Ferritic Nb-alloyed Cr-Steel in simulated strip casting process

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Nb alloyed ferritic Cr-steel is usually produced by continuous casting with following hot and cold rolling procedure. In the laboratory scale the possible new route via strip casting was studied. The scope of the investigation in simulated process route was the development of microstructure and precipitations. In the experiments process parameters similar to those of the real strip caster were chosen, then those of hot rolling and cold rolling of such cast strips. The quickly solidified layer was produced by immersion of a steel substrate under vacuum into melt. The microstructure showed small niobium precipitates in the grain matrix and at the grain boundaries. Their size and distribution was evaluated for different niobium contents and cooling rates in the as-solidified structure. The diffusion controlled change of the precipitate morphology was also analysed after preheating and rolling. Reprecipitation and precipitate growth, as well as dissolution of precipitations at the grain boundaries were observed. The effect of various cooling rates and niobium content on the shape and formation of niobium containing precipitates and on the grain boundary is discussed. Thermodynamic calculations using FactSage were carried out in order to predict the precipitation of Nb-rich phases in ferritic stainless steels. The effect of the chemical composition and temperature on the thermodynamic stability of these precipitates was evaluated.

KEYWORDS:
niobium, niobium carbide, precipitates, ferritic steel, strip casting, rapid solidification

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INTRODUCTION

Niobium is a fundamental alloying element in the steelmaking industry. Many of today's construction steels contain niobium as a microalloying element to reach a desired strength level, high ductility and creeping strength by precipitation hardening. In stainless steels niobium is added to prevent a chromium carbide precipitation and therefore to improve the corrosion resistance and in other applications to improve the high-temperature strength (1-3).

For steels with higher amount of precipitates the strip casting technology offers an interesting possibility for material processing. Characteristic for this technology is the high cooling and solidification rate of the strip as well as the integrated casting and rolling process. According to this, laboratory experiments were made to get new information about the fast solidification of niobium-alloyed, ferritic stainless steel. It was tested which parameters are critical for this procedure. Thus the laboratory experiment parameters were chosen to be similar to the real strip casting procedure.

The main issue of this investigation was to describe the precipitation behaviour of niobium-containing phases during the casting and rolling process. Size and shape of them are very important factors influencing the mechanical properties of the final product. From the results of this study it can be stated, how niobium precipitations in the ferritic matrix can be affected by process parameters.

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THERMODYNAMIC CALCULATIONS

In the first stage thermodynamic calculations of niobium precipitation in ferritic stainless steel were performed. For this purpose the FactSage program was used to identify and model the stable phases during cooling at temperatures between 1550°C and 1000°C. FactSage is based on the calculation of Gibbs energies of all possible phases. By minimising this Gibbs energy the most stable phase composition of the system is calculated. It is important to note that kinetic aspects are not considered – so the real microstructure can differ from these calculations.

In order to approximate real solidification behaviour, segregation of the alloying elements was included in the calculations. Niobium for example segregates strongly to the melt which can lead to precipitation directly from the liquid. Its partition coefficient k_{Nb} which is defined as $c_{Nb, solid} / c_{Nb, liquid}$ is around 0.3 (4).

A simplified chemical composition with 16% Cr, 0.3 to 0.9% Nb, 300ppm C, 250ppm N and Fe as balance was used for the calculation. The model calculates the stable fraction of solid steel and precipitates at a given temperature. The fraction of liquid steel is then used as the start composition for the next calculation at a lower temperature. In this way segregation is simulated. Additionally the formed fraction of solid steel is "cooled down" at the same temperature and the amount of precipitates which form in solid steel is calculated. The temperature step was set to 2 K. Anyway the calculations are simplified as for the model complete mixing in liquid and solid phase during cooling is assumed. Additionally there is no possibility to change the partition coefficients k_i with respect to the cooling rate when using FactSage. The results for 0.3 and 0.9% Nb are shown in Figure 1 and Figure 2.

At each niobium content Nb(C,N)x starts to precipitate directly from the melt as it was enriched with niobium up to 2.5% in the
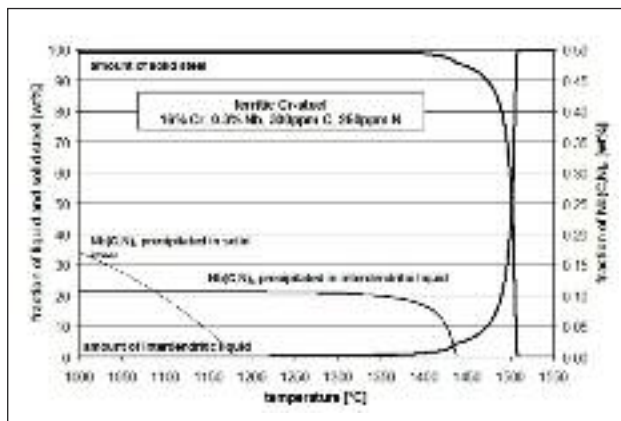
FIG. 1 *Phase formation of solid fraction and niobium precipitates during solidification and cooling of ferritic stainless steel with 0.3% Nb.*

