PRECIPITATION STRENGTHENING PRODUCED BY THE FORMATION IN FERRITE OF Nb CARBIDES

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A Nb microalloyed steel has been thermomechanically processed at laboratory through the use of plane strain compression sequences followed by simulated coiling. Tensile samples have been machined from the obtained specimens in order to investigate the effect of different variables: recrystallisation or accumulated strain before transformation, holding in austenite and coiling temperature on the final mechanical behaviour. Transmission electron microscopy observation of the precipitates has been carried out after coiling at different temperatures. It has been shown that when Nb remains in solution in austenite after hot deformation, it can precipitate in ferrite, leading to an important strengthening effect which is directly related to the concentration of Nb in solution before transformation and coiling temperature.

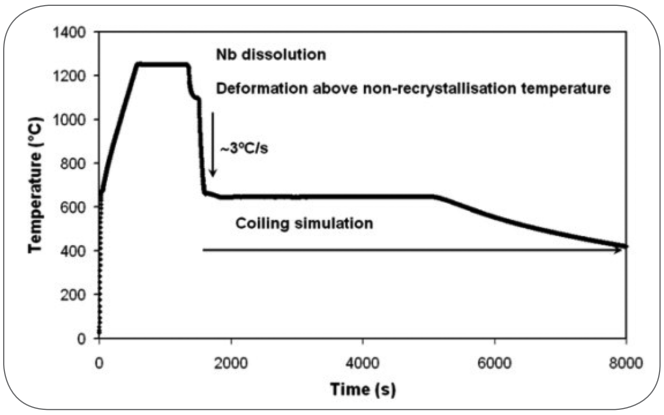
KEYWORDS: thermomechanical processing, niobium, coiling, precipitation strengthening, ferrite, microstructure, tensile

INTRODUCTION

Niobium delays austenite recrystallization during hot rolling interpass times due to solute drag when being in solution and also as a consequence of carbonitride strain induced precipitation [1,2,3]. These two phenomena result in a final ferrite grain refinement [4,5,6,7]. Precipitates formed in austenite are subjected to a relatively fast coarsening and lose part of their potential efficiency as ferrite strengtheners. Precipitation of Nb in ferrite is expected to be significantly finer and contribute to increase the tensile properties. Although extensive investigations have been carried out to characterize Nb (C,N) precipitation in austenite, there are fewer studies concerning precipitation of NbC in ferrite. Additionally, there are some controversial results, depending on the source. Some authors claim that when some Nb is left in solution after hot working, precipitation can take place during the coiling [8,9], while others consider that homogeneous precipitation of NbC is suppressed below about 700°C [10,11] and that there is no precipitation of Nb during coiling [12,13].
The purpose of this investigation was to study the eventual precipitation of Nb in ferrite during coiling and in the case of precipitation to estimate its contribution to the strength.

EXPERIMENTAL

An industrial Nb-steel [14] with composition: 0.06C - 0.35Si - 1Mn - 0.05Al - 0.0056N - 0.056Nb - 0.002Ti (wt-%) has been the base for the present work. Multipass thermomechanical plane strain compression tests were performed after reheating the specimens at 1250°C for 15 minutes in order to assure the total dissolution of Nb, followed by fast cooling to the deformation temperature.
Two different deformation sequences were applied in order to condition the austenite. The thermal cycle of the former sequence is shown schematically in Fig. 1. One deformation pass was applied at 1100°C at a strain rate of 1 s^{-1} and a strain ε=0.3, followed by holding time at the same temperature during 20s in order to ensure the recrystallization



▲ *Fig. 1* ***Example of the thermal cycle applied for one-pass deformation sequence plus coiling.***
Esempio di ciclo termico, per sequenza di deformazione a passaggio singolo seguito da avvolgimento.

