The Influence of Ti on the Hot Ductility of Nb-bearing Steels in Simulated Continuous Casting Process

Haiwen LUO, L. Pentti KARJALAINEN, David A. PORTER,1) Heidi-Marja LIIMATAINEN and Yan ZHANG2)

Materials Engineering Laboratory, University of Oulu, P.O. Box 4200, FI-N90014 Oulun Yliopisto, Finland.
E-mail: pentti.karjalainen@oulu.fi 1) Rautaruukki Oyj, Corporate R&D, P.O. Box 93, FIN-92101 Raase, Finland.
2) State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, P.R. China.

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The hot ductility of as-cast Nb, Ti and Nb–Ti bearing low-carbon steels has been assessed. Hot tensile testing of in-situ melted specimens, replica examinations and thermodynamic modeling showed that addition of 0.014–0.04% Ti to 0.1%C–0.03%Nb–0.005%N steel leads to a large volume fraction of fine strain-induced precipitates at temperatures up to 1 000°C which seriously deteriorate the hot ductility, in spite of the type of prior thermal history. Generally, three types of precipitates, i.e. coarse boundary precipitate, coarse frond-like and fine strain-induced precipitates, were found in Ti–Nb microalloyed steels with the different sizes and compositions, and the latter could be described by thermodynamic modeling. The current results are different from the previous ones published and a thermodynamic model was employed to explain this discrepancy. Accordingly, the beneficial effect of Ti can only be achieved in some instances at high nitrogen and low titanium contents, i.e. a low Ti/N ratio, which greatly encourages coarse precipitation at high temperatures and reduces the fine strain-induced precipitation. Therefore, only for electric arc steels typically with a high nitrogen level, a small addition of Ti might be considered to be advantageous to the hot ductility.

KEY WORDS: continuous casting; hot ductility; precipitation; niobium; titanium; nitrogen content; thermodynamic model.

1. Introduction

In continuous casting of low carbon steels containing Al, Nb, Ti or V, transverse cracking is sometimes observed in the subsurface zone of the slabs. In an attempt to reduce the frequency of these surface defects, extensive studies on the high temperature embrittlement of microalloyed steels have been undertaken since early 1980’s by Suzuki et al.,1,2) Ouchi and Matsumoto3) and by Mintz and his coworkers,4–8) among many others (see a recent review in Ref. 8)). It is well known that the hot ductility trough in microalloyed steels is controlled by deformation-induced ferrite film in the two phase austenite/alpha-ferrite region and grain boundary sliding in the low temperature region of austenite phase.1–8) The latter is usually encouraged by fine precipitation. Moreover, this low ductility can be almost fully recovered at the high temperature region of austenite phase due to the occurrence of dynamic recrystallisation.1,5–8) Some practical experiences indicate that the addition of Ti reduces the incidence of transverse cracking and improves the surface quality.8,9) Turkdogan10) suggested that in the Nb-microalloyed steels most of Nb can precipitate on the coarse TiN particles before the straightening stage of the slab, leaving less Nb in solution to precipitate out in a more detrimental form during straining. Abushosha et al.5) found that a 0.02% Ti addition was beneficial regarding the hot ductility of Nb-containing steels (0.023% Nb, 0.009% N), particularly after a slow cooling. Suzuki et al.11) similarly found that nitride-forming microalloying elements could improve hot ductility by causing niobium carbonitride precipitation at higher temperatures. In these tests, the thermal cycle of steel slab surface as it passes through the spray cooling and bending zones was simply simulated. Contrary to these observations, Comineli et al.7) recently reported a significant deterioration in ductility caused by a small addition of Ti to Nb-bearing steels. Mintz8) put forward the opinion that the beneficial effect of addition of Ti can be noted only when temperature fluctuations equivalent to those in real continuous casting are introduced into the hot ductility tests and the optimum levels of titanium and nitrogen are used.

Because there still exist highly conflicting results regarding the effects of Ti on hot ductility, the influence of 0.014–0.038% Ti alloying in Nb-bearing steels with a typical nitrogen content, i.e. about 0.005%, has been investigated using hot tensile testing of in-situ melted specimens and transmission electron microscopy. A thermodynamical model has been used to help understand the complex Nb–Ti precipitation occurring during the cooling stage. Finally, the conditions under which Ti can improve the ductility of Nb-bearing steels are discussed.
2. Experimental

The microalloyed steels used in this study were cast as 70 kg heats in a vacuum furnace and rolled in a laboratory rolling mill. Their chemical compositions are given in Table 1. Steel Nb only contains Nb and Steel Ti is only alloyed with Ti, while Steels Nb-loTi and Nb-hiTi contain both Ti and Nb, the former having a low and the latter a high Ti content.

