Original Article

Analysis of titanium nitrides precipitated during medium carbon steels solidification

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ABSTRACT

For certain applications, coarse titanium nitride (TiN) precipitates can be deleterious for the final properties of the material. Hence, in order to better understand the mechanisms involved in the generation of these precipitates, a characterization of the particles observed in steels with different titanium and nitrogen content was carried out. Samples from liquid steel (tundish), continuous casting billets and final product were evaluated using an Automatic Particle Analyzer (APA) coupled to a Scanning Electron Microscope (SEM). The location, frequency, size distribution and composition of the different particles observed were assessed. While only few TiN precipitates were observed in liquid steel samples, the density of this type of particles significantly increased in the continuous casting billets samples. Particles ranging from 1 to 10 μm were mainly found in the interdendritic zones of the as-cast structure. The density of TiN particles observed in these samples did not change after re-heating and rolling operations. A microsegregation model previously developed was adapted to predict TiN precipitation during solidification. A reasonable agreement was found between model results and measured data. Results of this analysis confirmed that the precipitated fraction of TiN increases as the product of steel Ti and N contents rises.

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1. Introduction

Titanium is normally added to steels for several purposes [1,2]. In some cases, the addition is performed to inhibit the formation of boron nitrides that impair steel hardenability [3,4]. In others, Ti addition has the objective of limiting grain growth during heating before rolling [5], or in the Heat Affected Zone (HAZ) of welded structures [6]. Titanium also plays an important role in the mechanical properties of the final product [7]. In Interstitial Free (IF) steels, the formation of titanium carbides and nitrides improves the drawing capacity, minimizing the aging of the material [8]. It has also been suggested that Ti could help in the modification of product microstructure, because the oxides that are formed promote acicular ferrite precipitation [9]. Also, the nitrides could be active

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in microstructure modification [9]. Titanium addition in Nb alloyed steels has proven to be effective to improve ductility of continuous casting products. This is because precipitation of niobium rich fine precipitates is minimized [10,11]. Nevertheless, the effect of Ti on high temperature ductility is still under debate [12,13]. Some recent studies have shown that titanium could refine austenitic grain size in the cast structure [14,15].

In any of the aforementioned applications, Ti addition can promote titanium nitride (TiN) precipitation during steel solidification. These TiN particles formed from liquid phase have cuboidal shape and relatively big sizes (1–20 µm) [3,16–19], compared with those formed in solid state during subsequent process stages, which sizes may range between 10 and 100 nm [6,18]. While the later have specific metallurgical functions, such as control of grain growth, the former can deteriorate material toughness, by promoting cleavage crack propagation [6,16,19–21]. In certain applications, like steels for ball bearings, these coarse precipitates can also impair fatigue properties [22].

In the present paper, the characterization of the size, density and composition of precipitates found in medium carbon steels with different Ti and N contents was performed. Samples from different stages of the process (liquid steel, as-cast billets and final product) were obtained for analysis. In addition, a previously developed microsegregation model was adapted to predict the formation of these precipitates during steel solidification.

2. Materials and methods

2.1. Analyzed samples

Samples were obtained from seamless pipes of eight different heats of medium carbon steels, with different titanium and nitrogen contents. The base composition of steel is indicated in Table 1, while the specific titanium and nitrogen contents in each of the analyzed heats are detailed in Table 2.

These pipes were rolled from round billets produced following the route: Electric Arc Furnace – Ladle Furnace – Continuous Casting. In one of the analyzed heats (C003), samples from three different pipes were obtained to verify consistency in the obtained results. To complement the analysis, liquid steel samples from tundish and as-cast samples from the continuous casting billets were also obtained in some of the studied heats, see Table 2. In all the samples, precipitates were characterized applying the technique described in the following section.

Pipe samples were sectioned longitudinally, as shown in Fig. 1(a). To assess possible differences in through thickness direction, the analyzed zone was divided into 10 smaller equal zones. Total scanned area was about 90 mm². In the as-cast material, 25 mm x 25 mm samples were prepared to characterize one billet radius, scanning also 90 mm² per sample, see Fig. 1(b). As-cast microstructure was revealed etching the samples with different reagents (Nital, Oberhoffer). In the sample taken from the center of the billet (sample C, Fig. 1(b)) additional studies were carried out to characterize central porosity. Finally, in lollypop samples taken from tundish, one of the faces was polished and an area of 90 mm² was also scanned to characterize the particles found.