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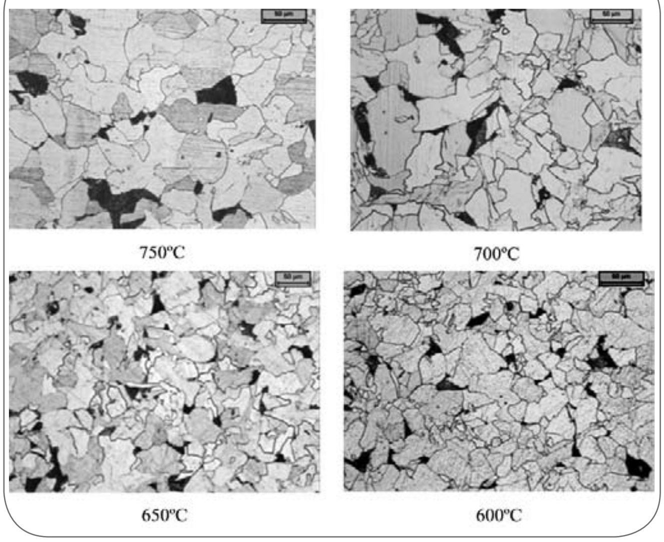

Fig. 2

Ferrite pearlite microstructures obtained at different coiling temperatures after one-pass deformation sequence.

Microstrutture di ferrite – perlite ottenute a diverse temperature di avvolgimento dopo una sequenza di deformazione a passaggio singolo.

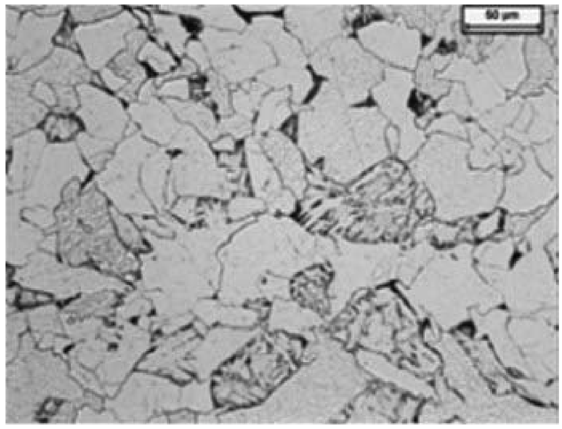

Fig. 3

Microstructure constituted by polygonal ferrite, acicular ferrite and pearlite obtained with one-pass deformation sequence, air cooling to 650°C, cooling at ~2°C/s to 500°C and coiling at this temperature.

Microstrutture costituite da ferrite poligonale, ferrite aciculare e perlite ottenute con una sequenza di deformazione a passaggio singolo, raffreddamento in aria a 650°C, raffreddamento a ~2°C/s a 500°C e avvolgimento a questa temperatura.

of austenite. The second sequence was designed in order to accumulate strain in austenite before transformation. It was similar to the one shown in the above figure, but had an additional deformation pass of $\varepsilon=0.3$ at 1000ºC (below the non-recrystallization temperature) and 1 s^{-1}, followed by 20s holding at this last temperature.

After the two deformation sequences, the specimens were cooled at ~3ºC/s to the coiling temperature, held there for 1h, followed by a slow cooling to room temperature within the furnace in order to simulate coiling conditions. A reference test was also performed that included after the deformation sequences (1-pass or 2-pass deformation) a holding stage in austenite at 870ºC during 1h in order to induce Nb precipitation in this phase before transformation. After this stage, the specimens were cooled at ~3ºC/s to the coiling temperature and coiling simulation was performed as described before.

Tensile specimens were machined from plane strain compression specimens. The tests were performed under strain control at a strain rate of 10^{-3} s^{-1}.

Metallographic samples were prepared using standard metallographic techniques and were etched with 2% nital for optical observations. The ferrite grain size and the volume fraction of pearlite were determined by quantitative metallography. Transmission electron microscopy (TEM) studies were carried out on thin foils and on carbon extraction replicas.

RESULTS AND DISCUSSION

The micrographs in Fig. 2 shows the microstructures obtained when using coiling temperatures in the range 750-600ºC after one pass deformation sequence. The microstructures are composed of polygonal ferrite and pearlite. Coiling temperatures below 600ºC lead to the formation of some acicular microstructures with volume fraction increasing with decreasing temperature. This is illustrated in the micrograph shown in Fig. 3. It corresponds to a specimen that has been air cooled to

Deformation sequence	Coiling temperature (°C)	Ferrite (%)	Ferrite grain size (µm)
1-pass + 1h 870ºC	650	95	26
1-pass	600	95	23
	650	96	28
	700	95	30
	750	94	33
2-pass+1h 870ºC	650	96	17
2-pass	600	96	13
	650	95	12
	700	96	14
	750	93	14

Tab. 1

Ferrite volume fraction and grain size, as a function of the processing conditions.

Frazione di volume della ferrite e dimensione del grano, in funzione delle condizioni di processo.