Formazione della frazione solida e dei precipitati di niobio durante solidificazione e raffreddamento dell'acciaio inossidabile ferritico con 0.3% Nb.
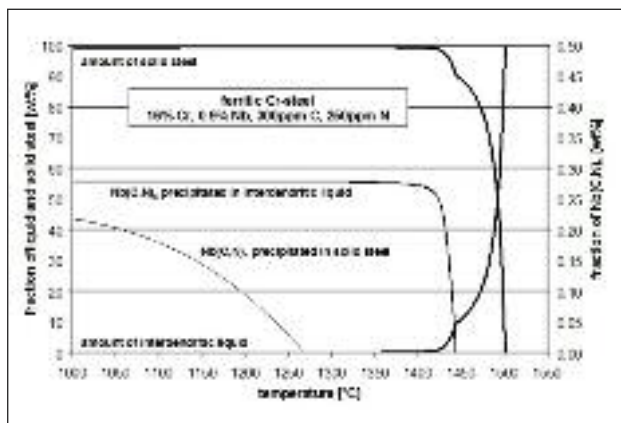

FIG. 2 *Phase formation of solid fraction and niobium precipitates during solidification and cooling of ferritic stainless steel with 0.9% Nb.*
Formazione della frazione solida e dei precipitati di niobio durante solidificazione e raffreddamento dell'acciaio inossidabile ferritico con 0.9% Nb.

case of 0.3% Nb and up to 4.5% in the case of 0.9% Nb when first precipitates occur. At this moment between 4.0 wt% (with 0.3% Nb) and 8.1 wt% (with 0.9% Nb) of liquid phase still remain. With this precipitation the amount of alloying elements Nb, C and N in the melt is immediately reduced which enhances solidification. Through this fact the solidification interval is reduced with increased niobium content. Precipitates forming in the liquid phase, as for example TiN, usually have a big size (> 10 μm) and hardly affect the grain size as they are no barrier for moving grain boundaries. On the other hand if the precipitates in the melt during fast cooling are sufficiently small, they get entrapped into the solidification front and act as a barrier even at very high temperatures at which the grain growth is fastest. In contrast $Nb(C,N)_x$ precipitates forming in the solid phase appear below 1182°C (with 0.3% Nb) and below 1268°C (with 0.9% Nb) when a considerable amount of grain growth is already finished. These precipitates are usually much smaller (< 1 μm) and appear in a higher amount compared to phases precipitated directly from the melt. So their contribution to grain growth limitation is also considerable. In

both cases increased niobium content leads to $Nb(C,N)_x$ precipitation at higher temperatures which is beneficial for decreasing grain growth during cooling. The higher the starting temperature for precipitation the more likely is their formation even at high cooling rates. Especially for strip casting where no extensive reheating is made before hot-rolling a good resistance to grain growth immediately after casting is critical. A special thermal treatment for dissolution and reprecipitation of $Nb(C,N)_x$ is not applied either.

The total amount of precipitates at room temperature only slightly increases with niobium content as it is mainly limited by the carbon and nitrogen content. Obviously the amount of niobium in all cases is higher than necessary for complete stoichiometric reaction with carbon and nitrogen.

Laves-Phase ($[Fe,Cr]_2Nb$) was predicted for the all steel compositions to form at the end of solidification, but the amount of 0.025% was very low.

In $Nb(C,N)_x$ precipitates the ratio of C/N slightly changes with falling temperature. The precipitates formed in interdendritic liquid show a ratio of about 2 which indicates a niobium carbide, while the precipitates formed in solid phase show a ratio of about 0.9 similar to Nb(C,N).

EXPERIMENTAL PROCEDURE

In this investigation the precipitation behaviour in the experimentally simulated strip casting process, hot and cold rolling was studied after each processing step. The rolling was carried out on laboratory scale rolling machines, while the solidification process of steel to a strip had to be modelled with dipping of a substrate (cold rolled sheet in the size of 30x100 mm) into the melt. The solidification experiments were performed in a vacuum induction furnace. Three variants of AISI 430 Cb were produced by addition of niobium to the base material of AISI 430 from industrial production (heat 0). The chemical compositions are given in Table 1. Electrochemical etching for selective attack of precipitations was chosen for sample preparation. The microstructure was examined qualitatively and quantitatively using optical microscope and image analysis software.

Additional samples were prepared by casting the melt into a triangle shaped copper mould which provided different cooling rates for each sample. This was controlled by introduced thermocouples. The experimental procedure was similar to the one described in Ref. (5). The temperature range between 1300 and 1400°C is most important for the first formation of niobium precipitates in these steels after finished solidification. In Cooling rates between 15 and 5800 Ks^{-1} in this temperature range were reached in samples investigated within this work. The cooling rates were either measured (copper mould experiments) or calculated (dipping experiments).