Cylindrical tensile specimens of 120 mm in length and 10.0 mm in diameter were machined from the rolled plates parallel to the rolling direction. A Gleeble 1500 thermomechanical simulator was employed to perform the hot tensile straining and the hot ductility was determined as the reduction of area (R.A.). The specimens were heated at 25°C/s in a shielding gas of argon up to the melting temperature to produce a molten length of 10–15 mm in the middle part of the specimen, which was supported by a slotted silica tube of 30 mm in length. This is called the in-situ melting technique. The occurrence of melting was determined visually and controlled by adjusting the final temperature manually.

Subsequently, specimens were either cooled directly to the straining temperature at the rate of 4 or 0.4°C/s, i.e. direct cooling, as schematically shown in Fig. 1(a), or first cooled to 100°C below the straining temperature and then heated back to the final test temperature, i.e. prechilled, to simply simulate a temperature cycling that occurs near the slab surface due to the water sprays below the mould in the practical continuous casting process (Fig. 1(b)). Specimens were held for 15 s at the final testing temperature before straining to failure at the slow strain rate of 0.0005 s⁻¹. After fracture the specimens were allowed to cool freely in argon. A few specimens were thermally cycled as shown in Fig. 1(a) to a final test temperature of 900°C without straining, and held for 15 s before cooling in argon.

The fracture surfaces of the strained specimens were examined using a scanning electron microscope (SEM). In addition, carbon replicas were prepared from samples taken adjacent to the fracture surface and etched in a 2% nital alcohol solution. At least two replicas were taken from each specimen. Precipitates were examined in an energy-filtered scanning transmission electron microscope (EFSTEM, Leo 912), and the chemical compositions of precipitates were analyzed using an energy dispersive spectrometer (EDS). Replicas from the specimens that were thermally cycled without straining were used to study the precipitation that occurred in the course of cooling. For some specimens, the size distributions of the numerous precipitates were analyzed by using the “Soft Imaging System” software of EFSTEM.

3. Results

3.1. Hot Ductility

The curves showing reduction of area (R.A.) as a function of the tensile test temperature for the four steels are given in Fig. 2. The minimum ductility is clearly dependent on the cooling rate but it is little affected by compositions. Compositional effect are, however, more apparent regarding the temperature where dynamic recrystallisation ceases and the ductility starts to drop. In this respect, it is evident that the addition of Ti has a marked deteriorating effect on the ductility of Nb-bearing steels at both cooling rates. Steel Nb shows a good ductility above 800°C, whereas the hot ductility of Steels Nb-loTi and Nb-hiTi stays low until 1000°C. Moreover, prechilling before straining deteriorated the ductility of both the Nb and Nb–Ti steels to almost the same degree at 800°C, but it had practically no influence above 900°C.

3.2. Fracture Appearance

Fracture surfaces corresponding to the ductility trough indicated a mixture of interdendritic and intergranular failure modes (Fig. 3), which is consistent with the previous observations. A number of inclusions, found to be alumina by EDS, were present on the dendrite nodules, as shown in Fig. 3(b). Aluminum has a high affinity for oxygen and the alumina particles can have formed during the original laboratory melting or during the in-situ melting prior to the test due to small amount of oxygen in shielding atmospheres. The alumina clusters seem to have been pushed ahead of the solidifying dendrite into the interdendritic regions. Such clusters will presumably impair the hot ductili-
3.3. Replica Examination

An extensive replica study showed that in the Nb steel directly cooled and strained at 900°C, a prominent precipitation of Nb(CN) had occurred at both cooling rates (Fig. 4). Despite this, the ductility is rather good, which can be attributed to the fact that only a small volume fraction of precipitates has formed as will be shown later. The higher ductility at the cooling rate of 0.4°C/s (R.A. = 60%) is associated with a mean precipitate diameter of 15 nm, while smaller precipitates with a mean diameter of 11 nm are found at the higher cooling rate of 4°C/s, which gave the R.A. of 36%.

In the Nb–Ti steels, three types of precipitates with different sizes and compositions were observed: (I) coarse particles arranged on what appeared to be prior austenite grain or subgrain boundaries, (II) large frond-like particles, and (III) very fine precipitates with a round or nearly cubic shape (Figs. 5–7). The coarse boundary precipitates are rich in Nb (the mole ratio of Ti to Ti/Nb varied from 0.4 to 0.45). They could form at grain boundaries even during the fast cooling before straining, and their sizes ranged from 30 to 120 nm (Fig. 5). Precipitation of frond-like particles occurs during both fast and slow cooling even without straining, indicating that they are formed during the

**Fig. 2.** Hot ductility curves for the Nb, Ti and Nb–Ti steels in-situ melted and (a) directly cooled at 4°C/s or 0.4°C/s, (b) cooled at 4°C/s with or without prechilling.