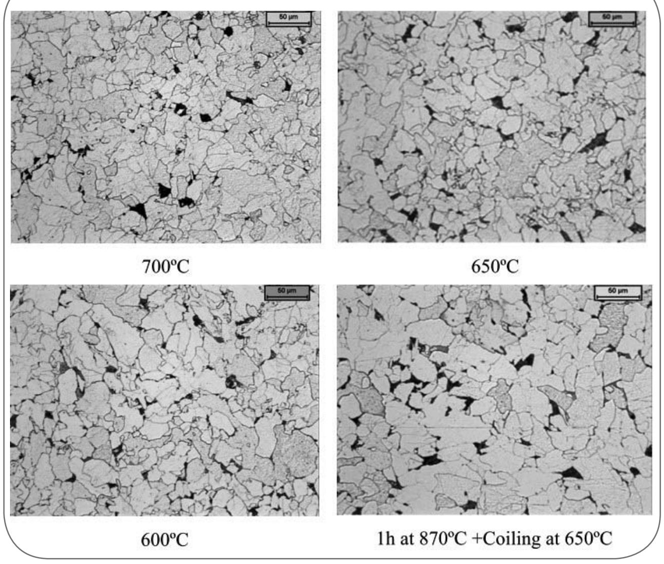

Fig. 4

Ferrite-pearlite microstructures obtained after two-pass deformation sequence and coiling at different temperatures. The microstructure of the reference test (1h at 870°C) is also shown for comparison.

Microstrutture di ferrite – perlite ottenute dopo una sequenza di deformazione a due passaggi e avvolgimento a diverse temperature. A fini comparativi viene mostrata anche la microstruttura delle prove di riferimento (1h a 870°C).

650ºC, leading to some polygonal ferrite being formed at prior austenite grain boundaries.

Subsequent fast cooling to 500ºC and simulated coiling at this temperature leads to some acicular ferrite and finally pearlite produces from the carbon enriched austenite.

The microstructures obtained at different coiling temperatures after a two-pass deformation sequence, are shown in Fig. 4. Ferrite-pearlite microstructures are obtained at coiling temperatures between 750 and 600ºC. As can clearly be seen, the application of the second deformation pass produces a significant refinement of the final microstructure which can be attributed to the accumulated strain in austenite before transformation. The volume fraction of ferrite and mean linear intercept are shown in Tab. 1 for the different tests. Pearlite is in the range 3-7% whereas ferrite grain size varies with the applied conditions. Decreasing the coiling temperatures produces some grain refinement for the one-pass deformation sequence, passing from 33 μm when coiling is performed at 750ºC to 23 μm at 600ºC. The effect of the coiling temperature on the ferrite grain size when applying a two pass deformation sequence is negligible leading to a value around 14 μm.

Holding the specimen during 1h at 870ºC has a small effect on the ferrite grain size after one-pass deformation sequence, but gives higher grain sizes after two-pass.

Tensile data have been plotted in Fig. 5 as a function of coiling temperature for the two deformation sequences. The reference tests have been identified by R. It is evident that the decrease of the coiling temperature has a strengthening effect, excepting for the case in which a 1h holding at 870ºC was applied before cooling to the coiling temperature. The difference in yield stress between the two materials coiled at 650ºC with

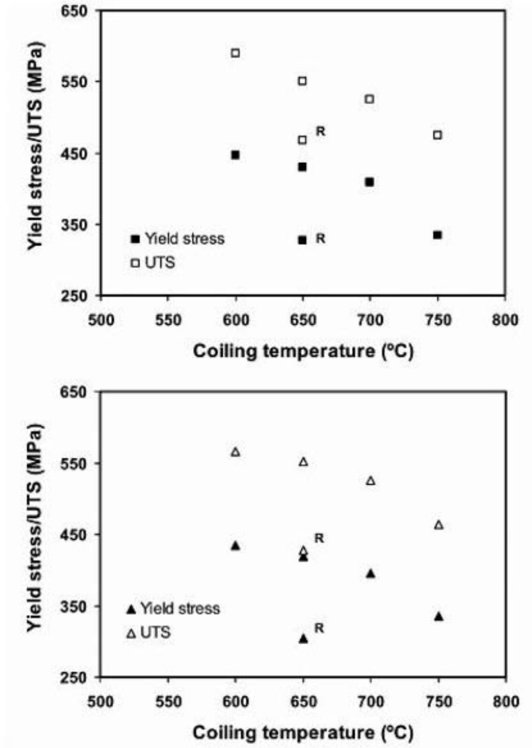

Fig. 5

Mechanical behaviour, as a function of the coiling temperature. R= reference test (1h at 870°C): a) 1 deformation pass and b) two deformation pass sequences.