Dipping experiments

On the surface of the substrate sheets an "inverse" solidification compared to the casting processstakes place. The heat is transported from the outside (melt) to the inside (sheet) and partly cumulates inside the substrate sheet. In the real process the heat is extracted from the system by the mould. Therefore in our experiments the temperature gradient decreases with dipping time. In order to model different strip thickness the superheat of the melt was varied, which caused steel layers with different thickness to freeze. With increasing superheat of the melt the frozen steel layer gets thinner.

Calculated cooling rates between 3400 and 5800 Ks^{-1} were achieved in the last stage of solidification at ca. 1400°C. After this initial fast cooling the steel layer warms again in the steel melt until the samples are pulled out of the melt. The dipping time was held

Heat	%C	%Si	%Mn	%Nb	%Cr	%Ni	%N	%Al	%Ti	%P	%S
0	0.047	0.24	0.37	0.006	16.2	0.19	0.033	0.003	0.003	0.021	0.004
03	0.031	0.20	0.23	0.313	16.2	0.12	0.024	0.005	0.007	0.017	0.009
06	0.029	0.21	0.23	0.645	16.0	0.11	0.024	0.006	0.009	0.018	0.008
09	0.032	0.18	0.19	0.964	15.8	0.13	0.025	0.008	0.011	0.019	0.009

TAB. 1   *Chemical composition of steel melts (0 = base material from industrial production).*

Composizione chimica dell'acciaio (0 = materiale di produzione industriale).

FIG. 3   *Steel strip after dipping experiment.*

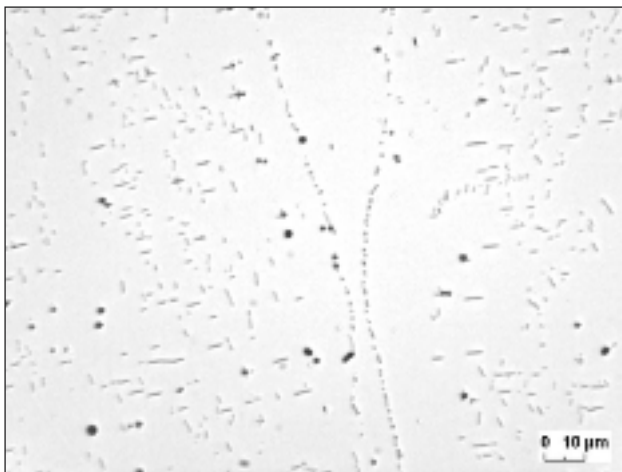*Nastro di acciaio dopo l'esperimento di immersione.*

FIG. 4   *Steel matrix with needle-like and round precipitates and grain boundary phase (0.6% Nb, 3400 Ks⁻¹).*

Matrice dell'acciaio con precipitati aghiformi e tondeggianti e fase ai bordi dei grani (0.6% Nb, 3400 Ks⁻¹).

constant of 1 s. The temperature at the contact between frozen steel layer and substrate varied between 1280 and 1440°C. Following a fast air cooling was performed.

An example of a substrate sheet with frozen steel after dipping experiment is shown in Figure 3. The liquidus temperature of the steel with 0.6% Nb was measured to be 1495°C. The thickness of the frozen steel layer depends on melt superheat and varied between 1.5 and 2.1 mm.

Hot and cold rolling procedure
Samples were hot rolled in one pass with the deformation degree between 22 and 29% after preheating in 10 min at 900°C. The cold rolling was performed in three passes with total deformation degree of 70% with respect to the as cast state. The final thickness of the layer was 0.4 to 0.8 mm.

RESULTS AND DISCUSSION
Phase identification
An example of a typical microstructure is shown in Figure 4. Most precipitates were small with needle-like or spherical shape and were distributed over the whole matrix. In the following evaluation they were subdivided into three groups:
• needle-like precipitates, length up to 6 μm, thickness below 1 μm;
• oblong precipitates, length up to 2.5 μm, thickness below 1 μm;
• small, spherical precipitates, diameter below 1 μm.
In all cases spherical precipitates were most frequent. Their distribution within the samples was not uniform. Inside the grains void corridors without any precipitates occurred.