**Fig. 3.** Typical brittle fracture surface of Steel Nb–hiTi after direct cooling to 800°C at 4°C/s and straining to fracture, R.A. = 11%.
(a) Fracture appearance. (b) Enlargement of the region shown by the arrow in (a).

**Fig. 4.** Precipitation of fine Nb(CN) in Steel Nb at 900°C.
(a) Cooling at 4°C/s, average particle size 10.8 nm, R.A. = 36%.
(b) Cooling at 0.4°C/s, average particle size 14.6 nm, R.A. = 60%.
cooling stage after solidification. Their maximum diameters varied from 40 to 250 nm. The Ti content in this type of precipitates varied locally, as demonstrated in Fig. 6(a). The Ti content was highest in the center of frond-like precipitate, which is consistent with the nucleation of frond. The content of Ti gradually decreases and its Nb content increases towards the extruding arms, indicating that the arms of the frond grow during cooling. Type III precipitates were usually formed during straining and were found extensively along grain and sub-grain boundaries and dislocation lines with Ti/(Ti+Nb) mole fraction varying from 0.54 to 0.69 (Fig. 7). They were round or almost cubic and as small as 5–20 nm in diameter. The hot ductility of the steels is mostly dependent on this kind of fine and dense precipitation.5–8) With increasing fracture-test temperature, the particles became coarser and richer in Ti, and the number of particles decreased significantly, see Fig. 8. Table 2 gives details of average precipitate diameters as a function of test temperature, cooling type and cooling rate together with corresponding reduction of area in the tensile tests. Details of some of the size distributions are given in Figs. 9 and 10. When the Ti content in the steel decreased, precipitates seem to become smaller, but the difference between the two mean diameters, i.e. 9.5 nm in Steel Nb–hiTi to 8.8 nm in Steel Nb–loTi, is not statistically significant. For the Ti steel, only Ti(CN) particles were found with an average diameter of 17.3 nm after the fast cooling at 1000°C. When prechilling was used before deformation particles become significantly coarser, so that for Steel Nb–hiTi cooled at 4°C/s the mean precipitate diameter was 12 nm at 900°C with prechilling and 9.5 nm with direct cooling. Ductility was, however, not affected.
Fig. 8. Fine precipitates with round or near-cubic shape after fracture at 1000°C in Steel Nb–hiTi.
(a) Cooling rate 4°C/s, average size 17.6 nm, R.A. 23%, Ti/(Ti+Nb) in precipitates 0.70–0.78.
(b) Cooling rate 0.4°C/s, average size 37.4 nm, R.A. 35%, Ti/(Ti+Nb) in particle of A: 0.78, B: 0.76.

Table 2. Mean precipitate diameters and reductions of area (R.A.) vs. test temperature and cooling rate.

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Test temperature (°C)</th>
<th>Type of cooling</th>
<th>4°C/s</th>
<th>0.4°C/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>900</td>
<td>Direct cooling</td>
<td>10.8</td>
<td>13.6</td>
</tr>
<tr>
<td>Ti</td>
<td>1000</td>
<td>Direct cooling</td>
<td>17.3</td>
<td>13.1</td>
</tr>
<tr>
<td>Nb-loTi</td>
<td>900</td>
<td>Direct cooling</td>
<td>8.8</td>
<td>10.0</td>
</tr>
<tr>
<td>Nb-hiTi</td>
<td>1000</td>
<td>Direct cooling</td>
<td>17.6</td>
<td>23.1</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>Prechilled</td>
<td>12.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Fig. 9. Size distributions of fine particles in Steel Nb and Steel Nb–hiTi at 900°C under the slow and fast cooling rates.

Fig. 10. Size distributions of precipitates in Steel Nb–hiTi at 1000°C at the two cooling rates.
4. Discussion

4.1. Influence of Cooling Rate and Temperature on Precipitation and Hot Ductility

For all the microalloyed steels examined, reducing the cooling rate distinctly improved the hot ductility, as is evident from Fig. 2. However, at both cooling rates the addition of Ti shifts the upper limit of the ductility trough to higher temperatures. As many researchers have pointed out,4,3,8 the improvement in ductility results from the coarsening of precipitates with reduction in the cooling rate. This increases the inter-particle spacing thereby reducing the strength difference between the grain interior and the weak precipitation-free zone adjacent to the austenite grain boundaries. Thus, formation and propagation of microcracks are suppressed. The present results support this view as can be seen from the size distributions of precipitates in the Nb and Nb–hiTi steels in Figs. 9 and 10. It is clear that both the mean particle size and the fraction of coarse particles are bigger at the slower cooling rate used. The percentage of precipitates in Steel Nb–hiTi steel with a diameter of less than 10 nm decreased from 65 to 40% as lowering the cooling rate, whereas in Steel Nb the change was from 62 to 46%. This seems to indicate that the slow cooling has a more prominent influence on precipitates in the Nb–Ti-containing steels than those in solely Nb-containing steels.