Comportamento meccanico, in funzione della temperatura di avvolgimento. R = prova di riferimento (1h a 870°C): a) un passaggio di deformazione e b) due passaggi di deformazione.

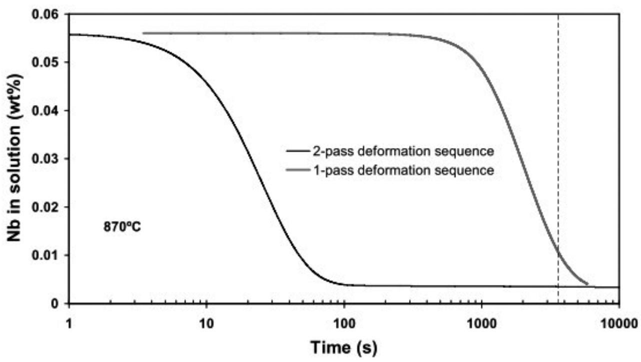

Fig. 6

Model predictions [15] for the precipitation of Nb in austenite at 870°C considering precipitation on a recrystallized austenite or strain induced precipitation.

Previsioni da modello [15] per la precipitazione di Nb in austenite a 870°C considerando la precipitazione su austenite ricristallizzata o precipitazione indotta da deformazione.

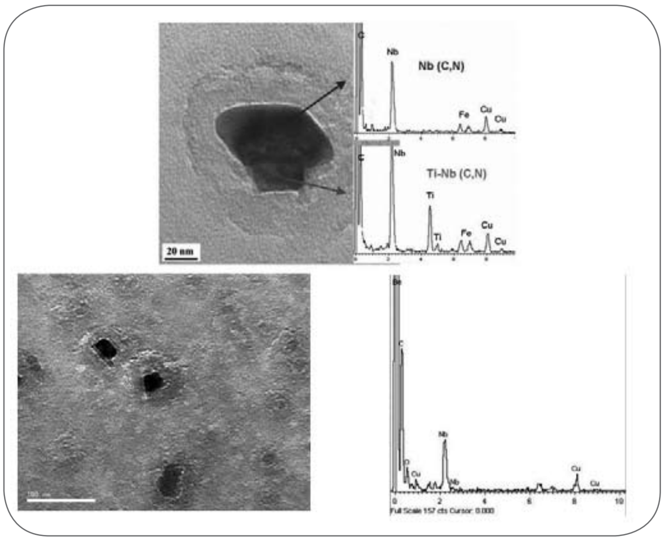

Fig. 7

Transmission electron micrographs and EDS analysis obtained on carbon extraction replicas after 1-pass deformation sequence, 1h holding at 870°C and coiling at 650°C.

Micrografie TEM e analisi EDS ottenute su repliche di estrazione al carbonio dopo sequenza di deformazione a passaggio singolo, permanenza 1h a 870°C e raffreddamento a 650°C.

and without holding at 870ºC is of about 105 and 115 MPa for 1-pass and 2-pass sequences respectively. After 1-pass deformation sequence, the ferrite grain size does not depend on the holding in austenite at 870ºC. This clearly indicates that the observed difference in strength cannot be attributed to the grain size.

The conditions for the holding in austenite were selected after applying a Nb(C,N) precipitation model (MOFIPRE [15]). According to this model, most of the Nb should precipitate in austenite during 1h holding at 870ºC in both recrystallized (1-pass sequence) and strained (2-pass sequence) austenites, Fig. 6. The predicted mean particle size for the precipitates formed in austenite during this holding are of about 25 nm for the one-pass and around 13 nm for the two-pass deformation sequence.

Transmission electron microscopy has been performed on carbon extraction replicas and on thin foils. The image in Fig. 7 corresponds to a relatively coarse Nb carbonitride precipitated on some residual Ti nitride. Nb carbonitrides of similar sizes have been found in association with AlN and also as individuals. The observed precipitates on the extraction replicas present rectangular, irregular, cube or spherical morphologies. The rectangular particles are usually the coarsest precipitates, whereas generally the finest precipitates are spherical with an approximate size of 5-20 nm.

