GRAIN REFINEMENT AND HIGH PRECIPITATION HARDENING BY COMBINING MICROALLOYING AND ULTRA FAST COOLING

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ABSTRACT

Microalloying with Nb has been proved to be a very effective mean to reduce the ferrite grain size as the deformation of the austenite is cumulated during rolling under T_{nr}, the non-recrystallisation temperature. Many parameters affect both the ferrite grain size and the precipitation kinetics during hot rolling Nb-bearing steel. Among these parameters the cooling rate and the coiling temperature can be easily controlled and play the most important roles in the control of the precipitation hardening. Ultra fast cooling was applied after the last pass of finishing rolling Nb and Ti-bearing steel. In all cases the Nb(C,N) precipitation was strongly retarded, increasing the precipitation hardening by the formation of finer precipitates. Moreover a non-negligible amount of Nb remained in solution. After cold rolling, precipitation hardening was still possible during annealing.
During this research work, several steel grades microalloyed with Nb and Ti were hot rolled and cooled using ultra fast cooling to different coiling temperatures to precipitate different amounts of Nb(C,N). Hot rolled strips were cold rolled and annealed at different temperatures. The kinetics of precipitation and recrystallisation were studied with emphasis on the mechanical property improvements.

KEYWORDS

Nb, precipitation hardening, ultra fast cooling, fine grains, hot rolling, cold rolling.

INTRODUCTION

The main parameters that determine the final ferrite grain size during hot rolling strips are: the chemical composition, the austenite grain size, the cooling rate between finishing rolling and coiling, the coiling temperature, the delay time between the end of rolling and cooling. Some of these parameters have been studied earlier [1], and their main effects on the ferrite grain size are summarised below:

- *Microalloy content*: the microalloying element Nb is a very important element widely used for the grain refinement. When in solid solution in the austenite, it retards its recrystallisation during rolling, and also lowers the kinetics of the $\gamma-\alpha$ transformation.

- *Cooling rate*: Using accelerated cooling (UFC: Ultra Fast Cooling) between the end of rolling and coiling increased the precipitation hardening efficiency and reduced the ferrite grain size. Accelerated cooling reduced the growth of ferrite grains during cooling, leading to finer microstructure and prevented NbC precipitation during cooling. This very important result shows that the microalloy content can be reduced to obtain similar strength level if fast cooling or ultra fast cooling is applied in place of the conventional (laminar) cooling.

- *Coiling temperature*: In all studied steels, decreasing the coiling temperature led to finer ferrite grains, provided ultra fast cooling is applied. If slow cooling is applied after rolling, the reverse situation is observed, as ferrite nucleates and grows during the cooling.

- *Rolling reduction (strain accumulation)*: Increasing the rolling reduction, especially in the last rolling passes cumulates the strain and reduces the austenite grain size. To have the maximum efficiency, the last rolling reduction must be immediately followed by fast cooling to avoid static recrystallisation of the austenite.

- *Finishing rolling temperature*: This parameter determines the amount of accumulated strain, especially in microalloyed steel when it is below T_{nr} and above Ar_3.

- *Time between the end of rolling and cooling (delay time)*: Hot torsion experiments have shown the strong difference between cooling immediately or 100 s after deformation. Independently of the cooling rate, specimens hold 100 s at 900 °C after deformation ($\varepsilon = 2$) had ferrite grain size 1 μm bigger than without holding time.

Figure 1 illustrates both effects of the cooling rate (represented by the time between the beginning of cooling from 900 °C and the austenite to ferrite transformation temperature Ar_3) and the delay time on Nb(C,N) precipitation in austenite for two Nb alloyed steels.

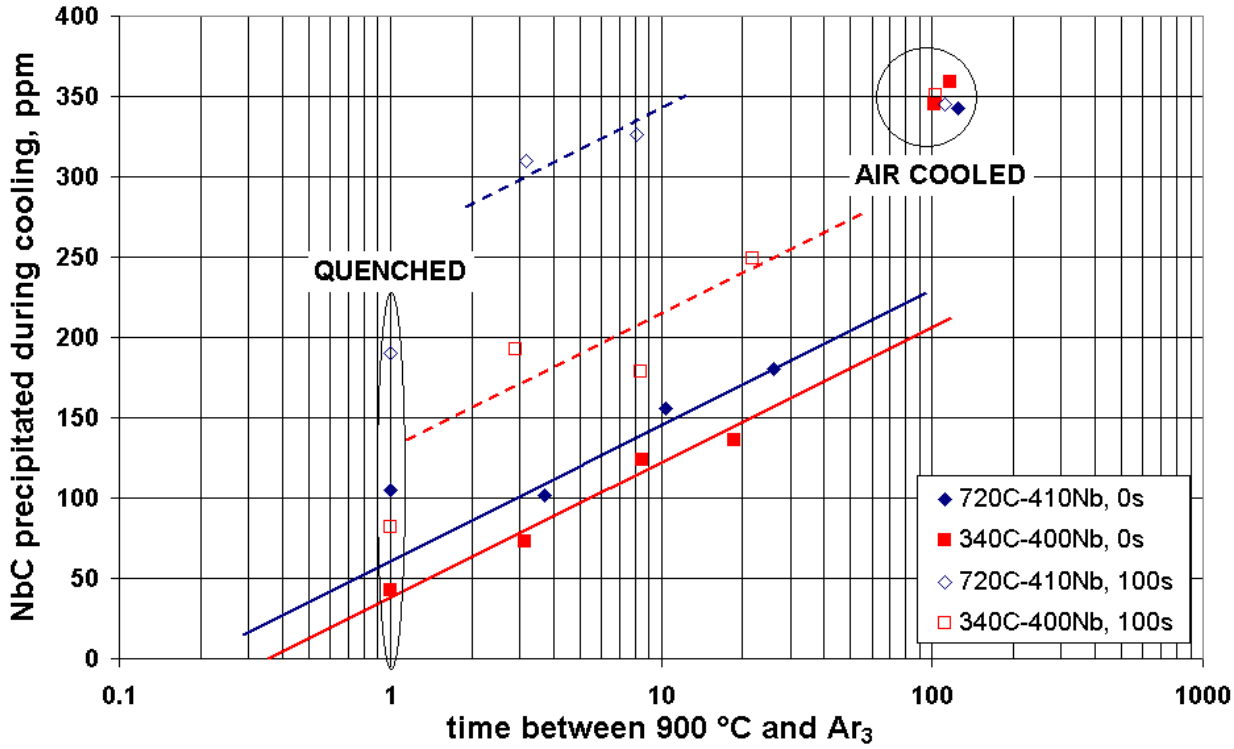

Fig.1. Effects of cooling rate and delay time on NbC precipitation in austenite after hot deformation by torsion ($\varepsilon = 2$) at 900 °C. C and N contents in ppm.