It should be mentioned that there also existed fine precipitates in strained specimens at 900°C after slow cooling besides a bigger percentage of precipitates became coarse (see Fig. 4). Slow cooling just increases the amount of precipitation occurring at high temperatures in a coarse form before straining leaving Nb and Ti in the matrix for subsequent fine strain-induced precipitation, as suggested by Mintz8) as well as Turdogan.10)

Higher deformation temperatures are also beneficial to ductility. When the test temperature increased from 900 to 1 000°C, a significant improvement of ductility was achieved in the Nb–Ti steels (Fig. 2). This was associated with a significant change in the precipitate size: the average particle diameter at 1 000°C was 17.6 nm whereas at 900°C it was only 9.5 nm. In particular, particles with diameter less than 10 nm were almost absent at 1 000°C, as shown in Fig. 10.

It can be concluded that deformation temperature and cooling rate make influence on hot ductility by affecting precipitates in steels, particularly their sizes. Figure 11 gives a clear dependence of hot ductility on the sizes of precipitates for Steel Nb–hiTi. A coarser size, usually resulting from a lower cooling rate or higher deformation temperature, always leads to a better ductility.

4.2. Modeling the Precipitation in Steels

The thermodynamics of precipitation in Nb–Ti steels can be described by the thermodynamic model,12–15) which are basis for current modeling and shown in details in Appendix I. The equilibrium compositions of precipitates at different temperatures were calculated using the data (Table 3) from Ref. 16).

Figure 12 shows the calculated equilibrium Ti/(Ti/Nb) mole fraction of the fine precipitates for the two Nb–Ti steels as a function of temperature. In the equilibrium calculation, the assumption is made that there are no solute concentration gradients in the austenite and precipitates. The solid lines in the figure are on the basis that bulk concentrations are equal to the initial concentrations since a certain supersaturation is necessary for precipitate nucleation. For instance, Kunze et al.17) reported that TiN particles only formed in the regions where the supersaturation was higher than 15 fold. The dash lines are also for equilibrium conditions with no concentration gradients in the matrix and precipitates, but on the assumption that (NbTi) (CN) precipitates in equilibrium at 1 150°C are removed from the system. The choice of 1 150°C is somewhat arbitrary; it is based on the observation that the highest mea-

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sured Ti/(Ti+Nb) mole ratio for any of the precipitates in Steel Nb–hiTi was 0.78, which corresponds to equilibrium at 1150°C. This approach allows a rough estimate to be made of the concentration differences that can arise in the precipitates due to slow diffusion within the precipitates, e.g. type II frond-like precipitates, and also of the concentration variation in the matrix resulting from coarse high-temperature precipitation during cooling. The data points in Fig. 12 show the measured mole fractions for the fine precipitates at the two test temperatures in the two steels. The fine precipitates are presumably formed at the test temperature and can be expected to have composition in local equilibrium with the matrix at the test temperature. The ‘local’ matrix composition can be affected by coarse high-temperature precipitation during cooling in which case local equilibrium could be represented by the dashed line in Fig. 12. Alternatively, outside of the coarse precipitates the local matrix composition can be considered close to the bulk composition. On this basis, the compositions of the fine precipitates can be expected to roughly vary between the full and dashed lines. The above approach ignores the micro-segregation that results from dendritic solidification. This will change the exact positions of the lines in Fig. 12. Overall, the measured Ti/(Ti+Nb) fractions agree with thermodynamic expectations.

The frond-like precipitates presumably formed during cooling when the center portion of the particles formed first at a high temperature producing a high content of Ti. As the temperature decreased, the branches grew with layers deposited at even lower temperatures and lower titanium contents.