In order to better characterise fine precipitates, TEM observations were also performed on thin foils. The dark field image in Fig. 8 has been obtained on a thin foil for the reference test after one-pass deformation sequence. Some fine Nb precipitation has taken place on some dislocations.

After 1-pass sequence and coiling at 750ºC fine precipitates can be observed, Fig. 9. Their distribution shows that different precipitation mechanisms have taken place. Rows crossing ferrite grain boundaries indicate that some precipitation

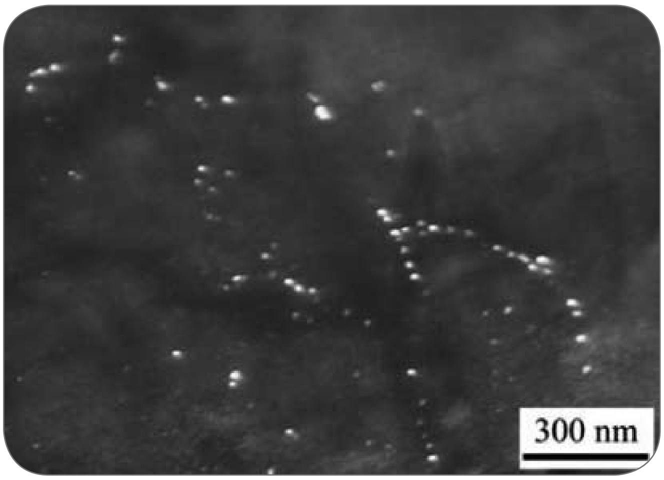

Fig. 8

TEM dark field image of a thin foil showing Nb carbonitrides precipitated at dislocations. one-pass deformation sequence, 1h at 870°C and coiling at 650°C.

Immagine TEM in campo scuro di una lamina sottile che mostra carbonitruri di Nb precipitati sulle dislocazioni. Sequenza di deformazione a passaggio singolo, permanenza 1h a 870°C e raffreddamento a 650°C.

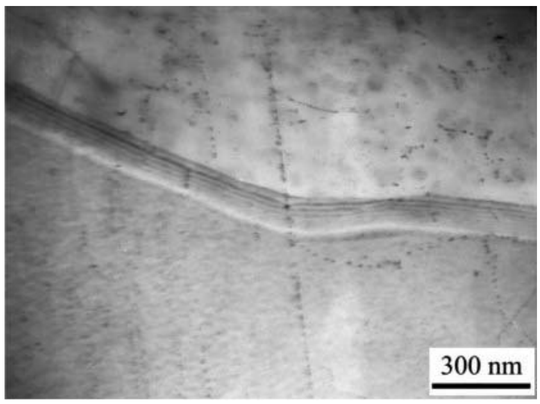

Fig. 9

TEM image of a thin foil showing different types of precipitation: interphase, on dislocations and randomly. 1-pass deformation sequence and coiling at 750°C.

Immagine TEM di una lamina sottile che mostra diversi tipi di precipitazioni: interfase, su dislocazioni, casuale. Sequenza di deformazione a passaggio singolo, permanenza 1h a 870°C e raffreddamento a 650°C.

has taken place at the austenite-ferrite interphase boundary during transformation, but precipitates can also be seen on dislocations or randomly distributed. Coiling at 600ºC produces a profuse and fine precipitation homogeneously distributed in the ferrite matrix, Fig. 10.

TEM results clearly show that when Nb is left in solution in austenite, precipitation can take place in ferrite during coiling. The observed strengthening with decreasing coiling

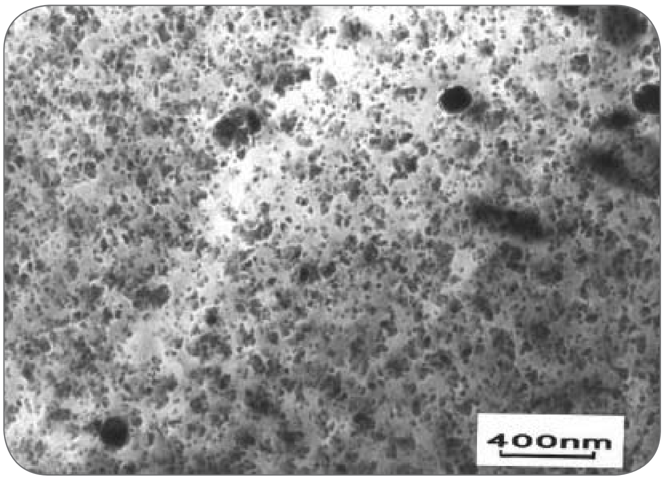

Fig. 10
TEM image of a thin foil showing fine precipitates homogeneously distributed in ferrite. 1-pass sequence and coiling at 600°C.
Immagine TEM di una lamina sottile che mostra precipitati fini distribuiti omogeneamente nella ferrite. Sequenza di deformazione a passaggio singolo, permanenza 1h a 870°C e raffreddamento a 650°C.