Phase identification was made using scanning (SEM) and transmission electron microscopy (TEM) for several samples. Using SEM only very big needle-like and spherical precipitates within the grains could be identified as NbC with nitrogen traces taking matrix effect into account. To characterize precipitates with diameters < 1 μm carbon extraction replicas were analyzed by TEM. An example for the precipitates found is shown in Figure 5. The precipitates were mainly characterized as Nb(C,N) with a needle-
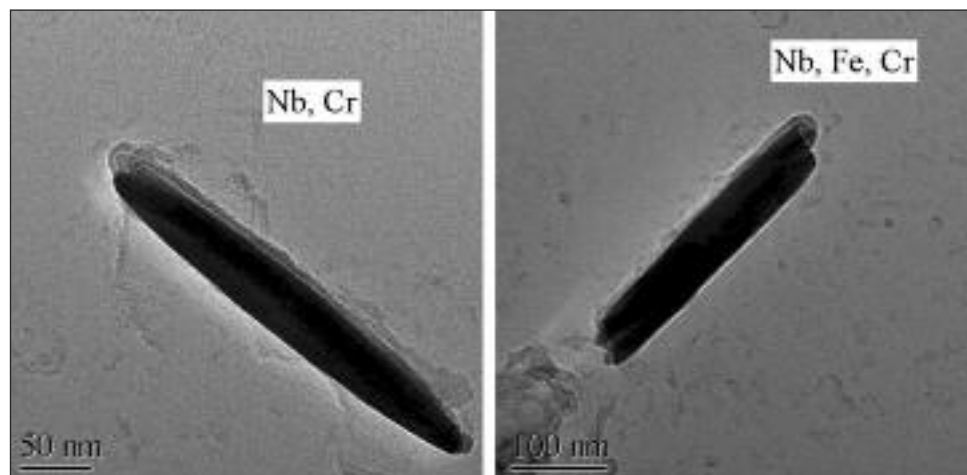
Fig. 5
Transmission electron micrographs and their analysis results by EDS (0.9% Nb, 250 Ks⁻¹).

Micrografie al microscopio elettronico a trasmissione e risultati delle analisi mediante EDS (0.9% Nb, 250 Ks⁻¹).

like or oblong shape.

No big precipitates (> 10 μm) were found in the samples, which means that if precipitation of Nb(C,N)$_x$ occurred even from the liquid phase, their growth was limited. This is probably attributed to the fast solidification and the limited time for niobium diffusion.

Laves-phase Fe$_2$Nb, as predicted by FactSage calculations and in other publications (3, 6), was not observed. It is believed that this phase is suppressed as a result of the high cooling rate. It normally forms after annealing at higher temperatures or because of segregation, which is damped at higher cooling rates. Additionally the predicted maximum amount of 0.025 wt% was probably too low to find this phase in the samples.

Grain size

The grain size increases with increasing superheat and decreasing solidification rate, as shown in another study on the solidification of ferritic stainless steel (7). Surprisingly a pronounced effect of the niobium content on the mean grain size was observed, that had a stronger influence than the solidification and cooling rate. It can be clearly seen from samples shown in figure 6 and Figure 7 which both were cooled with about 250 Ks^{-1}, that increased niobium content results in finer grain. The high solidification rate resulted in a columnar structure with precipitates at the grain boundaries and inside the grain. The mean grain size decreases with increasing niobium content regardless of the cooling rate as shown in Figure 8. As will be discussed later on, more niobium precipitates are present with 0.3% Nb, but at 0.9% Nb their mean size is much higher. Although fine dispersed precipitates are usually more effective for the prevention of grain growth than bigger ones, the main influence during the solidification process and following cooling is obviously the starting temperature of precipitation. As shown in the thermodynamic calculations the precipitation of Nb(C,N)$_x$ starts at higher temperatures with increasing niobium content and even in the melt. Thus at 0.9% Nb a higher amount of Nb(C,N)$_x$ precipitates was present at the end of solidification than at 0.3% Nb, which seems to be very effective to limit the grain growth at high temperatures. Additionally the precipitation of secondary Nb(C,N)$_x$ in solid steel starts at higher temperatures with increasing niobium content, which acts in the same way on limiting the grain growth.

Characterization of microstructure and precipitates

A quantitative analysis of the Nb(C,N)$_x$ amount and distribution using optical microscopy with image analysis. A lot of these precipitates found by TEM investigation were smaller than 0.5 μm. The amount of these very fine precipitations might be underestimated by optical microscopy. Additionally precipitates that were identified by optical microscopy as small and round might be also plate- or needle-like in 3D image as mainly small niobium carbonitride needles were found during TEM analysis.