The composition of the coarse irregular type I precipitates along the prior austenite grain/subgrain boundaries was far from the value predicted by the above thermodynamic model. Zhou and Priestner18) observed a very similar result and suggested that it could be attributed to the different segregation ratios of Nb and Ti in the interdendritic liquid during solidification. The interdendritic region was usually changed to austenite grain/subgrain boundaries after the delta-to-austenite phase transformation, which was supposed to be the reason for the formation of Nb-rich precipitates at austenite grain/subgrain boundaries. The segregation ratios for Nb and Ti in interdendritic liquid pools when the solidified fraction is 5% were estimated by Zhou and Priestner18) to be about 8 and 3, respectively. Taking this interdendritic segregation of the solute into account in equilibrium calculations and ignoring the back diffusion of Nb and Ti during the subsequent cooling could give calculation result consistent with the measurements, as shown in Fig. 13.

4.3. Influence of Titanium on Hot Ductility of Nb Containing Steels

In the present case, the addition of Ti always obviously deteriorated the hot ductility of the Nb-bearing steels no matter how much Ti was added. However, Abushosha et al.5) observed that an improvement could be achieved with slow cooling when 0.02% Ti was added to a steel containing 0.11–0.023Nb–0.009%N (%wt). The discrepancy between these results may be explained on the basis of the different compositions of the steels tested, because the density and composition of the precipitated particles depend on the exact composition of the steel. This can be shown using the thermodynamic model described above. The results of the calculations are illustrated in Fig. 14 and lead to the following conclusions:

1. When 0.014–0.04%Ti was added to Nb steel, the volume fraction of precipitates in the Nb–Ti steels is as about 2–4 times as that in the corresponding Nb steels at temperature range of 800–1000°C.
2. For a given nitrogen content, a higher Ti/N, i.e. a higher titanium content, produces a larger volume fraction of precipitates. For instance, the volume fraction of precipi-
tates in Steel Nb–hiTi is almost two times as that in Steel Nb–loTi at the temperature range 800–1000°C (Fig. 14(a)).

(3) In the Abushosha’s Nb–Ti steel with a high level of nitrogen but small addition of Ti, i.e., a lower ratio of Ti/N, the volume fraction of precipitates increases more slowly at temperature range 900–1150°C, as revealed by curves 1, 2 and 3 in Fig. 14(a). The equilibrium compositions of precipitates formed at these temperatures are Ti_{0.65–0.8}Nb_{0.35–0.1}C_{0.2–0.34}N_{0.66–0.8} (curve 2 in Fig. 14(b)), mainly nitrides.

(4) The content of nitrogen has hardly any influence on the volume fraction of Nb(CN) in Nb-containing steels at the temperatures range of 800–1000°C (curves 4 and 5 in Fig. 13(a)), which is the typical temperature range for straightening of the slabs.

(5) It is well known that the hot ductility of microalloyed steels depends on the volume fraction and size of precipitates. In Nb and Nb–Ti bearing steels, strain-induced Nb(CN) or (Ti_{x}Nb_{1−x})(C_{y}N_{1−y}) particles formed at 900°C are both very fine, about 10 nm, according to the observation shown in Figs. 4 and 7. Therefore, the volume fraction of fine strain-induced precipitates may control the ductility. Table 4 lists the maximum volume fraction of precipitates at different temperatures for the Ti–Nb steels in Fig. 14. It should be noted that near a half of the precipitates formed below 1150°C when nitrogen content was around 50 ppm, but only about 25% at 80 ppm nitrogen content, i.e., higher nitrogen content with lower Ti/N will result in a higher driving force for high-temperature precipitation in a coarser form. These coarse particles have hardly any effect on the ductility. In other words, the volume fraction of strain-induced precipitates in the Abushosha’s Nb–Ti steel could be less than that in the corresponding Nb steel during the slow cooling since almost 75% solutes of Nb and Ti could form coarse precipitates above 1150°C (Table 4). Thus, the small improvement in the ductility of a Nb steel due to the addition of Ti found by Abushosha et al. is understandable. However, in the present Steel Nb–hiTi with ~0.005% N, the equilibrium volume fraction of precipitates is much larger than that in the corresponding Nb steel (curve 4), and half of the particles precipitated below 1150°C. This means that a larger volume fraction of fine precipitates could form in the straining stage where the solute concentration in solution at high temperature, i.e., 1150°C, might remain down to 900°C with subsequent deformation producing close to equilibrium precipitation. Consequently, ductility was deteriorated due to the addition of Ti and the ductility trough was extended to a higher temperature since the Ti–Nb complex precipitates can exist at higher temperatures.