Nb is generally used in HSLA steel for ferrite grain refinement because it strongly retards the austenite recrystallisation. The second effect increasing the final strip properties is precipitation hardening. The most efficient strengthening is caused by fine (coherent) Nb(C,N) precipitates formed in the ferritic phase during the coiling operation. In cold rolled HSLA steel, most of the precipitation hardening effect is lost due to the coarsening of Nb(C,N) precipitates during annealing. This detrimental effect appears when most of the initial Nb has been precipitated during the cooling or the coiling after hot rolling. It was shown recently [2] that increasing the cooling rate between the end of hot rolling and coiling in the temperature range 500-600 °C allowed the production of hot rolled strips containing sufficient amounts of Nb in solution. During continuous annealing after cold rolling, soluble Nb could precipitate as fine Nb(C,N) causing secondary precipitation hardening.

Hot rolling simulations were done using CRM pilot line to produce hot rolled strips containing different amounts of Nb in solution at the end of the process, by varying the initial steel composition, the cooling rate between rolling and coiling, and the coiling temperature. Those plates were cold rolled using 60% and 80% cold reduction, respectively, then annealed according to industrial cycles. Dilatometer samples were used to study the interaction between Nb(C,N) precipitation and ferrite recrystallisation during annealing.

1. EXPERIMENTAL

Seven low C low Mn steel compositions have been cast to study the effects of Nb and Ti on the formation of fine ferrite and precipitation hardening during hot rolling. Their chemical compositions are given in table 1. The theoretical temperature for the end of static recrystallisation, T_{nr} [3] and the temperature of NbC precipitation in austenite[4] are indicated and were calculated using the following equations:

$$T_{nr}, °C = 887+464wt\%C+890wt\%Ti-357wt\%Si+6445wt\%Nb-644wt\%Nb^{1/2}+363wt\%Al \quad (1)$$

$$T_{NbC}, °C = -6770/(LOG((wt\%Nb)*(wt\%C))-2.26)-273 \quad (2)$$

Table 1. Chemical compositions in 10^{-3} wt.%.

Steel	C	Mn	Nb	Ti	Alsol	N	T_{nr}	T_{NbC}
1251	57	530	-	-	44	4.6	926	-
1252	52	520	19	-	35	5.3	955	1013
1254	50	520	50	-	27	5.3	1095	1120
806	62	500	59	3	43	4.8	1156	1168
1255	55	520	52	19	46	5.4	1131	1137
1134	57	540	54	25	50	6.2	1146	1146
1135	58	520	54	57	52	8.8	1173	1148

A 5 passes rolling scheme was used, starting from 30 mm thick blocks to obtain 4 mm thick sheets, with 40 % reduction in the last pass. Each steel composition was reheated one hour at 1250 °C, then hot rolled in 5 passes, finally air cooled to 600 °C and coiled at that temperature or fast cooled (150 °C/s) to the coiling temperature of 600 °C, 550 °C or 500 °C. The full rolling and cooling cycle is shown in figure 2.
Tensile specimens with 50 mm gauge length (A_{50}) were used to characterise the tensile properties of hot rolled strips. Ferrite grain sizes were determined using the line intercept method on pictures obtained from light optical microscopy, and Vickers hardness measurements were done using 5 kg diamond loads.
Nb and Ti quantification in both precipitates and solution were obtained by means of electrolytic dissolution and inductively coupled plasma spectroscopy (ICP-OES).[5] 4 mm thick strips were cold rolled with 60 % and 80 % reduction to obtain sheets with 1.5 and 0.9 mm thickness,

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respectively. Annealing cycles were done on tensile specimens in salt baths, reproducing industrial galvanising cycles (see figure 3).

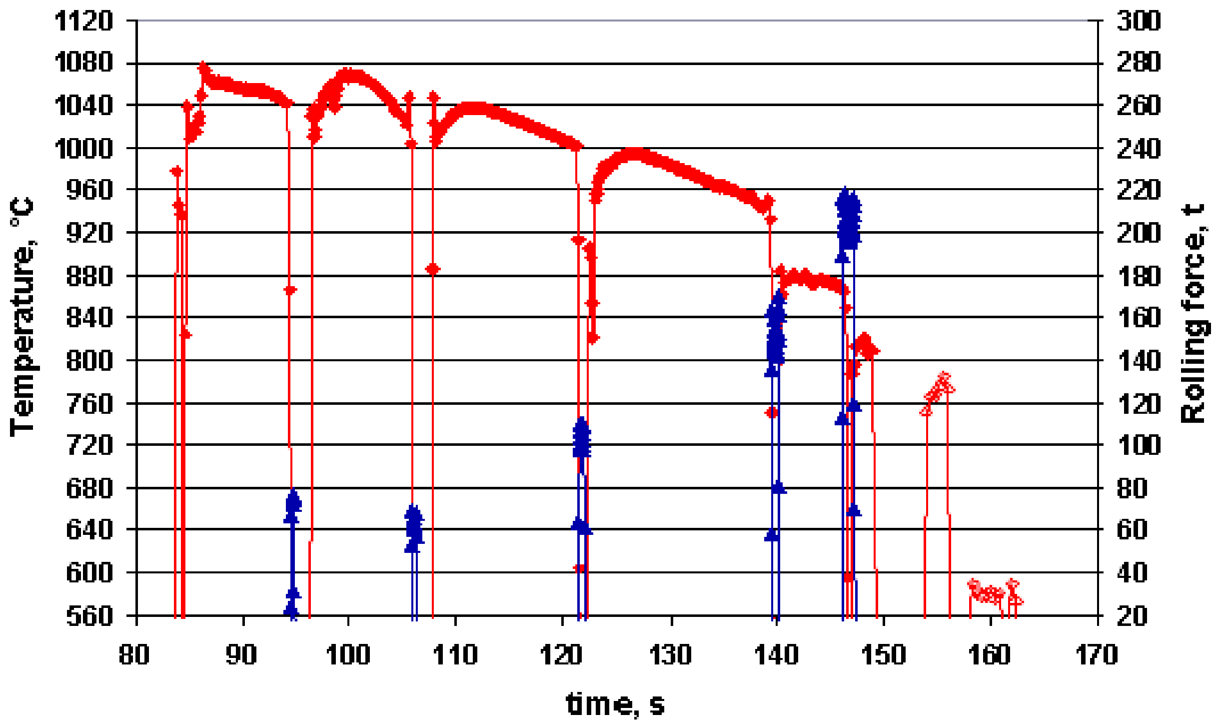

Fig.2. Surface temperature (measured by pyrometers) and rolling force during the 5 passes rolling cycles performed on the pilot line to simulate the finishing.