temperature goes in agreement with the observed increase of the density of fine precipitates in ferrite. The size of the precipitates has been determined from TEM images obtained on thin foils. The particle size distributions for different processing conditions are shown in Fig. 11. Only particles with sizes lower than 20 nm have been taken into consideration for this quantification.
The finest precipitation has been observed in the sample coiled at 750ºC, leading to a mean value of 6 nm, with about 40% of the precipitates with sizes in the range 4-6 nm. The coarsest particles are observed in the specimen held during 1h at 870ºC and coiled at 650ºC. In this case, the mean particle size is around 10nm. In the specimen coiled at 600ºC, around the 55% of the precipitates have sizes between 6 and 8 nm, but an important fraction of particles are over this range. The result is a mean precipitate size of about 9 nm. It has to be mentioned that was not always possible to obtain a dark field image of the precipitates because quite often the contribution of the precipitates to the diffraction pattern was quite weak. As a consequence, the obtained particle sizes are probably slightly overestimated.
Nb microalloying is generally used to condition the austenite by thermomechanical processing and obtain fine ferrite grain sizes leading to improved mechanical properties. In addition to this, it is generally accepted that Nb in solution in austenite leads to some strengthening of the final microstructure that cannot be attributed to the ferrite grain size refinement. However, there is some controversy when trying to explain the metallurgical mechanism which is responsible of this strengthening. Some authors attribute it to a high dislocation density at the interior of the non-polygonal ferrite grains usually observed in Nb containing steels, while others attribute it to precipitation.
In the present case, the ferrite microstructure is relatively coarse because the deformation sequences were designed aiming to investigate the eventual precipitation of Nb in ferrite over reaching austenite refinement. Some ferrite grains present irregular shapes while others are polygonal. This is true for all the processing conditions, including the one in which the holding in austenite before coiling has produced an important precipitation before transformation. This indicates that even a low fraction of Nb in solution is able to produce non-polygonal grains.
TEM observations do not indicate the presence of a high volume fraction of dislocations, but clearly demonstrate precipi-