For Steel Nb–loTi with the lower Ti/N close to Abushosha’s Nb–Ti steel, although the volume fraction of precipitates in equilibrium decreased with the decreasing Ti content (curves 1 and 3 in Fig. 13(a)), the chemical driving force for precipitation at a high temperature, compared with precipitation in Abushosha’s Nb–Ti steel, also decreased because of the lower nitrogen content as stated above, and may not have been high enough for precipitation. In such a case, the supersaturation from the concentration in solution at a higher temperature could remain down to the straining temperature. Then, extensive strain-induced precipitation could also occur during the deformation. Moreover, the strain-induced precipitates seem to become finer with the decreasing Ti content as definitely found by Comineli et al. Both of these factors make the ductility of Steel Nb–hiTi is still poorer than that of Steel Nb. Even if less Ti than 0.014% is added to 0.03%Nb–0.005%N steel, the same trend can also be expected since the chemical driving force for precipitation at high temperature further decreases and precipitates become finer with the decreasing Ti content, although not investigated experimentally here. However, the extent of the deterioration of ductility can be smaller since the volume fraction of strain-induced Ti–Nb complex precipitation could decrease with the decreasing Ti content.

### Table 4. Calculated volume fraction of precipitates in Nb–Ti steels at various temperatures from Fig. 14.

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Curve No.</th>
<th>%N</th>
<th>%Ti</th>
<th>Volume fraction 900°C</th>
<th>900°C</th>
<th>1050°C</th>
<th>1150°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel Nb–loTi</td>
<td>Curve 1</td>
<td>0.0053</td>
<td>0.014</td>
<td>Absolute (×10⁶)</td>
<td>6.40</td>
<td>5.04</td>
<td>3.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Relative (%)</td>
<td>100</td>
<td>79</td>
<td>57</td>
</tr>
<tr>
<td>Abushosha’s Nb–Ti steel</td>
<td>Curve 2</td>
<td>0.008</td>
<td>0.02</td>
<td>Absolute (×10⁶)</td>
<td>6.56</td>
<td>5.73</td>
<td>4.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Relative (%)</td>
<td>100</td>
<td>87</td>
<td>73</td>
</tr>
<tr>
<td>Steel Nb–hiTi</td>
<td>Curve 3</td>
<td>0.0059</td>
<td>0.038</td>
<td>Absolute (×10⁶)</td>
<td>11.3</td>
<td>9.22</td>
<td>6.70</td>
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<tr>
<td></td>
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<td></td>
<td>Relative (%)</td>
<td>100</td>
<td>82</td>
<td>59</td>
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<tr>
<td>Steel Nb</td>
<td>Curve 5</td>
<td>0.0050</td>
<td>0</td>
<td>Absolute (×10⁶)</td>
<td>3.11</td>
<td>0.84</td>
<td></td>
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<tr>
<td>Abushosha’s Nb steel</td>
<td>Curve 6</td>
<td>0.009</td>
<td>0</td>
<td>Absolute (×10⁶)</td>
<td>3.04</td>
<td>1.40</td>
<td></td>
</tr>
</tbody>
</table>

(Relative value is the ratio of the volume fraction of precipitates at a given temperature to that at 900°C)

### 4.4. Influence of Nb on Hot Ductility of Ti-containing Steels

The addition of Nb only occasionally resulted in a deterioration of the ductility of Ti-containing steels. For instance, the ductility of Steel Nb–loTi at 1000°C after the fast cooling and at 900°C after the slow cooling is worse than that of Steel Ti, as shown in Fig. 2. This influence is not so prominent as the influence of Ti in Nb-containing steels, which can be explained by the fact that Ti has a much stronger affinity with N than Nb has so that fine Ti(CN) particles can precipitate at higher temperatures even without Nb. It is noted that there is no obvious difference between the sizes of precipitates in both steels, as shown in Table 2. Therefore, that occasional deterioration of ductility by the addition of Nb might be attributed to the smaller concentration product of complex carbonitride (Ti_{x}Nb_{1−x})(C_{y}N_{1−y}) than that of Ti(CN), which leads to a bit larger volume fraction of precipitates.

### 4.5. Influence of Temperature History on Hot Ductility

The effect of prechilling of the specimen to a lower temperature, to the austenite or the austenite-ferrite regime, before tensile straining has been investigated by Ouchi and Matsumoto. The hot ductility of C–Mn–Al and C–Mn–Nb–Al steels was found to be deteriorated and an enhanced
precipitation of AlN or Nb(CN) in the ferrite formed and in the austenite phase was suggested to be a reason for impaired ductility. The influence of thermal fluctuations in the course of cooling on the hot ductility was investigated by Cardoso et al.\textsuperscript{19} in C–Mn–Al steels and by Mintz et al.\textsuperscript{20,21} in C–Mn–Al, C–Mn–Nb–Al and C–Mn–Al–Ti steels. Impaired ductility due to enhanced precipitation and the formation of ferrite during undercooling was recorded in the Ti-free steels, but no effect was found in the Ti-bearing steel where the formation of TiN prevents further precipitation of AlN.