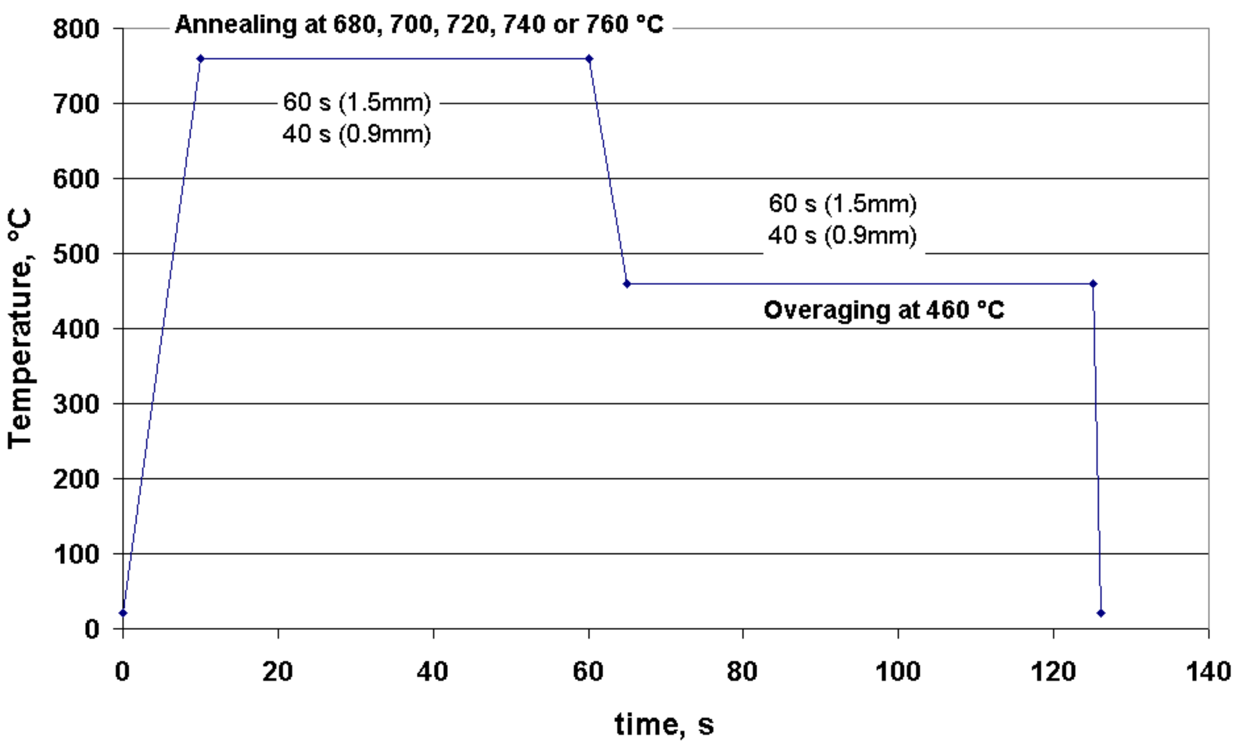

Fig.3. Annealing cycles performed in salt bath on cold rolled tensile specimens of different thickness.

2. HOT ROLLING SIMULATION: PRODUCTION OF PLATES WITH DIFFERENT AMOUNTS OF Nb IN SOLUTION

The measured values of the yield stress and tensile strength of studied steels, hot rolled and coiled at 600 °C, with and without fast cooling are reported in Figure 4. The effect of fast cooling on the precipitation hardening in Nb-alloyed steel is clearly seen, as both the yield and tensile strengths increased in the final strips. Figure 4 shows also, that Ti additions in Nb-bearing steel are detrimental for the NbC precipitation hardening efficiency. Suzuki *et al*. have shown that, during the casting stage, Ti additions change the precipitation mode of Nb(C,N) in austenite and their composition.[6]

In steel containing 0.1 wt%C, 0.005 wt%N, 0.03 wt%Nb and 0.001 wt%Ti, TiN and AlN precipitate at high temperature (T>1130 °C) and $NbC_{0.7}N_{0.3}$ form at T<980 °C. These precipitates precipitated along prior austenite grain boundaries.

In steel with 0.018 wt%Ti and 0.0005-0.0025 wt%N, $Nb_{0.5}Ti_{0.5}(C_{0.5-0.8}N_{0.5-0.2})$ precipitates formed at T<980 °C. They precipitated on TiN nucleation sites inside γ grains. Ouchy *et al.* summarised the improvement of high temperature ductility brought by Ti additions and/or reduction of N content in the steel as follows:[7]

1. Suppression of AlN precipitation;
2. Change in chemistry of carbonitrides from $Nb(C_{0.6}N_{0.26})$ with molar ratio C/Nb > 2 to $NbC_{0.86}$;
3. Complete suppression of NbN.

The detrimental effect of Ti on Nb precipitation is confirmed with the Nb quantification by electrolytic dissolution and ICP spectroscopy. The results of this quantification are given in figure 5 as the ratio of Nb not precipitated (thus kept in solution) relative to the initial Nb content. In the steel containing 500 ppm Nb and 200 ppm Ti initially, only 10 % Nb was left in solution after air cooling and coiling at 600 °C, *versus* 43 % in the steel without Ti. Increasing the cooling rate clearly increased the amount of Nb left in solution in the 3 studied steel compositions. Decreasing the coiling temperature slightly affected the Nb precipitation in Ti-free steels. From these results it can be considered that about 50 % of the initial Nb precipitated in austenite during the rolling stage or was not fully dissolved during the reheating stage, and the remaining Nb precipitated during the cooling and/or the coiling operations. Note that in spite of its detrimental effect on Nb, Ti may be useful for the better control of the precipitation. From figure 5, in Ti-free steels the coiling temperature seems to have little effect, but due to the quantification technique, it is very likely that some precipitates of Nb were not quantified and counted in the soluble part due to their small size. This can occur to precipitates with size below 20 nm (filter size). This assumption was confirmed by hardness measurements showing increasing hardness with increasing soluble Nb. In fact, the quantified NbC precipitates are coarse and incoherent and were mainly formed in the austenite. These are not strengthening. In the soluble part very fine (coherent) precipitates formed in ferrite are those responsible for precipitation hardening.