Effect of cooling rate

In the as-solidified state of the samples the size and distribution of precipitations is dependent on the cooling regime. At very low cooling rates (< 100 Ks^{-1}) the majority of precipitates is needle-like or oblong with a size of up to 10 μm. At cooling rates of about 3000 Ks^{-1} the needles were below 5 μm in length, while most of them were around 2 μm. As cooling rate further increased the precipitates became smaller (< 2 μm in diameter). On the other hand a great number of precipitates can be observed in the microstructure at highest cooling rates of 5800 Ks^{-1} – most of them below 1 μm in diameter. The shape of these niobium carbonitrides is also influenced by the cooling rate. In the samples with the lowest cooling rate they are real plates that look like needles in cross-section.
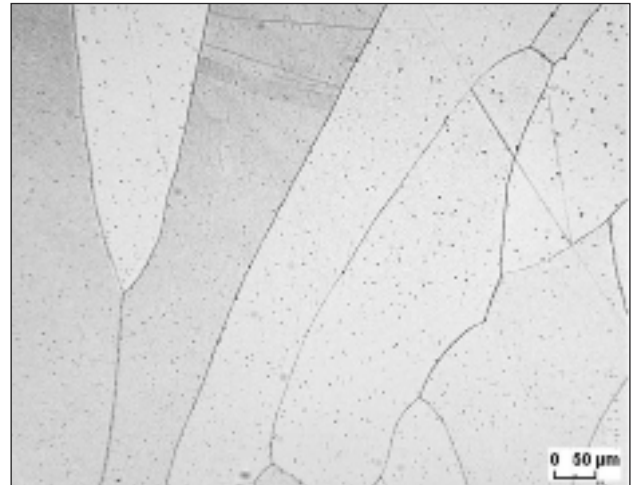

FIG. 6 *Grain size of as-solidified samples with 0.3% Nb cooled at 250 Ks^{-1}.*

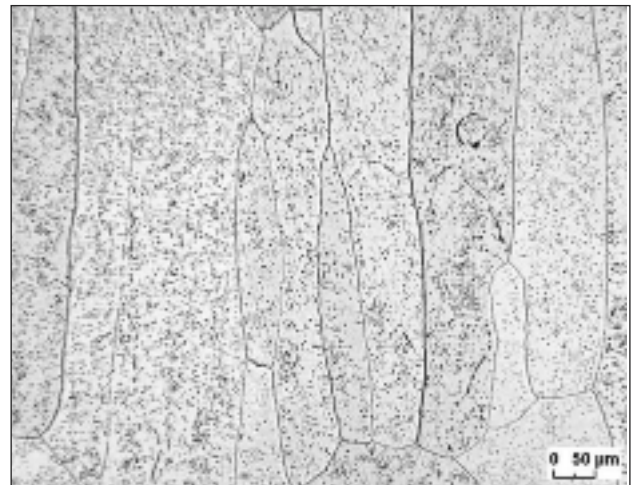*Dimensione del grano di provini come-solidificati con 0.3% Nb raffreddati a 250 Ks^{-1}.*

FIG. 7 *Grain size of as-solidified samples with 0.9% Nb cooled at 250 Ks^{-1}.*

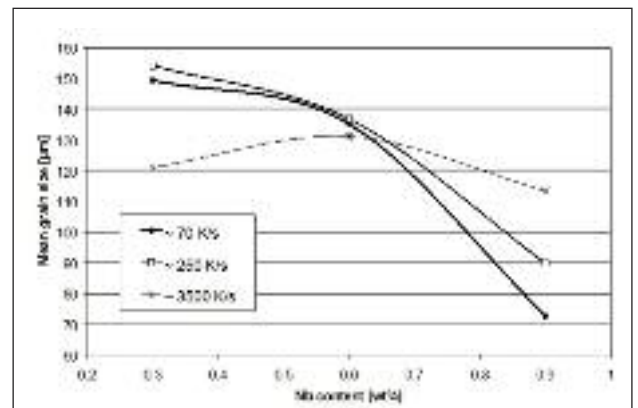*Dimensione del grano di provini come-solidificati con 0.9% Nb raffreddati a 250 Ks^{-1}.*

FIG. 8 *Grain size of as-solidified samples at different niobium contents.*

Dimensione del grano di provini come-solidificati con diversi contenuti di niobio.

FIG. 9
Distribution of niobium carbonitride precipitates at different cooling rates (0.6% Nb, as-solidified state) (optical microscopy).

