1. Introduction

Non-metallic oxide precipitates are a negative product of refinery processes, and therefore should be efficiently removed from liquid steel. The main purpose of the oxides removal is lowering the oxide concentration in steel and obtaining the most favourable physical and chemical form of de-oxidation products. On the other hand, a small amount of fine oxide inclusions or their precipitation during crystallization processes can significantly influence the way in which the structure of the cast steel is formed. The positive effect of non-metallic oxides precipitates on the steel structure is principally related to their similar sizes, of 1 µm, and the uniform distribution within the metal volume [1-6]. This can happen when the precipitates are formed during the steel crystallization. Therefore prior to casting, the steel should contain an appropriate amount of oxygen needed for the precipitates formation. The mechanism of the oxide precipitates formation in the crystallization process can significantly influence the chemical composition of the precipitates. Another factor which strongly influences the chemical composition of precipitates is the liquid steel enrichment in dissolved elements: Al, Mn, Si, O and S on the crystallization front. This causes not only a gradual change of the composition of the precipitates, which evolve over the crystallization process, but also decreases the steel crystallization temperature. The scale of this effect depends on the cooling rate of steel during casting[1, 4, 10-12]. The most important precipitates are formed in steel according to the following reactions[1,4,10,11]:

\[
\begin{align*}
[\text{Si}] + 2[\text{O}] &= (\text{SiO}_2) \\
\log K &= 30110/T - 11.40 \\
2[\text{Al}.] + 3[\text{O}] &= (\text{Al}_2\text{O}_3) \\
\log K &= 64900/T - 20.63 \\
[\text{Al}] + [\text{N}] &= (\text{AlN}) \\
\log K &= 12900/T - 0.96 \\
[\text{Mn}] + [\text{S}] &= (\text{MnS}) \\
\log K &= 8627/T - 4.745
\end{align*}
\]

where: \( K \) – equilibrium constant of chemical reaction, \( T \) – temperature [K].

Computer calculations for de-oxidized steel with Mn, Si and Al, at the cooling rate of 50 K/min, were performed for determining the amount of non-metallic precipitates during continuous casting of steel. The simulation was based on
a computer program, the block diagram of which is shown in Figure 1.

The Ueshima mathematical model was used for modelling as it corresponds to the conditions of the directional heat removal during the dendritic crystallization [19,20]. In the case of δ phase crystallization, all components of the alloy tend to cluster in the liquid phase. Under these conditions the precipitates can be formed during the crystallization process [6-8, 13-18]. The concentration of component “i” of liquid steel on the crystallization front depends on the operation of two factors: the rate of advancement of the crystallization front and the diffusion rate of a component in the solid phase. The back diffusion effect takes place during crystallization, when part of the steel component joins the crystallization front and diffuses inside the crystal. The magnitude of the back diffusion effect on an individual component of liquid steel is characterized by the back diffusion parameter \( \alpha_i \).

\[
\alpha_i = \frac{D_i \cdot f_S}{l^2} \quad (5)
\]

The crystallization with diffusion was calculated by means of the Wołczyński equation [18]

\[
C^*_S = k \cdot C_0 \cdot \left[ l + \alpha \cdot k \cdot f_S - f_S \right]^{\frac{k-1}{l-\alpha k}} \quad (6)
\]

where: \( \alpha_i \) – back diffusion parameter, \( D_i \) – diffusion coefficient \([\text{m}^2\cdot\text{s}^{-1}] \), \( l \) – distance \([\text{m}] \), \( t \) – time \([\text{s}] \), \( C_0 \) - initial concentration of solute in the liquid, \( C^*_S \) - concentration of a given solute in the solid phase, \( f_S \) – participation of solid phase (fraction of mass), \( k \) - equilibrium partition coefficient for solid/liquid phase interface.

The temperature dependences describing the diffusion coefficients and equilibrium division coefficients for steel components are given in Table 1 [1, 8]

### TABLE 1

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>( D_i \times 10^{-4} \text{ m}^2 \text{ s}^{-1} )</th>
<th>( k \delta/L )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>0.76exp(-223472/(RT))</td>
<td>0.77</td>
</tr>
<tr>
<td>S</td>
<td>4.56exp(-214443/(RT))</td>
<td>0.05</td>
</tr>
<tr>
<td>Si</td>
<td>8exp(-248710/(RT))</td>
<td>0.77</td>
</tr>
<tr>
<td>C</td>
<td>0.0127exp(-81301/(RT))</td>
<td>0.19</td>
</tr>
<tr>
<td>P</td>
<td>2.9exp(-229900/(RT))</td>
<td>0.23</td>
</tr>
<tr>
<td>Al</td>
<td>5.9exp(-241186/(RT))</td>
<td>0.6</td>
</tr>
<tr>
<td>O</td>
<td>0.0371exp(-96349/(RT))</td>
<td>0.03</td>
</tr>
<tr>
<td>N</td>
<td>0.008exp(-79078/(RT))</td>
<td>0.32</td>
</tr>
</tbody>
</table>

where: \( l \) – liquid Fe, \( R \) – gas constant \([\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}] \), \( k \delta/L \) – equilibrium division coefficient.

### 3. Results of computer simulations

Calculations were performed under conditions of the thermodynamic equilibrium between the metallic liquid phase and non-metallic solid phase with the use of constant equilibriums of reactions during which MnO, SiO2, Al2O3, MnS and AlN are formed [1, 4, 7, 10-12]. The chemical composition of the analyzed steel is presented in Table 2, and the results of computer simulations in Figures 2 – 7.