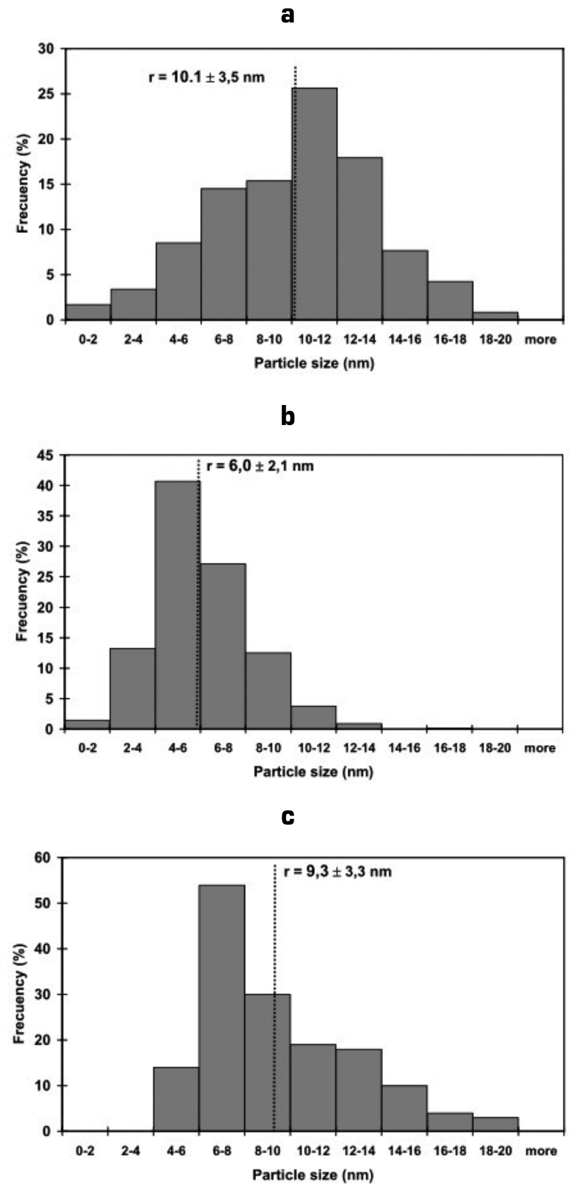

Fig. 11
Particle size distributions obtained by TEM after one-pass deformation sequence a) 1h at 870°C+coiling at 650°C, b) coiling at 750°C and c) coiling at 600°C. Only particles with sizes lower than 20 nm have been considered.
Distribuzioni della dimensione delle particelle ottenute mediante TEM dopo sequenza di deformazione a passaggio singolo a) 1h a 870°C + raffreddamento a 650°C, b) avvolgimento a 750°C e c) avvolgimento a 600°C. Sono state considerate solo le particelle con dimensioni inferiori a 20 nm.

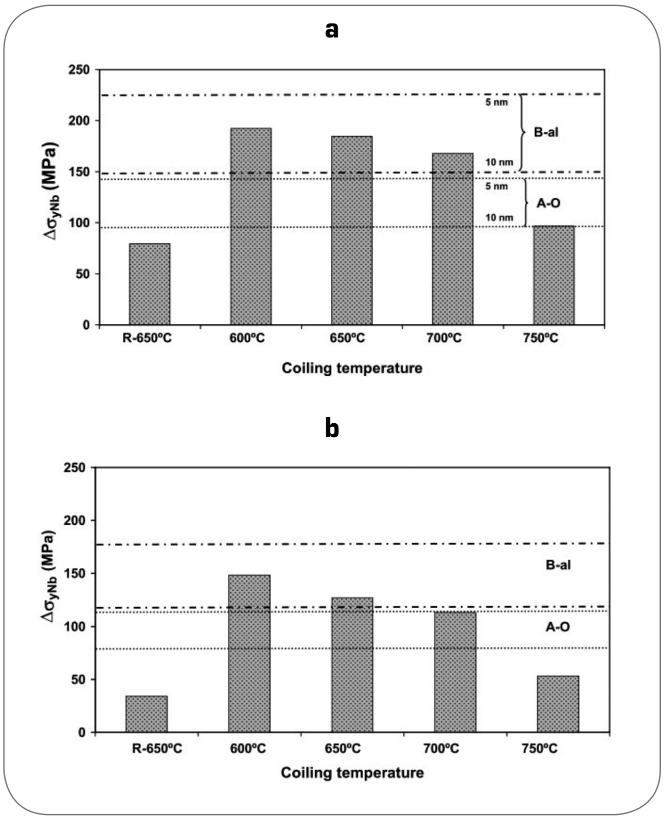

Fig. 12

Contribution of Nb to the yield stress for the different thermomechanical tests a) one-pass and b) two pass sequences. Hatched lines correspond to the predictions of Eq. (3), see text.

Contributo del Nb a determinare il limite di snervamento per le diverse prove termomeccaniche a) sequenza a passaggio singolo e b) a due passaggi. Le linee tratteggiate corrispondono alla previsione in base all' equazione (3), vedi testo.

tation in ferrite. Particularly important are the results obtained on the reference specimens as compared to those obtained on directly coiled ones. The higher precipitation strengthening has been obtained for the coiling temperature of 600ºC. At the coiling temperature of 750ºC some rows of precipitates are observed which indicates some interphase precipitation. At 600ºC a profuse homogeneous precipitation occurs which explains the significant increase of the tensile properties.
The contributions of different strengthening mechanisms to the yield stress, σ_y, can be expressed through the following equation:

$$\sigma_y = \sigma_0 + \sigma_{ss} + k_d d^{-1/2} + \sigma_\rho + \sigma_{ppt} \quad (1)$$

where σ_o is the lattice friction stress, σ_{ss} is the contribution from elements in solid solution, d is the average grain size of ferrite, kd a constant, σ_d is the eventual contribution from dislocations, σ_{ppt} is the precipitation strengthening term. Three first terms on the right hand side can be estimated using Pickering´s equation [16] leading to:

$$\sigma_y = 88 + 37Mn + 83Si + 15.1d^{-1/2} + \sigma_\rho + \sigma_{ppt} \quad (2)$$

in which the content of solutes is expressed in weight per cent.