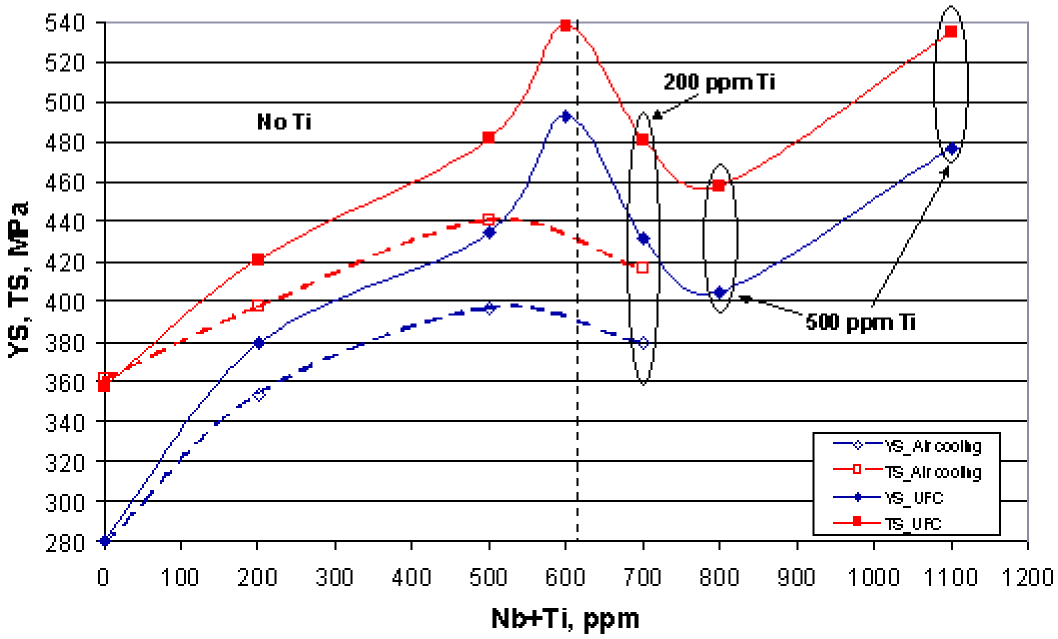

Fig.4. Tensile properties of hot rolled steels with different Nb and Ti additions showing the effect of the cooling rate before coiling at 600 °C.

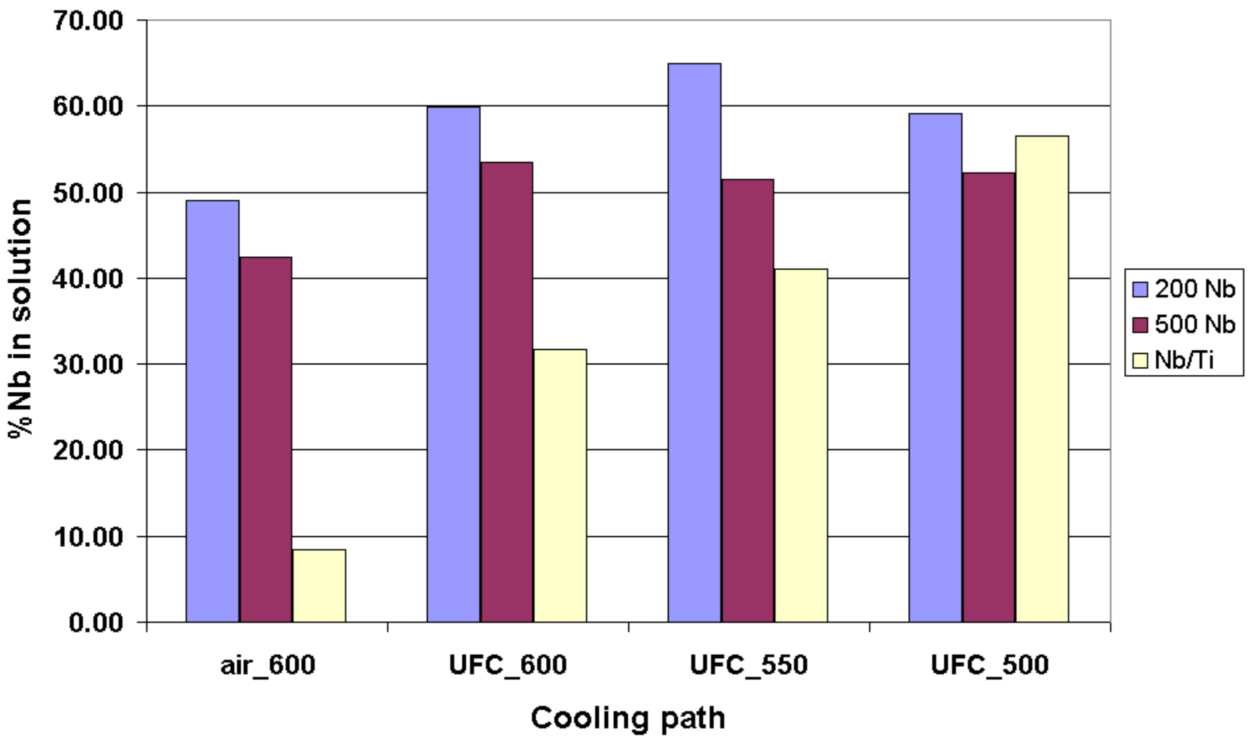

Fig.5. Amount of Nb kept in solution (relative to the initial Nb content) after hot rolling and cooling with air or ultra fast cooling to different coiling temperatures.

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Figure 6 is a tensile strength versus ferrite grain size plot for industrial coils.[8] It is clearly seen that low carbon steels microalloyed with Nb have finer grains and consequently higher tensile strength than conventional low carbon steel. Additional points indicated in red were obtained in laboratory using ultra fast cooling before coiling. It can be seen that the strength level is increased due to the accumulation of both effects: grain refinement and precipitation hardening.