Here, the prechilling before straining had no influence on ductility at the test temperature range of 900–1000°C, as shown in Fig. 2, although precipitates seem to be a little bigger if prechilling was used, which can be attributed to a longer time for the growth of precipitates before straining. Prechilling might encourage a higher volume fraction of precipitation, thereby counteracting the improvement due to coarser precipitation. However, at 800°C the ductility of both the Nb and the Nb–hiTi steels was impaired by this treatment. It is noted that Ar\textsubscript{3} temperatures of both steels are around 730°C according to the empirical equations used in Ref. 22). This means that the temperature drop of 100°C before the straining at 800°C resulted in the formation of some ferrite. As a consequence of this, the volume fraction of precipitated particles might increase prominently because the precipitates have a much lower solubility in ferrite than in austenite, as also observed before.\textsuperscript{23} Some ferrite formed at a low holding temperature may persist up to the test temperature similarly as the precipitate particles decreasing the hot ductility.

Cardoso et al.\textsuperscript{19} and Mintz et al.\textsuperscript{20,21} concluded from their results that, in practice, because thermal fluctuations occur in the continuous casting, the Ti-alloying has a beneficial influence. However, no evidence can be given to support this opinion in the present case. In conclusion, the addition of Ti does not show any advantages regarding the hot ductility even after prechilling.

4.6. Commercial Implications

It can be concluded that influence of Ti on the hot ductility of as-cast Nb-containing steels depends on whether the addition of Ti encourages more or less precipitation during straining. According to the above equilibrium precipitation model, a higher Ti content at a given nitrogen content, corresponding to higher Ti/N ratio, will result in more intense strain-induced precipitation, which means that the addition of Ti at a typical level of nitrogen, e.g. 50 ppm, will impair the hot ductility and possibly increase the incidence of cracking in slabs. At a high level of nitrogen, e.g. around 80–100 ppm, however, a small addition of Ti, e.g. 0.02% Ti, can be beneficial to hot ductility by encouraging Nb to precipitate out together with Nb at higher temperatures during the slow cooling and leaving less Nb in solution for strain-induced precipitation at lower temperatures, as found by Abushosha et al.\textsuperscript{5}.

Soft cooling encourages coarse precipitation at higher temperatures before straightening resulting in a marked improvement in ductility. Furthermore, straining at higher temperatures, e.g. 900°C instead of 800°C, has a pronounced positive influence on ductility of Nb-containing steel. Particularly, at 1000°C, strain-induced precipitates with diameter less than 10 nm are always absent in the Nb–Ti steels, and correspond to a much-improved hot ductility of the Nb–Ti steels. Therefore, slow cooling and high straining temperature could help to reduce the incidence of cracking in slabs in the continuous casting.

5. Conclusions

(1) There are three types precipitates in Nb–Ti microalloyed steels with the different sizes and compositions: coarse boundary particles, large frond-like and fine strain-induced particles. The last type of precipitate mostly influences hot ductility of as-cast Nb and Nb–Ti microalloyed steels in the austenite temperature range. Any method of reducing their volume fraction or coarsening their size would improve the hot ductility.

(2) Slow cooling encourages precipitation in a coarse form prior to straining and reduces the volume fraction of fine strain-induced precipitates. The temperature of straining has a more marked influence on particle size and hot ductility. Even in Ti–Nb microalloyed steels, fine precipitates (<10 nm) are practically absent for the straining temperature of 1000°C or higher.

(3) The addition of Ti to Nb-bearing steels can have two kinds of effect on precipitation and hot ductility correspondingly. For 0.1%C–0.03%Nb–0.005%N steel, additions of 0.015–0.04%Ti led to a worse ductility both in direct cooling and when prechilling was applied. Contrary to this, an addition of 0.02% Ti to 0.11%C–0.023Nb–0.008%N steel resulted in a small improvement of hot ductility after the slow cooling as investigated by Abushosha et al.\textsuperscript{5}. The discrepancy can be reasonably explained by thermodynamic calculation model. In the former case, a large volume fraction of fine strain-induced precipitates is available because Ti can precipitate out together with Nb. In the latter case, however, the total volume fraction of precipitates is restricted at high level of nitrogen but low level of titanium, and most of them precipitate at higher temperatures as a coarse form, mainly as (TiNb)N. This leaves less solutes for subsequent fine strain-induced precipitation and finally favors the ductility.

(4) Only for electric arc steels with typically a high level of nitrogen, a small addition of Ti can be considered to be beneficial.