Distribution of niobium carbonitride precipitates at different cooling rates (0.6% Nb, as-solidified state) (optical microscopy).
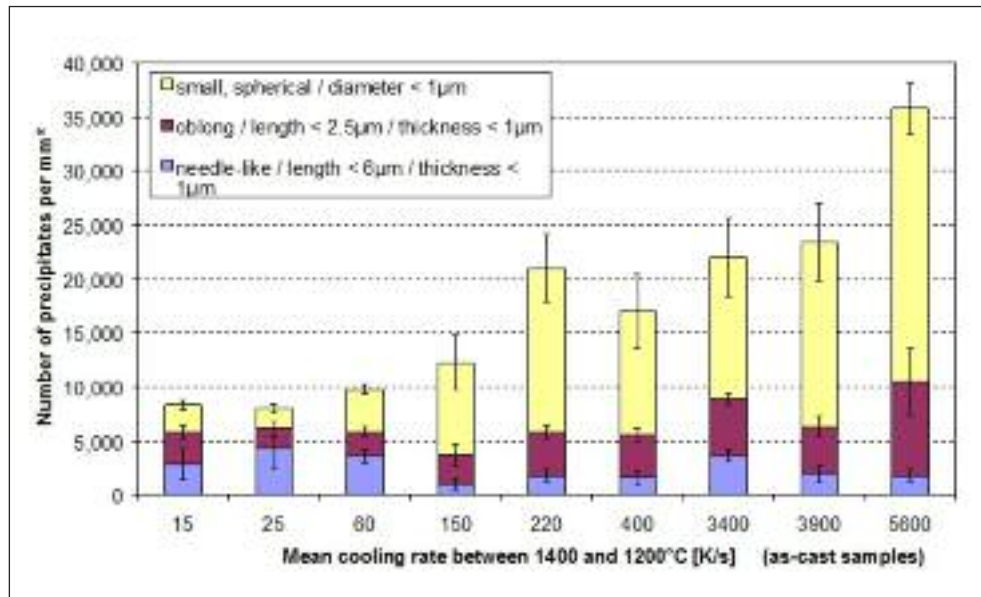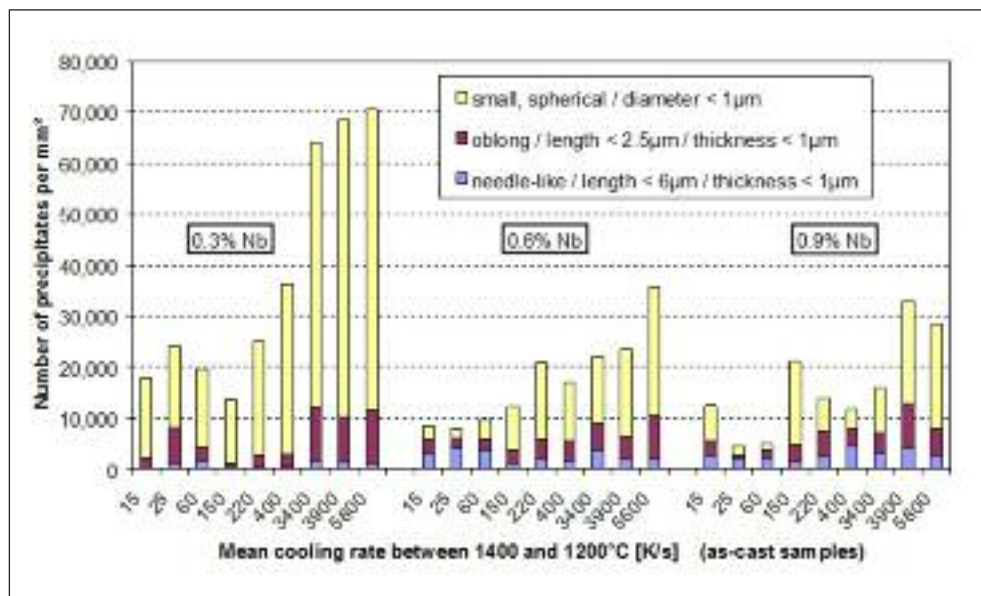

FIG. 10
Distribution of niobium carbonitride precipitates at different niobium contents (as-solidified state) (optical microscopy).

Distribuzione dei precipitati di carbonitruri di niobio per diversi contenuti di niobio (stato come-solidificato) (microscopia ottica).

With increased cooling rate the precipitates become shorter and more spherical. A lot of spherical niobium carbonitrides precipitates were analysed at the highest cooling rate in these solidification experiments. The results are summarised in Figure 9.

It can be seen, that the total number of niobium carbonitrides increases with increasing cooling rate. Especially the number of fine, spherical precipitates shows a steep increase, which can improve the mechanical properties through strengthening and impeding grain growth. On the opposite the number of coarse needle-like precipitates decreases.

The reason for an increasing number of precipitates and their decreasing mean size at higher cooling rates is their forming mechanism. Whereas at high cooling rate the driving force for matrix precipitation is high due to strong non-equilibrium conditions the diffusion and growth of precipitations predominate under low cooling rates. A similar trend was observed for the grain boundary precipitates.

Effect of niobium content
Niobium content shows surprising effect as the number of preci-

pitates does not increase with higher niobium content, but decrease (see Figure 10). On the other hand at 0.9% Nb the inclusions were longer (up to 8 μm) and like needles, while at 0.3% Nb they had a round shape and were much smaller (up to 4 μm). One possible explanation is that according to the thermodynamic calculations at lower niobium contents the main part of precipitation occurs at lower temperatures. As the diffusivity is reduced and the undercooling is increased, more sites for precipitation become favourable. On the other hand at high niobium contents, most niobium precipitates at higher temperatures where the diffusivity is high. For this reason the first precipitates are enlarged and grow in the equilibrium plate-like form. Despite the decreasing number of precipitates with increasing niobium content in the steel, the total amount of $Nb(C,N)_x$ only slightly increases.