2.2. Characterization of the precipitates

The obtained samples were polished and analyzed by means of a Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS). Inclusion and precipitates population was evaluated using an Automatic Particle Analyzer (APA) software incorporated to the SEM. This software is

| Table 1 – Base composition of the steel in wt.%. |
|-----------------|-------|---|---|---|---|---|---|---|
| C               | Mn    | Si | Cr | Mo | Nb | Al | S  | Ca |
| 0.25            | 0.35  | 0.21 | 1.00 | 0.70 | 0.025 | 0.03 | 0.0015 | 0.0012 |

| Table 2 – Ti and N content in the analyzed cases. |
|-----------|--------|---------|---------|---------|--------|
| Heat      | Ti (%) | N (%)   | Ti/N (-) | Ti*N (10^-4%)² | Sample       |
| C001      | 0.022  | 0.0064  | 3.45     | 1.408     | Pipe        |
| C002      | 0.025  | 0.0081  | 3.09     | 2.025     | Tundish/Billet/Pipe |
| C003      | 0.023  | 0.0044  | 5.23     | 1.012     | Tundish/Billet/Pipe |
| C004      | 0.020  | 0.0063  | 3.16     | 1.264     | Tundish/Billet/Pipe |
| C005      | 0.012  | 0.0045  | 2.67     | 0.540     | Pipe        |
| C006      | 0.011  | 0.0055  | 2.00     | 0.605     | Pipe        |
| C007      | 0.012  | 0.0046  | 2.61     | 0.552     | Pipe        |
| C008      | 0.019  | 0.0048  | 3.96     | 0.912     | Pipe        |

Fig. 1 – Samples for analysis. (a) Seamless pipes, (b) continuous casting bars.
based on gray level distinction of closed features in a determined field observed with Back-Scattered Electrons (BSE). Particle morphology characteristics (e.g. area, diameter, aspect ratio, etc.) are calculated and its spectrum is collected and quantified for the list of elements set. The obtained spreadsheet is post-processed with an in-house developed software. Firstly, the program applies a set of sorting rules to eliminate those indications that are not precipitates or inclusions (scratches, pores, grinding material, dust, etc.). After that, the elemental composition of the remaining indications is converted into the corresponding oxides, sulfides and nitrides. Finally, the particles are classified into different families [23,24].

In order to identify the nitrides with better precision, the minimum particle size was lowered to 1.4 μm (instead of the 2.7 μm used in the original procedure). Most of the precipitates normally look darker than the steel matrix with the BSE detector, which allows an easy identification by the APA. However, as the analyzed steels contain niobium in their composition (Table 1), Nb precipitates would appear brighter than the steel matrix. Hence, samples were analyzed twice, setting the APA brightness threshold to assess particles darker and brighter than the steel matrix. Anyway, as it is shown in the following section, the number of bright precipitates in the analyzed samples was relatively low, so the analysis was mainly focused in the dark particles, observed with the usual procedure.

3. Results and discussion

3.1. Typically observed particles

Preliminary analysis revealed the presence of three types of particles within the steel matrix: oxides, sulfides and nitrides (or carbonitrides), together with their possible combinations. As an example, Fig. 2 shows the distribution between the different families for one of the analyzed samples. It is clear that, for the particles size range evaluated in this work, nitrides are the predominant particles, followed by oxy-sulfides, oxides and sulfides. The same pattern is observed in most of the samples. Dark nitrides mainly contain Ti, with small amounts of Nb, as shown in Fig. 3(a). Their shape is cuboidal, with sharp edges, as reported in the literature [17]. In some cases, these TiN particles are associated with oxide inclusions that remain in the liquid steel after the secondary metallurgy stages. Brighter particles have high niobium content with traces of Ti, see Fig. 3(b). Nevertheless, as mentioned before, the number of Nb-rich particles was very low compared to Ti-rich precipitates.

Fig. 3 – Nitrides and/or carbonitrides typically observed in the analyzed samples. (a) Ti-rich precipitates, (b) Nb-rich precipitates.
3.2. **Particles density in the analyzed samples**

Particle densities measured in all the final product samples are summarized in Fig. 4(a). For the sake of clarity, only those families with larger amounts of particles are shown: oxides, sulfides, oxy-sulfides and nitrides. Although there are some variations from one heat to another, a high proportion of nitrides are detected in most of the analyzed cases. Good consistency of results was also verified in the three samples obtained from the same heat (C003).

