The Impact of the Production Stages of Grade D Steel on its Contamination and the Chemical Composition of Nonmetallic Inclusions

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Abstract. Optical and electronic microscopy methods are used to evaluate the contamination of grade D carbon steel with nonmetallic inclusions in steel samples taken at various stages of steelmaking (electric arc furnace (EAF) discharge → ladle furnace (LF) → vacuum deoxidation (VD) → continuous casting) at an electric furnace melting shop. Steel contamination with nonmetallic inclusions and inclusion chemical composition are assessed. It is demonstrated that the aluminum deoxidation of the semiproduct leads to the formation of corundum nonmetallic inclusions (Al₂O₃) in molten steel. The total amount of corundum reaches 52% for all the stages of steelmaking process. The identification and evaluation of nonmetallic inclusions demonstrates that deoxidation performed at all the stages of secondary steelmaking reduce the amount of inclusions. After vacuum deoxidation and adding Al and SiCa, corundum inclusions become globular in shape with a particle size less than 6 μm. When the continuously cast billet has solidified, the total amount of nonmetallic inclusions does not change, whereas silicate inclusion content decreases and corundum contamination grows, with corundum inclusions being of an irregular shape. A heavy corundum contamination is caused by aluminum secondary deoxidation during steel casting as well as by the fact that the molten residue in the pouring nozzle is carried into the solidifying continuously cast billet.

1. Introduction

Nowadays the advent of modern technologies for the production and transportation of hydrocarbons at locations with harsh operational environment calls for the making of steel grades with high mechanical, physical and chemical properties. A steel manufacturing process is the major factor which affects steel quality and determines chemical, physical and structural heterogeneity of finished products as well as the presence of nonmetallic inclusions. The inclusion cleanliness of steel is an important parameter which determines steel quality, and existing steelmaking processes may effectively reduce the amount of inclusions [1–5]. Somehow, even small quantities of impurities may reduce impact strength; besides, corrosive nonmetallic inclusions (NMI) worsen the corrosion resistance of steel. Hence, the production of steel grades with a low content of NMI is a topical and challenging task of metallurgy.
Controlling the formation, shape, distribution as well as phase composition of NMI has a major effect on steel quality [6]. It has also been demonstrated that the inclusion cleanliness of steel has a significant impact on the formation of contact fatigue defects in rail steel [3].

2. Main part
NMI composition and final oxygen content in steel are conditioned by deoxidizers used, their composition, quantity, addition sequence and methods of adding into molten steel [7–9].

Currently aluminum has been most widely applied as a deoxidizer at the initial stages of ladle treatment (when molten steel has been discharged from the furnace). Aluminum has the highest deoxidation power compared to other commonly used deoxidizing agents, such as Si, Mn, etc. When aluminum is used for steel killing, corundum inclusions as well as Al₂O₃ inclusions emerge. Aluminum residual content in steel as well as aluminate inclusions content heavily affect the stability of the continuous casting process [10, 11]. Moreover, Al₂O₃ content determines the degree of inclusion deformation at rolling temperatures and triggers the formation of contact fatigue defects [9, 12, 13]. In order to reduce the negative impact of aluminum inclusions on the teeming of steel and steel quality, molten steel may be treated with calcium compounds. Thus, calcium carbide CaC₂ was added as a deoxidizer at the initial stages of steel production (when a semifinished product was discharged from the furnace). It has been established that calcium affinity to oxygen is much higher than that of aluminum [14–16]. Somehow, calcium carbide has not been widely used for killing steel. It has been revealed that carbide calcium may reduce the total amount of inclusions in a continuously cast billet. The authors also demonstrate that if calcium carbide, and not aluminum, is added at the initial stages of steel ladle treatment, the NMI content in samples grows. Somehow, the phase composition of inclusions alters because of the decrease in aluminum oxide content (Al₂O₃) [7, 9].

Nowadays aluminum and calcium based compounds, silicocalcium being the most common one, are added to molten steel at the final stages of ladle treatment, namely, before casting. This is done in order to improve steel castability, reduce the impact of corundum inclusions on steel quality and decrease the amount of nonmetallic inclusions. Consequently, the chemical composition and shape of aluminate inclusions may alter. Adding calcium compounds does not always have a positive effect and may trigger the formation of new types of corrosive nonmetallic inclusions, like Type I and Type II.

Such inclusions heavily deteriorate steel corrosion resistance [4, 5], impact strength [2, 3] and fatigue strength [12, 13]. It has been demonstrated that when calcium is added, (CaO·Al₂O₃)+CaS complex oxysulfide inclusions of different shapes emerge and may trigger the build up of molten metal in the pouring nozzle. Consequently, it deteriorates steel castability and contaminates the continuously cast billet with nonmetallic inclusions [10, 17].

The paper is focused on the assessment of the effect of steel production stages at an electric furnace melting workshop (electric arc furnace (EAF) discharge → ladle furnace (LF) → vacuum deoxidation (VD) → continuous casting) on the chemical composition and NMI contamination of steel at different stages of steel production.

