Sources of Nitrogen in Pig Iron and Crude Steel for its Analytical Modelling in BOF Production

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Abstract

Nitrogen rate control in the steelmaking process has become an important topic in recent years. The need for nitrogen control in steel results from its negative influence on the properties of the produced steel. There are a few exceptions where nitrogen in steel has a positive effect, e.g. nitriding of austenitic stainless steel. In general, nitrogen causes deterioration of tensile strength, ageing resistance and mechanical properties of steel, such as toughness and formability of steel. Nitrogen also affects the degree of recrystallisation. Nitrogen is contained in steel in the form of inclusions, and the accurate determination of the sources of nitrogen in steel allows the creation of new options and the modification of existing ones for the management of these inclusions in the steel cycle. Describing the impact of these sources is a fundamental objective in further addressing the problem of optimising nitrogen management in steelmaking. Predicting nitrogen levels at different stages of production will allow informed decisions to be made, optimising efficiency and meeting market demands, while providing solutions for process control, resource utilisation and carbon footprint reduction, ensuring high quality steel for a wide range of applications.

Keywords: nitrogen, steel, pig iron, nitrogen sources, BOF

1. Introduction

The growing demand on steel cleanliness, particularly in the automotive sector, necessitates precise nitrogen control in oxygen converters to ensure quality. High-end steel grades now require nitrogen levels around 20 ppm. This focus on nitrogen control stems from its largely detrimental impact on steel properties, though some exceptions exist (e.g., nitriding of austenitic stainless steel). Generally, nitrogen degrades crucial mechanical characteristics [1]. Specifically, elevated nitrogen levels are associated with a reduction in tensile strength, compromised aging resistance, and diminished mechanical properties including toughness and formability. Furthermore, nitrogen influences the extent of recrystallization within the steel microstructure [2]. Consequently, precise nitrogen rate control is paramount for producing steel with desired performance attributes [3].

2. Sources of nitrogen in molten metal

The main way of controlling the nitrogen content in the converter method of steelmaking is to ensure low nitrogen values in the converter charge [4, 5].

Molten pig iron: Molten pig iron typically contains around 70-80 ppm of nitrogen. CO bubbles, formed during the decarburisation reaction, absorb nitrogen from the metal bath and carry it to the surface. Research has shown that liquid pig iron has little effect on the final nitrogen content of the steel. For every 20 ppm increase in nitrogen content in liquid pig iron, the nitrogen content of the pig steel increases by only 1–2 ppm (Figure 1) [5].

Steel scrap: Steel scrap is one of the main sources of nitrogen in the crude steel produced in the basic oxygen furnace (BOF) [5]. The amount of nitrogen in steel scrap depends on the type of scrap and its quality, which is divided into so-called classifications depending on the specified chemical composition of the steel grades produced [6, 7].

The nitrogen content depends on the quality of the steel scrap and ranges from 40 to 200 ppm. The amount of nitrogen in the final crude steel also depends on the size of the scrap pieces, since larger ones are more difficult and time-consuming to melt (Figure 2) [5]. During the melting process of heavy pieces of steel scrap, a smaller amount of CO is generated, which cannot extract nitrogen from the molten metal in sufficient quantities, leading to an increase in the amount of nitrogen in the crude steel.

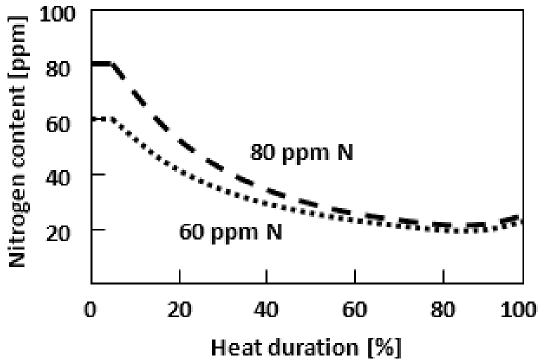

Figure 1 – Dependence of the nitrogen content of pig iron on the nitrogen content of crude steel.

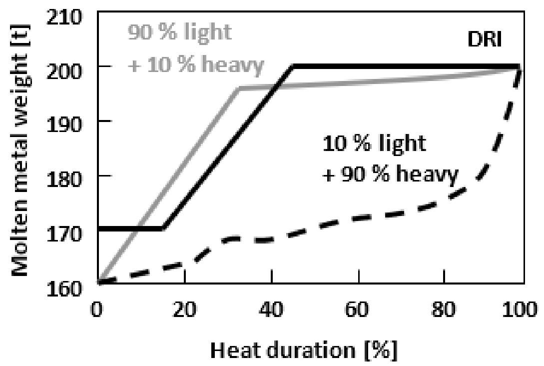

Figure 2 – Dependence of the melting speed of steel scrap on nitrogen content in the melt during heat.