Effect of rolling
Samples of the solidification experiments were reheated and hot-rolled. After this treatment no recrystallization was observed but a deformation texture in rolling direction. At the grain boundaries dissolution of niobium precipitates had started, as their mean
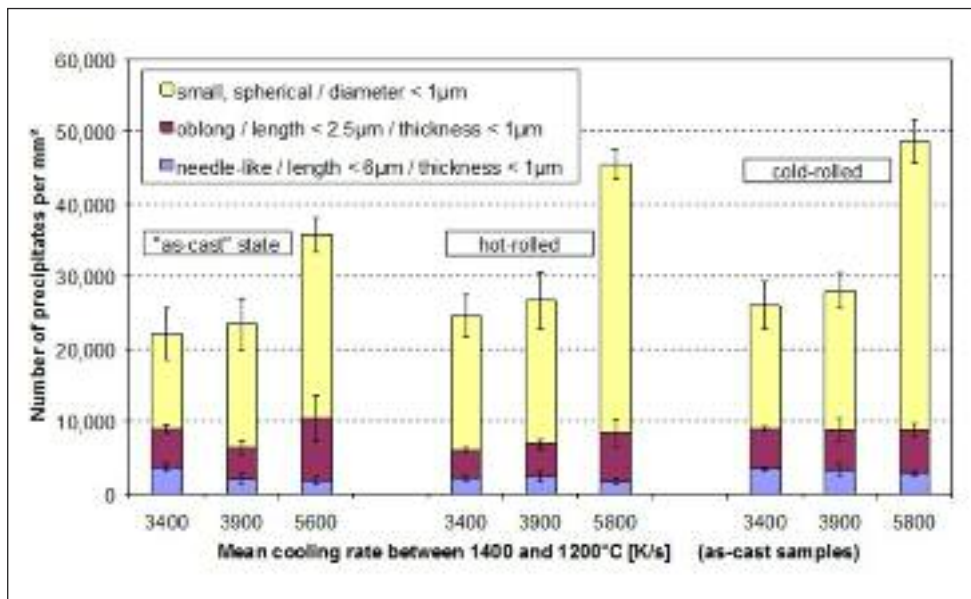
FIG. 11
Evolution of precipitate size distribution after solidification and hot and cold rolling (optical microscopy).

Evoluzione della distribuzione della dimensione dei precipitati dopo solidificazione e laminazione a caldo e a freddo (microscopia ottica).
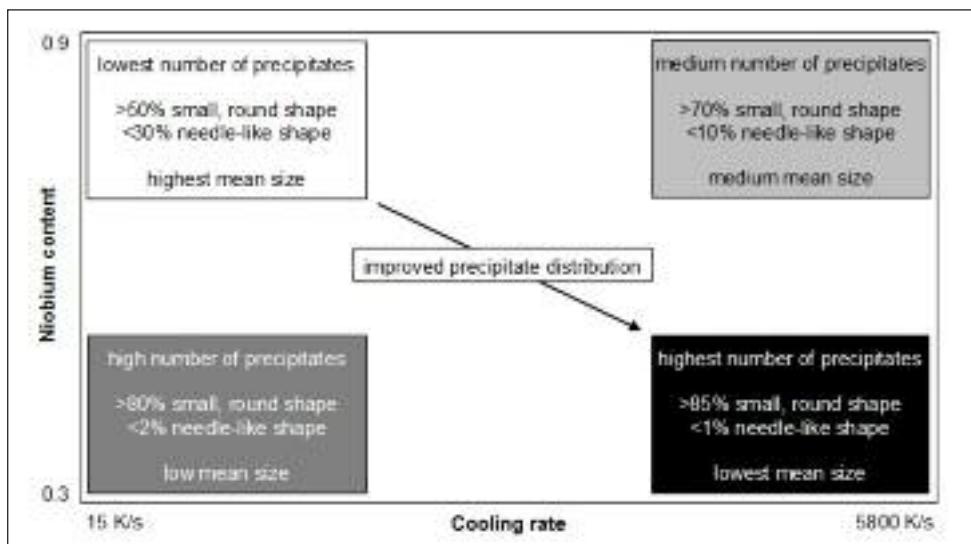

Figure 12: Precipitation behaviour for different niobium contents and cooling rates.

Comportamento nella precipitazione per diversi contenuti di niobio e diverse velocità di raffreddamento.

size decreased and the needle-like precipitates changed towards a spherical shape. On the other hand the matrix was obviously still supersaturated in niobium as many new small precipitates (< 1 μm) were formed. When they reprecipitate at lower temperatures they do so on new-formed dislocations or around other precipitates in a more equilibrium form. As a result more and finer precipitates exist in the steel matrix.

Especially at highest cooling rates the precipitates were spread more completely in the steel matrix and the voids were smaller after hot-rolling. Obviously the lower the cooling rate after solidification is the more completely the supersaturation of niobium in the matrix already decreases. The potential for precipitation is then lower when hot-rolled. On the other hand at highest cooling rates the supersaturation rests until preheating before rolling and creates new, fine precipitates in the steel matrix. In result only few differences are found for samples of low cooling rate before and after hot rolling.