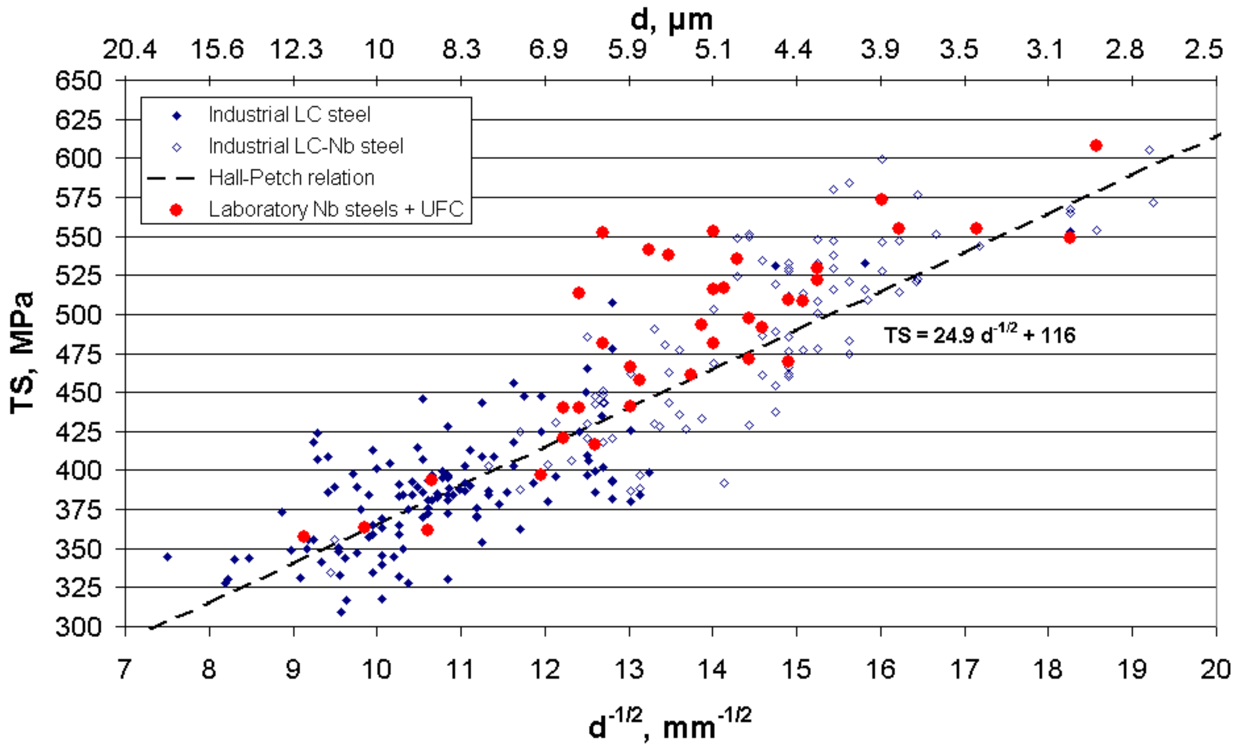

Fig.6. Hall-Petch relation from industrially produced steel and laboratory rolled Nb-steel.

Several strips have been produced with different amounts of Nb in solution (mixed with very fine precipitates), ranging from 10 to 65 % of the initial Nb content (200 or 500 ppm).

3. COLD ROLLING AND ANNEALING: INDUSTRIAL CYCLES

In order to check the potential hardening due to the remaining Nb in solution, some hot rolled strips were reheated 100 s in salt bath at different temperatures between 670 °C and 770 °C. Figure 7 shows that up to 70 MPa increase of the tensile strength is due only to precipitation hardening in steels reheated at 720 °C. This confirms that using ultra fast cooling before coiling at 600 °C kept sufficient Nb in solution.

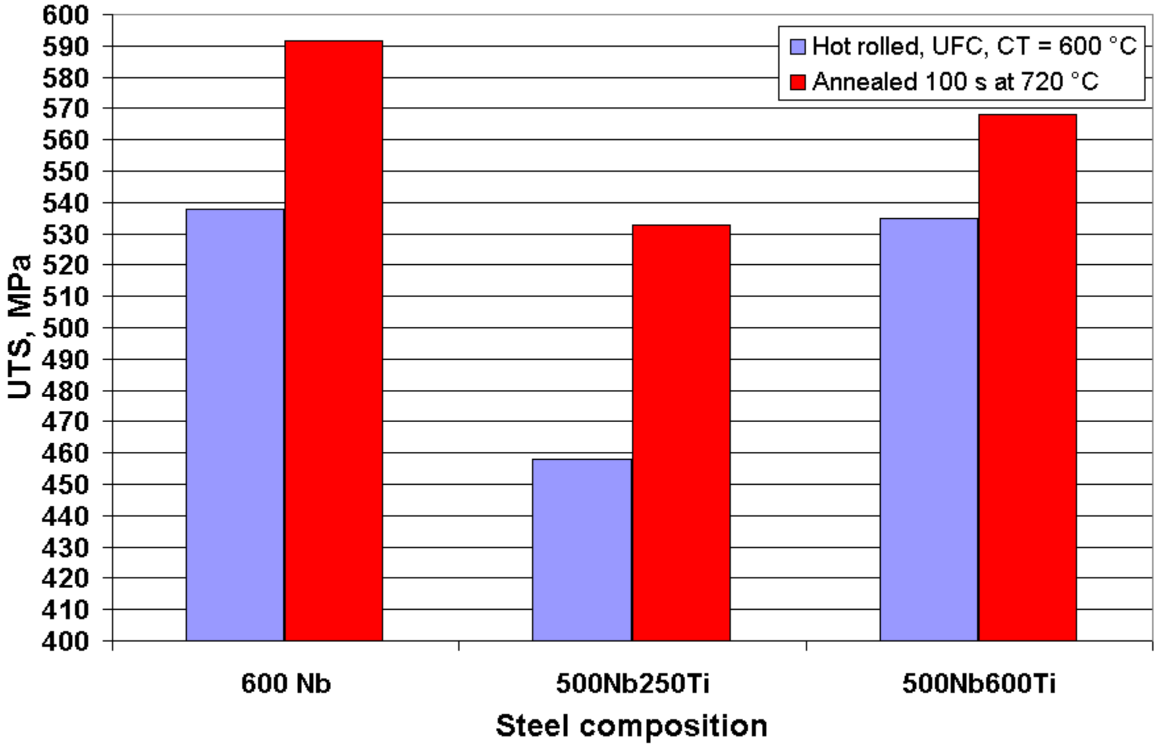

Fig.7. Ultimate tensile strength increase due to Nb precipitation hardening after annealing hot rolled strips ultra fast cooled and coiled at 600 °C (No cold rolling operation). Nb and Ti contents in ppm.