High-purity oxygen: High-purity oxygen with a purity of at least 99.5 % oxygen is blown during steel production in BOF. The remaining consists of argon and nitrogen, the amount of nitrogen in high-purity oxygen in the production of selected deep-drawing steel grades not to exceed 50 ppm [8]. The nitrogen content of the molten metal is determined by two opposing processes: the dissolution of nitrogen from the high-purity blowing oxygen into the high-temperature reaction zone, and the melt's reaction with CO bubbles emitted during the blowing process. According to equation (1) based on [9], the nitrogen content in the crude steel at the end of oxygen blowing is decisively influenced by the partial pressure of nitrogen in the blowing oxygen. High oxygen activity at the phase interface during the latter stages of oxygen blowing prevents nitrogen absorption from technically pure oxygen into the melt [5].

$$[N] = 0{,}0024 + 0{,}053\sqrt{P_{N_2}} + 0{,}00009\tau \qquad (1)$$

where: [N] is Nitrogen content in crude steel at the end of heat [%]; P_{N_2} is Partial pressure of nitrogen in blowing high-purity oxygen [Pa]; τ is Blow time of high-purity oxygen [min]

To prevent the nitrogen in the blowing oxygen from having an excessive impact on the final nitrogen content of the crude steel, it is essential to ensure that the nitrogen content of the technical oxygen does not exceed 0.2 % by volume, or 0.01 % by volume for the production of steels with extremely low nitrogen content [5, 10].

Nitrogen from the atmosphere: During tapping from the BOF, nitrogen in the air supersaturates the stream of outgoing steel. The amount of nitrogen absorbed from the atmosphere during this process is mainly influenced by the surface area of the molten steel that comes into contact with the air. The greater the liquid steel-atmosphere reaction area, the more nitrogen will be absorbed into the molten steel from the air [11, 12]. Therefore, it is required that the steel flows through the taphole in a continuous, splash-free stream. The time taken for the steel to flow from the converter to the ladle must be optimal. If the tapping takes too long through a narrow taphole, the amount of nitrogen in the molten steel will increase. The optimum tapping of the steel is determined by the diameter and condition of the taphole surface, and the amount of steel to be tapped. Each time a steel sample is taken for chemical analysis, the chemical composition of the gas above the melt surface changes.

The longer it takes to tilt the vessel to sample the steel (longer turndown), the more the chemical composition of the gas above the liquid metal surface will approach that of air, which contains up to 79% nitrogen. Since slag does not always cover the liquid steel surface uniformly, liquid steel may come into contact with large amounts of atmospheric nitrogen. This poses a particularly great danger due to the elevated nitrogen content of the steel.

Metal stirring by the nitrogen: The application of bottom bubbling nitrogen through porous blocks or blowing plugs ensures thermal and chemical homogenization of the melt. When nitrogen is used to mix the melt, it causes the partial pressure of nitrogen in the gas phase of the emulsion to increase, resulting in dissolution of the nitrogen into the metal. If only nitrogen is used for stirring, the amount of nitrogen in the crude steel increases by 25 ppm compared to a melt that has not been stirred with nitrogen. If blowing with a gaseous mixture (50 % N_2 + 50 % Ar) was deployed the increase in the final amount of nitrogen in the steel was only minimal [12].

Carburizers: Another source of nitrogen in BOF steel production is the carburizers. According to the literature [5], which assumes full nitrogen transfer from the carburizing coke to the steel, up to 3.3 ppm of nitrogen would pass from 100 kg of added carburizing coke to an 180-ton batch of steel. However, under realistic conditions, only 72.9% of the coke's total nitrogen content passes into the steel. The total nitrogen increment during tapping process is 10-40 ppm, of which the carburizing coke contributes the majority [13].

Ferroalloys: The presence of nitrogen in ferroalloys can compromise the quality of steel production, particularly when ferroalloys are consumed in high quantities during tapping. This increases the risk of nitrogen in steel originating from ferroalloys if the steel does not boil at the bottom of the ladle during tapping [14].

3. Discussion

For metal analysis for nitrogen, 79 samples of pig iron after desulphurization and 68 samples of crude steel after heat were collected. The data obtained on the nitrogen content were processed and evaluated using Microsoft Excel 365 with the Lumivero XLSTAT 2019 statistical add-in. Combining the results of the chemical analysis of the samples and the heat logs data allows us to establish a ranking of the influence of various relevant factors on nitrogen content in metal based on correlation coefficient values - *r*. As shown in Table 1, the amount of nitrogen in desulfurized pig iron is primarily influenced by the temperature of the pig iron, the silicon content of the pig iron, and the amount of sulphur removed. This is related to desulfurization time, which affects the consumption of desulfurization mixture and the amount of nitrogen blown. The amount of nitrogen in the crude steel is primarily influenced by the amount of oxygen added during the afterblow process, the consumption of covering slag, and the temperature of the tapping crude steel.

Table 1 – Influence of individual factors on the nitrogen content of pig iron and crude steel.

Desulfurized pig iron		Crude steel	
Factor	**r**	**Factor**	**r**
Pig iron temperature	– 0.4645	Consumption of high-purity oxygen for afterblow	0.5075
Silicon in pig iron	– 0.2983	Covering slag	0.4534
Amount of sulphur removed	0.2541	Temperature of tapping crude steel	0.1448
Weight of desulphurisation mixture	0.1722	Tapping duration	– 0.0552
Amount of nitrogen blown (as carrier gas)	0.1337	Total consumption of high-purity oxygen	0.0448

4. Conclusion

This article briefly describes the sources of nitrogen in the desulfurized pig iron and crude steel. The combined influence of these factors determines the final nitrogen content of the metal, as well as the quality of the produced steel, which is now receiving much attention. Accurately determining the sources of nitrogen in steel enables the development of new methods and the improvement of existing ones to control these inclusions in the BOF steelmaking process.

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