Steel samples of two heats of grade D steel were investigated; their chemical composition is given in Table 1.

Upon the discharge from the furnace, molten steel was deoxidized with aluminum AB 87 at the amount of 0.9 kg/ton. The amount of the aluminum added was calculated to achieve oxygen content not greater than 4 ppm after killing.

Then steel was ladle treated and vacuum deoxidized in order to obtain the final chemical composition; steel composition and the amount of the materials consumed are given in Tables 1 and 2. The weight of steel in the steel-teeming ladle was 150 tons.

Inclusions were identified with optical (using Leica 8 C) and electronic (using FEI Versa 3D) microscopy methods. NMI phase composition was assessed by recalculating the TDS analysis data
with the help of the Thermocalc application. The evaluation of NMI contamination was performed automatically with the Axalit Soft application in compliance with the GOST 1778–70 method P.

**Table 1.** Chemical composition of the samples, taken in different stages of D steel treatment.

| Element, % | EAF smelting | After vacuum deoxidation | Continuous cast billet | EAF smelting | After vacuum deoxidation | Continuous cast billet |
|-----------|--------------|----------------------------|------------------------|--------------|----------------------------|------------------------|
| Ca        | –            | 0.0001                     | 0.0011                 | –            | 0.0001                     | 0.0011                 |
| Al        | 0.0217       | 0.0140                     | 0.025                  | 0.0237       | 0.0154                     | 0.018                  |
| C         | 0.3643       | 0.4342                     | 0.465                  | 0.3743       | 0.4442                     | 0.475                  |
| Si        | 0.2288       | 0.2082                     | 0.226                  | 0.2008       | 0.2062                     | 0.216                  |
| Cr        | 0.1337       | 0.142                      | 0.153                  | 0.1237       | 0.132                      | 0.143                  |
| Ni        | 0.0858       | 0.0868                     | 0.087                  | 0.0838       | 0.0848                     | 0.0865                 |
| Ti        | 0.0017       | 0.0013                     | 0.001                  | 0.0016       | 0.0014                     | 0.0012                 |
| Cu        | 0.1755       | 0.1754                     | 0.175                  | 0.1645       | 0.1654                     | 0.1760                 |
| Mo        | 0.018        | 0.0169                     | 0.017                  | 0.019        | 0.0179                     | 0.017                 |
| Sn        | 0.009        | 0.0092                     | 0.009                  | 0.008        | 0.0082                     | 0.008                 |
| P         | 0.0089       | 0.0099                     | 0.010                  | 0.0115       | 0.0128                     | 0.0130                 |
| S         | 0.0444       | 0.0149                     | 0.007                  | 0.0468       | 0.0037                     | 0.006                 |

**Table 2.** Amount of introduced charge materials during deoxidation of steel with aluminum.

| Materials, kg | LF–1 | LF–2 | LF–3 | LF–4 | VC | LF–1 | LF–2 | LF–3 | LF–4 | VC |
|---------------|------|------|------|------|----|------|------|------|------|----|
|               | heat 1 |       |      |      |    |      |      |      |      |    | heat 2 |       |      |      |      |    |
| ALBRA         | 87    | –    | –    | –    | 10 | 40   | –    | –    | –    | 10 |
| Alsiflux      | 366   | –    | 110  | –    | –  | 213  | –    | 100  | –    | – |
| CaO           | 313   | 740  | 245  | 414  | 798| 328  | 500  | 167  | –    | – |
| Al            | 30    | 30   | 13.2 | 36.5 | 6.8| 0.4  | –    | 13.2 | 27   | – |
| FeSiMn18      | –     | 238  | 85   | –    | –  | 373  | –    | 85   | –    | – |
| Anthracite    | –     | 210  | 66   | –    | –  | 28   | –    | 27   | –    | – |
| FeSi65        | –     | –    | 75   | –    | –  | –    | –    | –    | –    | – |
| Rice husk     | –     | –    | –    | 180  | –  | –    | –    | –    | –    | – |
| SiCa          | –     | –    | –    | 98.5 | –  | –    | –    | –    | 84.4 | – |

Upon the discharge from the furnace, molten steel was deoxidized with aluminum AB 87 at the amount of 0.9 kg/ton

The identification of nonmetallic inclusions with optical and electronic microscopy methods reveals that oxide NMI are presented by the following compounds (Figure 1 and 2):

- corundum (Al₂O₃; \( T_{mel} = 2050^\circ C; \rho = 3.96 \text{ g/cm}^3 \)) with a content of not less than 50% of the total amount of NMI (see Figure 2a),
- calcium aluminate compounds containing (xCaO·yAl₂O₃) with alumomagnesian spinel (MgO·Al₂O₃) at the centre of the inclusion particle (see Figure 2b);
- silicates containing MnO·SiO₂·Al₂O₃, (spessartite Mn₃Al₂Si₃O₁₂; \( T_{melt} = 1195 ^\circ C, \rho = 4.18 \, g/cm^3 \)) (see Figure 2c).

Figure 1. Relative fraction of oxide non-metallic inclusions detected at all stages.