Hot rolled strips containing different amounts of Nb in solution were cold rolled with 60 and 80 % reduction. Cold rolled sheets were then reheated following the annealing cycles given in figure 3. Tensile properties were measured on A_{50} specimens and microstructure observations combined with hardness measurements were done to follow the recrystallisation during annealing.

In figure 8 the comparison between microstructures and tensile properties is made for the steel containing initially 500 ppm Nb hot rolled and coiled at 600 °C after having been cooled in air, and with the fast cooling device, respectively. In the air-cooled steel (precipitated Nb = 259 ppm, soluble Nb = 191 ppm), the following observations can be done:

- at low annealing temperature (680 °C), strong increases of both the yield stress and tensile strength are measured but the microstructure is not fully recrystallised;
- there is a range of temperatures where the microstructure is fully recrystallised, but the tensile properties drop with 15 MPa regarding the initial (hot rolled) properties, due to NbC precipitates coarsening;
- at higher temperatures (in most of the cases the annealing temperature 760 °C is above Ac_1) the strength slightly increases, due to the presence of very little amount of martensite or bainite formed after intercritical annealing.

In the ultra fast cooled steel (precipitated Nb = 220 ppm, soluble Nb = 253 ppm), the annealing behaviour is different:

- at low annealing temperatures (680 °C and 700 °C) the strength increase is huge (up to 200 MPa) but the microstructure is not recrystallised;
- the recrystallisation temperature has been raised, the kinetics of recrystallisation strongly retarded;
- there is a range of temperatures where the microstructure is nearly fully recrystallised and precipitation hardening is efficient (+ 60 MPa when compared to the cold rolled and annealed air-cooled steel);

- at the higher temperature 760 °C, which is above Ac_1, NbC precipitation occurs in austenite during intercritical annealing, and the precipitation hardening effect is lost.

The same observations were made for steels with different initial Nb and Ti contents. Nb kept in solution was found to strongly retard the ferrite recrystallisation, and is very efficient for precipitation hardening during annealing.

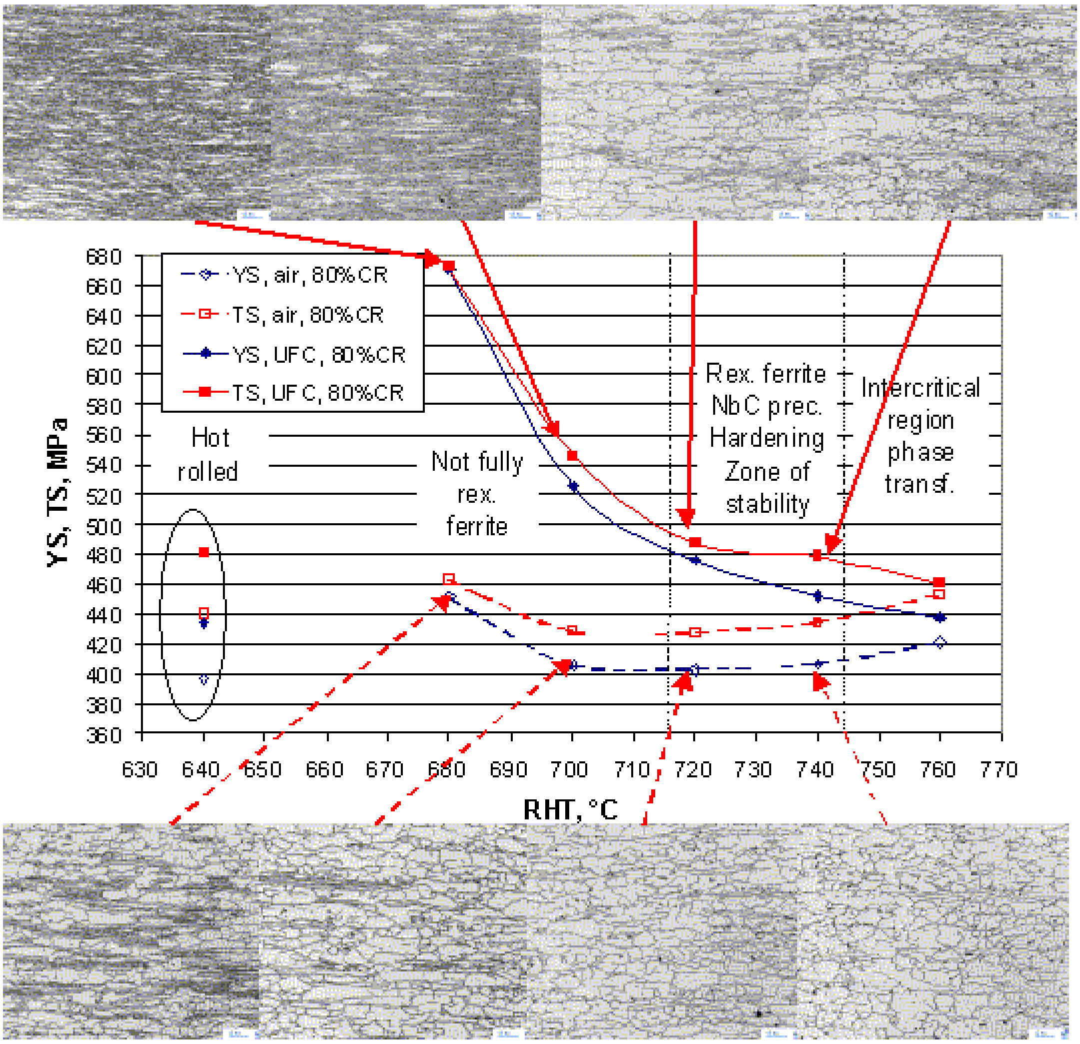

Fig. 8. Microstructure and tensile property evolution after annealing cold rolled steel 1254 (500 ppm Nb), after hot rolling and processing with different cooling patterns.