In order to evaluate the effect of processing steps on the density of particles, samples taken at the liquid steel, after casting and in the final product are analyzed in three of the studied heats (Table 1). Results of this analysis are presented in Fig. 4(b). For all the evaluated heats, the particle density measured in final product is similar to that obtained in as-cast samples. The same result is observed for the different particles families considered, suggesting that hot rolling and heat treatment stages do not introduce major modifications in these precipitates. It means that neither dissolution nor coalescence of particles occurs during the thermomechanical treatment. This is in agreement with previous studies that reported that “coarse” TiN precipitates formed during solidification are not altered by subsequent process treatments [16].

However, in the case of liquid steel samples, a different pattern is observed. While the densities of oxides, oxy-sulfides and sulfides are similar to those obtained in as-cast and final product samples, the amount of nitrides is significantly lower. This result suggests that these particles precipitate during steel solidification. With the aim of verifying this observation, further analysis was performed and is discussed in the next section.

3.3. **Location of the particles in the as-cast structure**

Analysis of the as-cast material revealed that TiN particles were mainly located in the segregated areas of the dendritic structure. As an example, Fig. 5(a) shows the segregation pattern observed after the sample was etched (Oberhoffer). The dark areas indicate the segregation pattern developed by the dendritic growth. Titanium rich particles are located preferentially in these darker zones, suggesting that they are precipitated at the end of the solidification process. In addition, the analysis of the sample taken from the center of the as-cast billet (sample C in Fig. 1) showed the precipitation of these particles at the solidification front. Shrinkage of the steel in the final stages of solidification removes interdendritic liquid exposing the dendrites. Fig. 5(b) shows one of these regions, were several TiN particles can be observed.

3.4. **Precipitated fraction**

By means of the APA measurements carried out with the SEM, it is possible to determine not only the density of particles but also the fraction of area occupied by them. Assuming that the volumetric fraction is equal to the measured area fraction [25], the amount of TiN precipitates (wt%) can be calculated as indicated by Eq. (1):

$$m_{\text{TiN}}(\%) = 0.01 \cdot A_{\text{TiN}}^{\text{eq}} \cdot \frac{\rho_{\text{Fe}}}{\rho_{\text{TiN}}} \tag{1}$$

where $\rho_{\text{Fe}}$ and $\rho_{\text{TiN}}$ are iron and TiN densities respectively (7800 and 5420 kg/m\(^3\) [26]). In order to evaluate the effect of steel composition on the amount of coarse titanium nitrides precipitated during solidification, different studies were performed. Fig. 6 shows the effect of the product Ti/N and the ratio Ti/N on the mass fraction of precipitates. These results indicate that the amount of TiN precipitates is more affected by the product of titanium and nitrogen concentration than by their ratio, which is in agreement with the conclusions obtained by other researchers [3].

3.5. **Precipitates size**

In most of the analyzed samples, the average size of the different particles found was around 3–5 μm. This is well
above the sizes typically reported in the literature for TiN precipitated in solid state [27], which suggests that the coarse particles observed in the present work are formed in liquid state. The typical size distribution obtained in the analyzed samples is shown in Fig. 7(a). This distribution can be adequately described with a log-normal type function, similar to the one applied for the size distribution of “fine” TiN particles (1–10 nm) [28], Eq. (2) and Fig. 7(b):

\[ p = \frac{1}{d \cdot \sigma \cdot \sqrt{2\pi}} \cdot \exp \left[ -\frac{(\ln d - \mu)^2}{2\sigma^2} \right] \]  

(2)
As shown in Fig. 8(a), the average size of TiN particles tends to increase with the distance to product surface. However, in the case of oxides, the particle size is not affected by their position in the product, Fig. 8(b). This behavior can be explained by the fact that oxides are already present in the liquid steel before solidification starts but titanium nitrides precipitate and grow in the interdendritic liquid.