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Appendix. Thermodynamic Modeling on Ti$_2$Nb$_{1-x}$C$_x$N$_{1-y}$ Precipitation

In this model, the solubility of complex precipitate with the NaCl type structure can be estimated as many researches have reported. 12-15 Nb and Ti sites are on one sub-lattice (fcc structure), and C and N on the other sub-lattice (fcc) in the complex precipitates of Ti$_2$Nb$_{1-x}$C$_x$N$_{1-y}$. Thus, it could be regarded as a complete ideal solid solution of NbC, NbN, TiC and TiN when the interaction between C and N or Ti and Nb is ignored. Thus, the activity of binary compound in the precipitate can be described as:

\[ a_{\text{NbC}} = x_{\text{NbC}}/(x_{\text{NbC}} + x_{\text{NbN}} + x_{\text{TiC}} + x_{\text{TiN}}) \]  (A-1)

\[ a_{\text{NbN}} = x_{\text{NbN}}/(x_{\text{NbC}} + x_{\text{NbN}} + x_{\text{TiC}} + x_{\text{TiN}}) \]  (A-2)

\[ a_{\text{TiC}} = x_{\text{TiC}}/(x_{\text{NbC}} + x_{\text{NbN}} + x_{\text{TiC}} + x_{\text{TiN}}) \]  (A-3)

\[ a_{\text{TiN}} = x_{\text{TiN}}/(x_{\text{NbC}} + x_{\text{NbN}} + x_{\text{TiC}} + x_{\text{TiN}}) \]  (A-4)

where \( x_{\text{NbC}}, x_{\text{NbN}}, x_{\text{TiC}} \) and \( x_{\text{TiN}} \) are the mole fraction of NbC, NbN, TiC and TiN respectively, and equations of equilibrium could be expressed as follows:

\[ \ln a_{\text{NbC}} + \ln a_{\text{NbN}} = \Delta G_{\text{NbC}}/RT \]  (A-5)

\[ \ln a_{\text{NbN}} + \ln a_{\text{TiC}} = \Delta G_{\text{NbN}}/RT \]  (A-6)

\[ \ln a_{\text{TiC}} + \ln a_{\text{TiN}} = \Delta G_{\text{TiC}}/RT \]  (A-7)

\[ \ln a_{\text{TiN}} = \Delta G_{\text{TiN}}/RT \]  (A-8)

where \( \Delta G \) is the standard free energy of formation of binary compound and equal to

\[ \Delta G_{\text{NbC}}/RT = 2.3 \log K_{\text{NbC}} + \ln(A_{\text{TiC}}/10^4 A_{\text{TiN}}) \]

\[ + (e_{\text{Nb}}^c + e_{\text{N}}^c) x_{\text{Nb}} + (e_{\text{C}}^c + e_{\text{N}}^c) x_{\text{C}} \]  (A-9)

\[ \Delta G_{\text{NbN}}/RT = 2.3 \log K_{\text{NbN}} + \ln(A_{\text{TiC}}/10^4 A_{\text{TiN}}) \]

\[ + (e_{\text{Nb}}^c + e_{\text{N}}^c) x_{\text{Nb}} + (e_{\text{N}}^c + e_{\text{N}}^c) x_{\text{N}} \]  (A-10)

\[ \Delta G_{\text{TiC}}/RT = 2.3 \log K_{\text{TiC}} + \ln(A_{\text{TiC}}/10^4 A_{\text{TiN}}) \]

\[ + (e_{\text{Ti}}^c + e_{\text{N}}^c) x_{\text{Ti}} + (e_{\text{C}}^c + e_{\text{N}}^c) x_{\text{C}} \]  (A-11)

\[ \Delta G_{\text{TiN}}/RT = 2.3 \log K_{\text{TiN}} + \ln(A_{\text{TiC}}/10^4 A_{\text{TiN}}) \]

\[ + (e_{\text{Ti}}^c + e_{\text{N}}^c) x_{\text{Ti}} + (e_{\text{N}}^c + e_{\text{N}}^c) x_{\text{N}} \]  (A-12)

When the solubility products of NbC, NbN, TiC and TiN is given, the chemical driving force for precipitation of Ti$_2$Nb$_{1-x}$C$_x$N$_{1-y}$ is:

\[ \Delta G_{\text{chem}} = RT \left[ x_{\text{TiC}} \ln(x_{\text{TiC}}/x_{\text{TiN}}) + (1-x_{\text{TiC}}) \ln(x_{\text{TiN}}/x_{\text{TiC}}) \right] + y \left[ x_{\text{TiC}} \ln(x_{\text{TiC}}/x_{\text{TiN}}) + (1-x_{\text{TiC}}) \ln(x_{\text{TiN}}/x_{\text{TiC}}) \right] \]  (A-25)