4. DILATOMETRIC STUDY OF RECRYSTALLISATION AND PRECIPITATION

Dilatometer samples with 0.9 mm thickness, 4 mm width and 10 mm length have been reheated at different temperatures between 680 °C and 740 °C and held at this temperatures different times. The aim was to study the effect of soluble Nb on the ferrite recrystallisation kinetic. Figure 9 shows the microstructure and hardness evolution during annealing at 680 °C and 720 °C, respectively, the steel containing initially 500 ppm Nb hot rolled and cooled at 150 °C/s to the coiling temperature 600 °C (precipitated Nb = 220 ppm, soluble Nb = 253 ppm).

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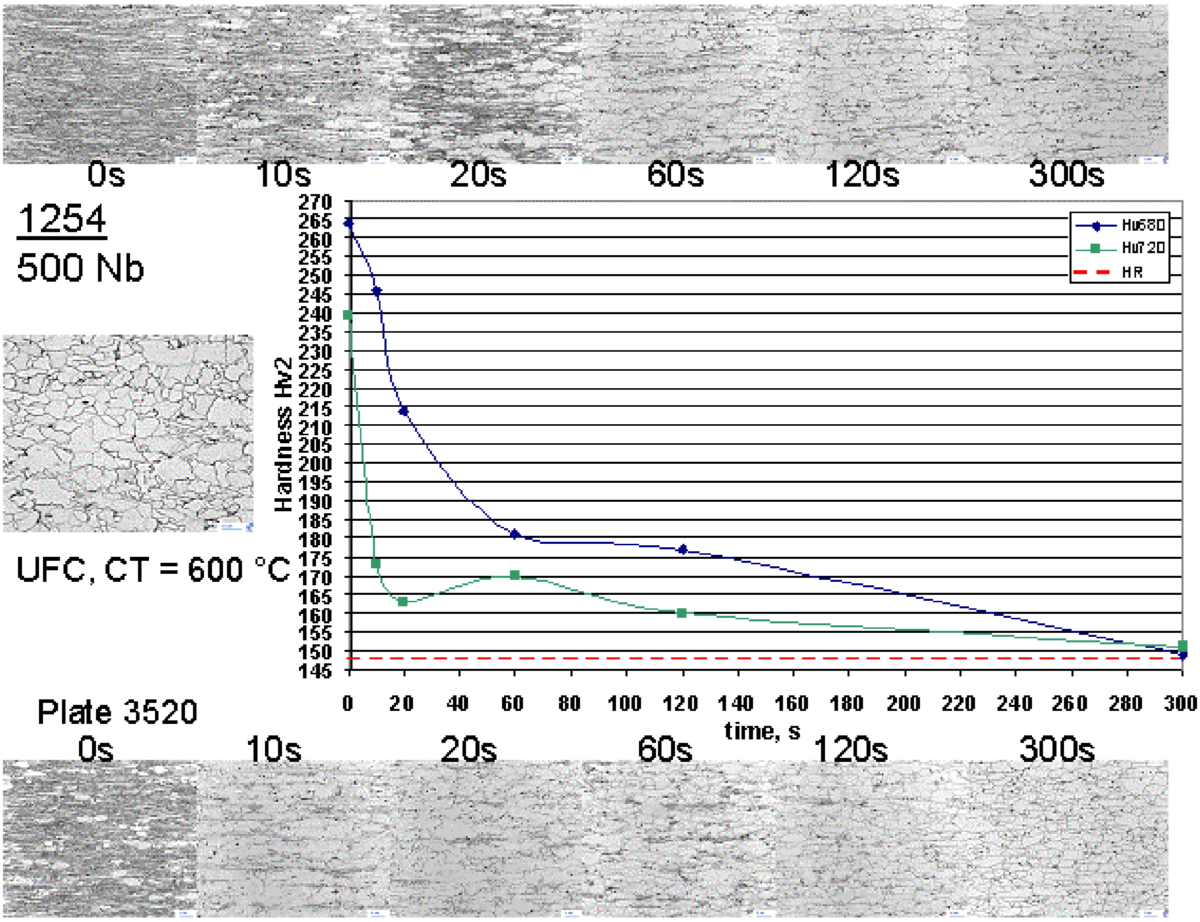

Fig. 9. Microstructure and hardness evolution after annealing cold rolled steel 1254 (500 ppm) at 680 °C (top) and 720 °C (bottom).

During isothermal holding, the dilatometer samples contracted, likely due to creep. However, depending on the amount of Nb in solution the contraction behaviour differed. Following this contraction, it was possible to detect the end of the ferrite recrystallisation. The function representing the relative contraction of the sample at a given temperature was called y(t) and was calculated from the dilatation curves at each time t using the relation:

$$y(t) = \frac{l(t) - l_0}{l_f - l_0} \quad (3)$$

where l(t), l_0 and l_f correspond to the sample length at time t, at the beginning of the holding and at the end of the holding, respectively.

At each annealing temperature, the Johnson-Mehl-Avrami (JMA) analysis was carried out by fitting the experimental data to the JMA equation:[9]

$$y(t) = 1 - \exp\left[-k(t)^n\right] \quad (4)$$

where

$$k(T) = A\exp\left(\frac{-Q}{RT}\right) \quad (5)$$

and y(t) is the sample contraction proportional to the ferrite recrystallisation, t, the time, T, the temperature, A, the frequency factor, Q, the activation energy, k(T), the temperature-dependent rate constant and n, the Avrami exponent. R is the gas constant, 8.314 $JK^{-1}mol^{-1}$. n and k can be determined experimentally by modifying equation (4) to:

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$$\ln\left(\ln\left(\frac{1}{1-y(t)}\right)\right) = \ln k + n\ln(t) \qquad (6)$$