The contribution of Nb to the yield stress, $\Delta\sigma_{yNb}$, can be estimated by substracting the solute and grain size contribution from the experimental value. The obtained contribution for the different thermomechanical schedules are shown in Fig. 12. As a general rule, it can be said that decreasing the coiling temperature in the range 750-600ºC increases the contribution of Nb to the yield stress.
However, such contribution is lower in the two-pass deformation sequence due to some strain induced precipitation taking place in austenite. Such precipitation that contributes indirectly to the steel strengthening through ferrite grain size refinement also reduces the Nb in solution available to precipitate in ferrite. This explains the lower $\Delta\sigma_{yNb}$ values obtained for the two-pass sequence in comparison with the one-pass. Modelling [15] of the strain induced precipitation in austenite during the 20s holding after the second deformation pass allows estimating ~0.045% Nb left in solution.
Precipitation strengthening depends on the particle size and interparticle spacing of the precipitates and can be expressed through Ashby-Orowan's equation [17,18]:

$$\sigma_{ppt}\,(MPa) = k\frac{\sqrt{f_v}}{r}\ln\frac{r}{6.125\times10^{-4}} \quad (3)$$

where fv is the volume fraction of the particles, r is the average precipitate diameter in μm and k is a constant. In the Ashby-Orowan's (A-O) equation k adopts a value of 10.8 MPa μm [19], but Buessler et al. (B-al) reported a value of 17 MPa μm for the case of Nb precipitation in ferrite [20].
This equation has been applied in order to estimate the expected contribution of precipitation to the yield stress. For the one-pass deformation sequence it has been assumed that all the Nb in the steel (0.056%) is available to produce precipitation in ferrite, while for the 2-pass sequence only 0.045%Nb has been considered. Calculations have been done using precipitate sizes in the range 5 nm $< r <$ 10 nm corresponding approximately to those determined from TEM measurements, Fig. 11. The hatched lines in Fig. 12 represent the different stress levels reached, depending on the k coefficient and mean size of precipitates.
It can be seen that, in agreement with previous results on Nb microalloyed steels, A-O equation underestimates the observed strengthening, while B-al equation gives better predictions. The two testing conditions that are out of B-al band are the reference tests and the one corresponding to coiling at 750ºC. In the former of them, almost all Nb has precipitated in austenite, Fig. 6, leading to relatively coarse particles >10 nm. For the coiling at 750ºC, the assumption made considering all the Nb has precipitated in ferrite clearly overestimates actual precipitation. The best agreement between B-al predictions and experiments is reached for the coiling made at 600 ºC for which homogeneously distributed fine precipitation has been observed, Fig. 10. Reasonably good predictions are also obtained for the coiling performed at 650 and 700ºC. This indicates that within this range of coiling temperatures most of the Nb contributed to the precipitation strengthening.
TEM observations clearly demonstrate that a fine homogeneous precipitation of Nb is possible in ferrite during coiling when enough Nb is left in solution after thermomechanical sequences. This precipitation leads to a significant strengthening of the steel.

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ABSTRACT

MIGLIORAMENTO DELLE CARATTERISTICHE MECCANICHE MEDIANTE PRECIPITAZIONE PRODOTTO DALLA FORMAZIONE DI CARBURI DI Nb NELLA FERRITE

Parole chiave: acciaio, processi, precipitazione

Un acciaio microlegato al Nb è stato trasformato termomeccanicamente in laboratorio attraverso sequenze di compressione planare seguite da avvolgimento simulato. Da questo materiale sono stati ricavati provini di trazione mediante lavorazione dei pezzi ottenuti, al fine di studiare l’effetto delle diverse variabili sul comportamento meccanico finale:
ricristallazione o tensioni accumulate prima della trasformazione, permanenza in campo austenitico e a temperatura di avvolgimento. Dopo l’avvolgimento a differenti temperature è stata effettuata l’osservazione dei precipitati al microscopio elettronico a trasmissione.
È stato dimostrato che, quando il Nb rimane in soluzione nell’ austenite dopo deformazione a caldo, può precipitare nella ferrite, portando ad un importante effetto di miglioramento delle caratteristiche meccaniche che è direttamente collegato alla concentrazione di Nb in soluzione prima della trasformazione e della temperatura di avvolgimento.