in general when inter-granular failure is the main mode of failure, the coarser is the precipitation at the boundaries the better is the hot ductility and that will reflect in the less likelihood of transverse cracking occurring. Thus, slower cooling rates in general after solidification would still be expected to be beneficial. However, there are other ways of improving ductility if needed. Increasing the product of [Ti][N] above that required for stoichiometry will lead to coarse particles and this is particularly so for high N steels.

A Nb addition does not give problems as has been found with HSLA steels. Indeed it improves the hot ductility since in addition to TiN preventing the detrimental fine deformation induced NbC precipitation from forming, the high N content causes the TiN to precipitate at high temperatures and in consequence the NbC precipitation will be coarser.

Finally, it may not be necessary to achieve the stoichiometric Ti/N ratio for TiN, as the high Al level seems sufficient to remove all the N from solution as AlN and the low S level and high Mn level prevent AlN from precipitating detrimentally at the boundaries. However, a high Ti addition may be necessary to encourage the NbC to come out at a high temperature. Indeed the work of Wang et al [25] suggests that, if commercially the S can almost be eliminated from the steel, there should be no cracking problems and B and Ti may then not be needed. Further work is needed to explore these possibilities.

Conclusions

1. The hot ductility of the Nb containing, high Al, TWIP steels containing B was good >40% RA in the straightening temperature range 800-1000°C.

2. Precipitate volume fraction was not influenced by the test temperature; the precipitation was mainly fixed on solidification although reheating might cause some limited growth. The slow cooling rate for the ingot after casting is so slow that any further possible growth on reheating would have only a small influence on ductility.

3. As ductility is so good in these steels due to the addition of B, trans-granular as well as inter-granular plays an important role in the fracture process.

Because trans-granular failure in these steels is the main mode of failure, the faster cooling rate of 60°C/min after reheating to 1250°C may by giving finer particles give better ductility provided they do not precipitate at the boundaries. Hence, a further study on particle sizing and distribution in relation to the hot ductility performance is required.

4. A high product of [Ti][N] will give improved ductility and a higher N level gives some further benefit.

5. Because, the addition of B so improves ductility by itself, reducing the Ti level to the stoichiometric for TiN will only marginally cause a deterioration in ductility. Indeed, even working with Ti at levels below the stoichiometric may be acceptable but further work is required before that can be recommended.

6. Nb is beneficial as the precipitation of Nb(CN), on the Ti particles at higher temperatures, will probably generally coarsen the precipitates so not only is the fine deformation induced precipitation avoided but a coarser precipitation will enhance ductility.

7. A V addition to the Nb containing made the hot ductility slightly worse in contrast to the benefit it often gives when added to HSLA steels. Further work is required to establish the reason for this.

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