In the continuous casting process, the cooling rate at the solidification front decreases with the distance to steel surface, while the opposite trend is verified for the local solidification time. Several studies reported in the literature for particles precipitating in the interdendritic liquid (like MnS or secondary oxides) have shown that an increment of the cooling rate promotes a higher density of precipitates with smaller sizes [29-31]. It has been pointed out [29] that lower cooling rates can promote a less copious nucleation and/or favor the particles coarsening (for example through an Ostwald-ripening process) due to the longer solidification times. So, a similar effect is expected to happen for the case of TiN particles formed in the interdendritic liquid.

4. Model to predict TiN precipitation during solidification

4.1. Theoretical background

In order to estimate the change of solute content in the interdendritic liquid during steel solidification, a previously developed multicomponent microsegregation model was applied [32,33]. In this model, an elemental volume located between two neighboring secondary dendrite arms is considered. As the solidification progresses, the solid–liquid interface moves from the side of the elemental volume lying at the dendrite axis, to the opposite. Among other assumptions, the model considers that thermodynamic equilibrium is attained at the solid–liquid interface and that liquid phase is completely mixed. The diffusion of alloying elements in the solid phase is solved by applying a numerical method. Additionally, the model can also predict the ferrite delta/austenite (δ/γ) phase change produced by the peritectic reaction in medium carbon steels. Further details have been given elsewhere [32,33].

In the present work, the original model was extended to allow the precipitation of TiN particles during solidification. As the concentration of Ti and N in the interdendritic liquid increases, they can react forming TiN precipitates, according to the following reaction:

\[
[Ti] + [N] = TiN \xrightarrow{K_{TiN}} \frac{a_{TiN}}{f_{Ti}f_{N}}
\]  

where the equilibrium constant \(K_{TiN}\) depends on temperature and can be expressed as follows [10]:

\[
\log K_{TiN} = \log f_{TiN} = \frac{17.040}{T} + 6.40
\]

The activity coefficients of Ti and N \(f_{Ti}, f_{N}\) depend on the concentration of the other elements segregated in the interdendritic liquid and can be calculated by means of the Wagner formalism for diluted solutions:

\[
\log f_i = \sum_{j=1}^{n} \frac{c_i^j}{\epsilon_j^i} \cdot (\%)
\]

where the interaction parameters \(\epsilon_j^i\) are taken from the work of Sigworth and Elliot [34]. The diffusion coefficient of Ti and N in ferrite and austenite as well as the corresponding partition coefficients were obtained from the literature [35,36].

In each time step, the model calculates the concentration of the different elements segregated in the interdendritic liquid. When the concentration of Ti and N exceeds the solubility limit, the amount of precipitated TiN and the liquid composition are updated. Calculations are continued until solidification is finished, so the total amount of precipitated TiN can be obtained.

4.2. Model results

For the different analyzed heats (Table 2), model results were compared with SEM measurements performed on pipe samples. Results are presented in Fig. 9(a), where a reasonable agreement between measured and calculated data is observed. As mentioned before, the measured fraction of TiN precipitates increases with the product of Ti and N concentrations in bulk steel (Fig. 6(a)). Simulations performed with the developed model also predict a similar trend, Fig. 9(b).
5. Conclusions

An intensive characterization of the precipitates observed in medium carbon steels with different titanium and nitrogen contents was carried out. In addition to the oxides and sulfides normally found in these steels, a higher number of Ti rich precipitates with sizes ranging from 1 to 10 μm were detected in the final product.

The density of these particles in the final product was similar to that measured in the as-cast material, indicating that hot rolling and heat treatment stages do not introduce major modifications. However, the amount of TiN particles measured in liquid steel samples was significantly lower, which suggests that precipitation takes place mainly in the final stages of steel solidification.

Further analysis of as-cast material showed that TiN particles are mainly located in the interdendritic regions of the microstructure, which confirms that precipitation principally takes place in the final stages of steel solidification. Moreover, it was also observed that the average size of these precipitates tends to increase with the distance to product surface, which can be explained by the fact that the local solidification time also increases with the distance to the surface.

Processing the information collected during SEM analysis it is possible to estimate the mass fraction of precipitated TiN. For the group of evaluated steels, this analysis revealed that the fraction of TiN increases with the product of titanium and nitrogen concentration in bulk steel.

Finally, a microsegregation model to predict the formation of TiN particles during steel solidification was implemented. Model results showed a reasonable agreement with the amount of TiN measured in the final product samples.

References


Conflicts of interest

The authors declare no conflicts of interest.