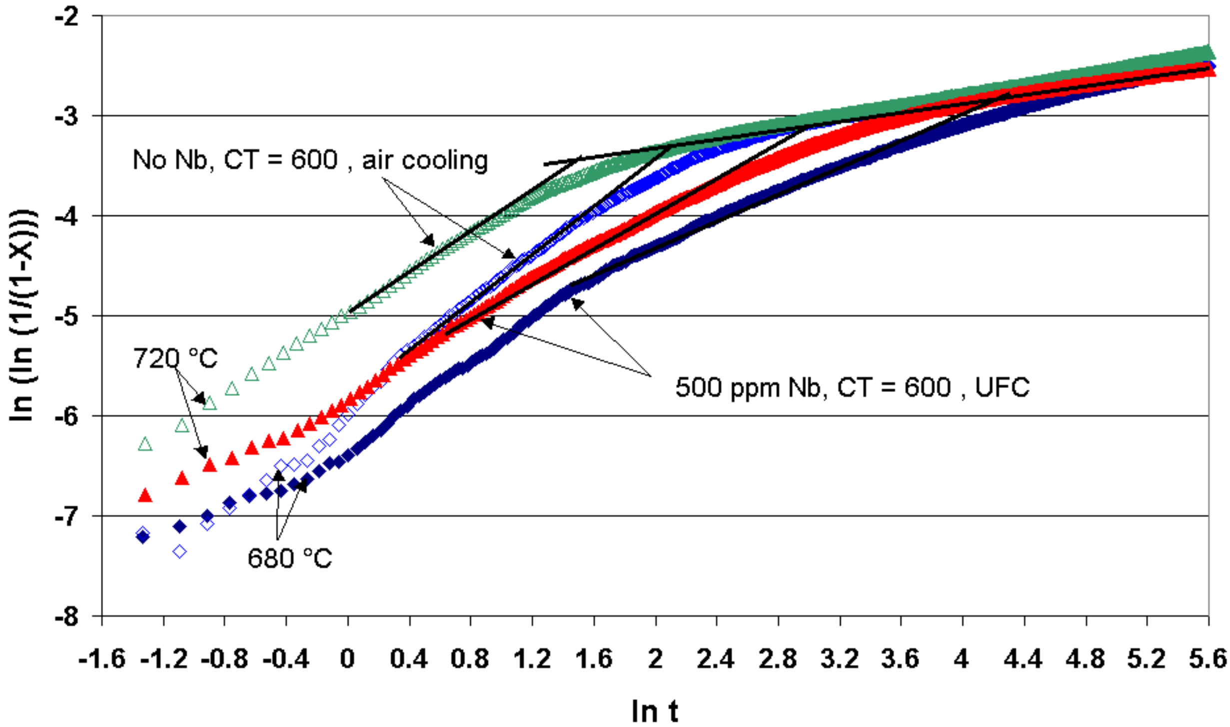

Fig. 10. JMA analyse during isothermal holding Nb containing steel. The change in the slope indicates the end of the ferrite recrystallisation.

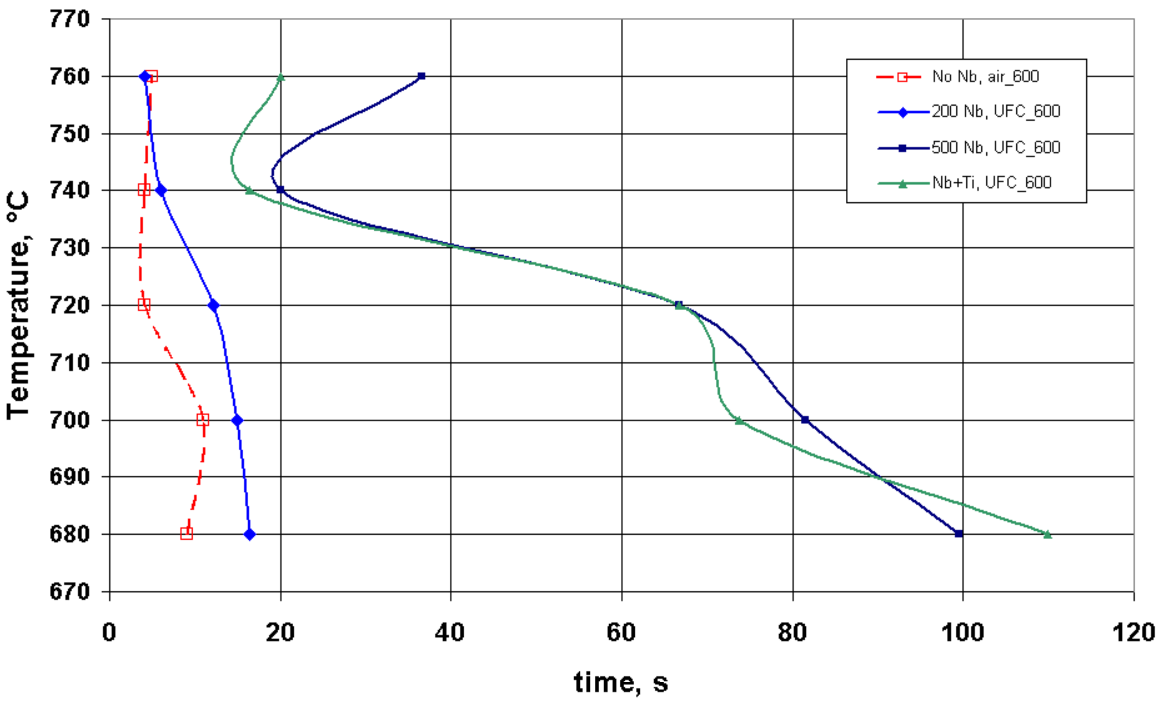

Fig. 11. Ferrite recrystallisation end determined by means of dilatometry for 4 steels with different amounts of Nb in solution.

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Figure 10 shows the double logarithmic plot for the Nb-free steel and the steel containing initially 500 ppm Nb, during annealing at 680 °C and 720 °C, respectively. It can be seen that the end of ferrite recrystallisation can be determined by the break of slopes. Using this method, the time for full recrystallisation could be determined for steels with different Nb and Ti contents. The results shown in figure 11 were in good accordance with microstructure and hardness measurements similar to those shown in figure 9. This method has to be generalised to the studied steels and the link between the amount of Nb in solution and the time for full recrystallisation may be done.

5. SUMMARY

7 steel compositions with different Nb and Ti contents have been hot rolled and cooled using different cooling patterns (air cooling / ultra fast cooling) to different coiling temperatures. It has been shown that accelerated cooling retarded the precipitation of hard NbC particles and kept Nb in solution. After cold rolling, Nb was shown to be able to precipitate during annealing, causing hardening. It has been proved that improved tensile properties can be reached after cold rolling and annealing Nb microalloyed steel with high consistency, provided the hot rolling, cooling and cold rolling and annealing parameters are controlled. Dilatometry was used to follow the ferrite recrystallisation during annealing. It was shown that the end of recrystallisation could be determined from the dilatometric curves. Using this method combined with hardness measurements and microstructure observations, the retarding effect of soluble Nb on the ferrite recrystallisation can be quantified.

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