After cold rolling (without any annealing) no significant difference in the microstructure was found between hot-rolled and cold-rolled samples. As no additional heat treatment except the self-heating during rolling was applied to them, grain growth, precipitate coarsening or reprecipitation could hardly occur. The size distribution after hot and cold rolling compared to the as-solidified state is shown in Figure 11.

It can be stated from this study that a short heat treatment at these low temperatures (900°C) before hot rolling – in most cases in-line during the casting and rolling process – has no negative effect on the precipitation distribution and is even beneficial.

CONCLUSIONS

The evolution of the shape and distribution of niobium precipitates has been studied for ferritic stainless steels. The simulation of the strip casting process was performed in dipping experiments with the aim of fast solidification and high cooling rates (up to 5800 Ks^{-1}). The change of microstructure during hot- and cold-rolling was examined. The precipitates in the matrix were identified using SEM and TEM analyses as $Nb(C,N)_x$, which occurred in needle-like or round shape with varying size. Fe_2Nb-Laves-phase was not detected in the microstructure.

Using image analysis niobium carbonitride occurrence depending on niobium content and cooling rate was quantified and compared to samples with lower cooling rates (< 500 Ks^{-1}). A short summary is shown in Figure 12. At the performed cooling rates of the samples differences in precipitate size distribution was observed.

Generally increased cooling rates caused the formation of more and smaller precipitates. This effect was more pronounced with higher niobium contents, where at low cooling rates a lot of needle-like niobium precipitates with a higher size up to 10 μm form. At higher cooling rates their relative amount is decreased. With low content of niobium (in this case 0.3%) these long precipitates hardly occurred and the precipitates were much finer (< 1 μm). Surprisingly the number of precipitates in the as-solidified state did not increase with niobium content but decrease. If the niobium content is very high (in this case 0.9%), the niobium precipitation starts at higher temperatures where the diffusivity is high and less precipitates of higher mean size form. With lower niobium contents the precipitation starts at lower temperatures and results in a finer distribution. This behaviour was predicted by FactSage calculations.

With niobium contents of 0.3 to 0.9% and the steel composition studied here a precipitation of $Nb(C,N)_x$ is also possible in the interdendritic liquid. With these precipitates and those which form in solid steel during cooling it is possible to impede grain growth in ferritic steels at high temperatures. This effect becomes more pronounced with increasing niobium content.

For optimized mechanical properties a fine precipitation distribution and small ferrite grain are desirable. While the niobium content should be as low as possible to form a sufficient amount of fine precipitates, increasing the niobium content can limit grain growth at high temperatures more effectively and lead to a higher strength level through solution hardening. In any case increasing the cooling rate improves the distribution of fine niobium carbonitrides.

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Abstract

Acciaio ferritico al Cr legato con Nb nel processo di Strip Casting simulato

Parole chiave:
acciaio inossidabile, simulazione, strip casting, solidificazione

L'acciaio ferritico al Cr legato con Nb viene solitamente prodotto mediante colata continua con susseguenti procedure di laminazione a caldo e a freddo. Nel presente lavoro è stata studiata in laboratorio una possibile nuova modalità mediante strip casting. Lo scopo della simulazione del processo in laboratorio era quello di esaminare lo sviluppo della microstruttura e delle precipitazioni. Negli esperimenti sono stati scelti parametri di processo simili a quelli realmente utilizzati nello strip casting, e in seguito parametri simili a quelli della laminazione a caldo e a freddo dei nastri. Lo strato solidificato rapidamente è stato ottenuto mediante immersione nella fusione di un substrato di acciaio sotto vuoto. La microstruttura ottenuta ha mostrato piccoli precipitati di niobio entro il grano e al suo bordo. La dimensione e la distribuzione dei precipitati è stata valutata in termini di diverso contenuto di niobio e di velocità di raffreddamento, nella struttura con l' acciaio allo stato di come-solidificato. Il cambiamento della morfologia del precipitato, controllato dalla diffusione, è stato analizzato anche dopo preriscaldamento e laminazione. Sono stati osservati riprecipitazione e ingrossamento dei precipitati, così come la loro dissoluzione al bordo del grano. Inoltre sono stati messi in evidenza gli effetti delle diverse velocità di raffreddamento e del contenuto di niobio sulla formazione e la morfologia dei precipitati contenenti niobio e sulla loro collocazione al bordo del grano.
Sono stati effettuati calcoli termodinamici, utilizzando FactSage, al fine di predire le caratteristiche della precipitazione delle fasi ricche di Nb negli acciai inossidabili ferritici. E' stata infine valutato l'effetto della composizione chimica e della temperatura sulla stabilità termodinamica di questi precipitati.