### TABLE 2

<table>
<thead>
<tr>
<th>Type of steel</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>S235</td>
<td>0.08</td>
<td>0.78</td>
<td>0.017</td>
<td>0.013</td>
<td>0.01</td>
<td>0.07</td>
<td>0.0005</td>
<td>0.005</td>
</tr>
</tbody>
</table>
4. Structure of cast steel

The microstructural analysis was performed for steel samples from the cast ingot 220 mm thick and 1500 mm wide. Apart from a preliminary identification, attempts were also made to establish the distribution of precipitates in a sample. The precipitates of the most diversified chemical composition and shape were searched for. The investigations were performed with the use of the SEM and X-ray microanalyses. The experiments were preceded by observation of samples in the optical microscope. Figures 8 to 10 illustrate the microstructure and distribution of precipitates in the steel sample collected from the central part of the ingot. Groups of tiny precipitates (Figs. 8 and 9) are presented in the microstructure (Fig. 11). The analysis of the X-ray microanalysis plots (Fig. 12) of the precipitates area (point 1) and the matrix (point 2) as well as the quantitative analysis results (Table 3) revealed that these precipitates could be identified as MnS. The precipitate composed of three particles is visible in the microstructure in Figure 13. The X-ray emission lines obtained from two different precipitates (points 1 and 2) (Fig. 14) as well as the results of quantitative analysis (Table 4) indicate the presence of clusters of MnS and Al₂O₃ precipitates.
Fig. 8. The non-metallic precipitates distribution in the cast steel ingot (SEM)

Fig. 9. The non-metallic precipitates distribution in the cast steel ingot (SEM)

Fig. 10. Morphology of the non-metallic precipitates from the cast steel ingot (SEM)

Fig. 11. Morphology and distribution of the non-metallic precipitates in the cast steel ingot

Fig. 12. EDS investigation obtained for the precipitate area (point 1) and the grid (point 2)

Fig. 13. Morphology and distribution of the non-metallic precipitates in the cast steel ingot (SEM)

**TABLE 3**

Results of quantitative analysis obtained for the area of MnS precipitates (point 1) and the matrix (point 2)

<table>
<thead>
<tr>
<th></th>
<th>C-K</th>
<th>Si-K</th>
<th>S-K</th>
<th>Mn-K</th>
<th>Fe-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>precipitate (pt 1)</td>
<td>1.53</td>
<td>1.28</td>
<td>10.20</td>
<td>18.83</td>
<td>68.16</td>
</tr>
<tr>
<td>matrix (pt 2)</td>
<td>1.36</td>
<td></td>
<td></td>
<td></td>
<td>98.64</td>
</tr>
<tr>
<td>atomic %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>precipitate (pt 1)</td>
<td>6.19</td>
<td>2.23</td>
<td>15.49</td>
<td>16.68</td>
<td>59.41</td>
</tr>
<tr>
<td>matrix (pt 2)</td>
<td>6.03</td>
<td></td>
<td></td>
<td></td>
<td>93.97</td>
</tr>
</tbody>
</table>
The observations revealed that fine and irregular MnS precipitates dominate in the sample collected from the ingot. The Al$_2$O$_3$ particles were also identified. The latter takes the form of characteristic irregular spatial clusters. The statistical analysis of selected ingot areas was carried out to provide a more detailed identification and to determine the distribution of precipitates in a cross-section of the cast ingot. Five steel samples cut from various areas of the cast ingot were analyzed. The sampling places are presented in Figure 15.

The statistical analysis of non-metallic precipitates in steel ingot was performed with the SEM method using the EDS detector and Thermo Scientific software. The advanced software module “Feature Sizing” was applied for the geometrical analysis of structural details and simultaneous chemical analysis. Having analyzed the picture obtained from the BSE detector and with the appropriately provided contrast threshold the authors could select elements of the structure, e.g. dark oxide precipitates. This created bases for determining areas of the material subjected to the subsequent chemical analysis. The measurements were performed individually for each determined area. Then the statistical analysis followed. It was based on ascribing individual particles definite sets on the basis of their geometrical and chemical identification. In the analyzed case, an area of 4.158 mm$^2$ was measured in each sample. The analyses covered 336 such areas at the 1000x magnification. The approximate duration of the analysis depended on the average number of particles classified for measurements, ranging from 1 to 4 hours. The obtained results of statistical analysis of precipitates in samples obtained for various areas (1 to 5) of the ingot are listed in Table 5.

The statistical analysis of the non-metallic precipitates distribution in the ingot reveals that during crystallization...
of steel mainly the MnS and Al2O3 precipitates are formed. Samples 1 and 2 contain the highest number of precipitates. These are non-metallic particles which did not manage to outflow and be assimilated by crystallizer slag, and which acting with the crystallization front, were absorbed by it. Steel samples collected from the central part of the ingot contain trace amounts of precipitates. Such distribution of non-metallic particles can be a result of good mixing of steel in the crystallizer, e.g. by the magnetic mixer.

5. Concluding remarks

The results of computer simulation were confirmed experiments performed by means of microscopic techniques carried out for the analyzed type of steel, where Al2O3 and MnS precipitates were observed to be formed. The differences related to the presence of these precipitates in samples are indicative of primary precipitates and products of refining processes, which entered the crystallizer with liquid steel. The computer simulations performed by the authors were made only for secondary precipitates. The content of oxygen dissolved in steel to be cast, ranges between 3 and 5ppm, signifying that the amount of oxides precipitated during the crystallization process is low. The ultimately low oxygen content in steel hinders the formation of SiO2 precipitates. The SiO2 precipitates identified by microscopic analyses are primary ones, i.e. they were present in liquid steel and were not a consequence of precipitation processes taking place during the crystallization. Hence the conclusion that it is necessary to leave some amount of non-metallic oxide precipitates (products of refining of steel) to form a fine structure of steel. The remaining non-metallic phases: sulphides and nitrides will also play an important role in this process.

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REFERENCES