Figure 2. The characteristic types of oxide non-metallic inclusions.

The evaluation of NMI contamination at different stages of metallurgical treatment at an electric furnace melting shop is presented in Figure 3.

Figure 3. Changes of steel contamination with different type of non-metallic inclusions on smelting stages.

The analysis reveals that the samples taken after killing steel at the initial stages of secondary metallurgy are most heavily contaminated with NMI (see Figure 3).
The LF treatment of steel reduces overall NMI content to approximately 0.0019% vol., with the prevalence of corundum based \((Al_2O_3)\) inclusions (see Figure 3b); silicate \((Mn_3Al_2Si_3O_{12})\) content reaches its lowest value of 0.0010% vol. The addition of 85 kg of FeSiMn18 and 75 kg of FeSi 65 results in the formation of globular-shaped corundum inclusions. Combined with argon blowing, it facilitates the transport of inclusions into slag. The amount of NMI with a high content of corundum increases in the samples taken after VD and adding 36.5 kg (81 m) of aluminum wire and 98.2 kg (204 m) of SiCa (see Figure 3); these corundum inclusions not always being of globular shape (see Figure 2b). Unlike calcium aluminates, corundum inclusions are hard to remove from molten metal and their residual amount is high in the samples taken both from the tundish as well as from the continuously cast billet. Moreover, corundum inclusion contamination increases after teeming into the tundish to 0.0022% ÷ 0.0030% vol. (see Figure 3). Killing steel with SiCa after VD alters the shape and composition of corundum inclusions; besides, silicate inclusion content increases to 0.0055% ÷ 0.0058% vol. (see Figure 3).

The increased contamination of steel with corundum NMI may be explained by the secondary oxidation of aluminum during casting, a partial erosion of the inner surface of the corundum pouring nozzle with molten metal flow, and an alteration of aluminum content after VD. In heat No. 2 corundum inclusion content remains unchanged after the continuously cast billet has solidified (see Figure 3b). The fact can be explained by adding a smaller amount of aluminum (see Figure 2) and, consequently, a lower content of aluminum in the molten metal (see Table 1, Figure 3b).

The data presented in Figure 3 prove that a reduced amount of aluminum results in a lower NMI contamination (see the left hand side of the curves in Figure 3), while an increased amount of aluminum leads to an increase in NMI contamination (see the right hand side of the curves in Figure 3).

In order to determine the efficiency of the current aluminum deoxidation methods, an aluminum deoxidation curve for steel was calculated using data available [18–23]. With this aim the \(K_p\) values of the equilibrium constant for aluminum deoxidation as a function of temperature were evaluated. The data calculated for the degree of molten steel deoxidation are presented in Figure 3. A comparison of the theoretical and empirical data reveals that the current method of killing steel with aluminum at a rate of 0.93 kg per ton can result in soluble oxygen content [O] of 3.7913 ppm (in the sample taken after killing steel in the ladle, heat No. 2).

The calculation of the deoxidation curve demonstrates that in order to keep oxygen content below 4 ppm, the amount of aluminum for killing steel in the ladle should be reduced from 0.93 to 0.70 ÷ 0.80 kg per ton (see Figure 4).

![Figure 4. Curve of steel deoxidation with aluminium.](image)

3. Conclusion
The analysis of NMI chemical and phase composition as well as the evaluation of NMI contamination prove that the amount of aluminum deoxidant needs to be decreased in order to reduce NMI contamination of the continuously cast billet. A theoretical analysis demonstrates that if dissolved oxygen content $[O]$ in killed steel is not to exceed 4 ppm, it is sufficient to reduce the amount of the deoxidizing agent from 0.93 to 0.7÷0.8 kg per ton.

An increased amount of dissolved aluminum leads to the growth of NMI content, with the inclusions being predominantly presented by hard melting non-deforming corundum particles ($\text{Al}_2\text{O}_3$) with the shape which makes the further pressure shaping process more difficult.

Secondary metallurgy decreases NMI contamination of steel and alters corundum inclusions, modifying their chemical composition and shaping them like spheres. It needs to be noted that following VD, during steel casting and solidification, corundum inclusions of unfavorable shape emerge.

Alongside with corundum inclusions, globular silicate inclusions containing the oxides ($\text{MnO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$) were identified. The latter emerge after killing molten steel with Si additions.

Steel semiproduct deoxidation should be performed at an early stage of steelmaking (when discharging steel from the EAF) using less aluminum: the amount of aluminum deoxidizer should be reduced $0.70 ÷ 0.80$ kg per ton.

Aluminum content is as follows:

$[\text{Al}]$ 0.020÷0.030% (for steels with restricted Al content)

$[\text{Al}]$ 0.020÷0.030% (for marketable workpieces).

Aluminum content should be adjusted after VD and not greater than by $0.005\%$. In case if aluminum content needs to be adjusted by a greater value, calcium silicon wire needs to be added at the amount of 1 kg per ton of steel immediately before discharge with molten steel killed in the ladle for $10 ÷ 15$ minutes.

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