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THE NITROGEN CONTENT MANAGEMENT IN THE OXYGEN CONVERTER STEELMAKING

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The nitrogen belongs to elements which have significant impact in steel mechanical properties. The influences of individual elements on the properties of solution of nitrogen in the metal bath, on the process of nitrogen dissolution in connection with decarburisation process and also influences of some important factors on the possibilities of nitrogen regulation during the refining period were investigated in this work. The path for production of steel with regulated nitrogen content relies on the combination of knowledge of nitrogen thermodynamics, mechanism and kinetics of nitrogen sorption and desorption, together with possibilities of steel melt properties prediction and also with metallurgical actions leading to the control of required chemical composition.

Key words: Nitrogen in the steel, nitrogen dissolution, refining, oxygen converter, charge

Reguliranje sadržaja dušika pri proizvodnji čelika u kisikovim konvertorima. Dušik spada u elemente koji značajno djeluju na mehanička svojstva čelika. U radu su istraženi utjecaji pojedinih elemenata na svojstva otapanja dušika u metalnoj kupci, proces izdvajanja dušika u vezi s procesom odugljičenja a također utjecaji nekih važnih faktora na mogućnost reguliranja dušika tokom perioda rafinacije. Put proizvodnje čelika s reguliranim sadržajem dušika oslanja se na kombiniranje znanja termodinamike dušika, mehanizma i kinetike sorpcije i desorpcije dušika, zajedno s mogućnošću predviđanja svojstava čelične taline, a također s metalurškim djelovanjem koje vodi kontroli zahtijevanog kemijskog sastava.

Ključne riječi: dušik u čeliku, izdvajanje dušika, rafinacija, kisikov konvertor, uložak

INTRODUCTION

The nitrogen is an indispensable part of the commercial steel grades. It has definite influence on the properties within most of the higher-quality steel grades. The nitrogen is considered as an impurity or as an alloying element. In general, nitrogen in steel is present interstitially, but it can also be presented in the form of nitrides.

The nitrogen content of the cast steel depends mainly on the type of technology.

In the converter processes with oxygen blowing, the nitrogen content depends on the purity of the blown oxygen, whereas at region of very high temperatures (more than 2000 °C, end of the oxygen jet) the nitrogen equilibrium distribution between gas and metal ranges from 0,002 to 0,005 %. In the electric arc furnaces, thanks to active interaction of electric arc, the nitrogen content of the steel ranges from 0,007 to 0,012 %.

Nowadays, modern steelmaking registers rising demand for better control and decreasing of dissolved gasses in the steel. The recognized nitrogen sources are as follows: nitrogen coming from the hot metal, scrap, ferroalloys and coke. Moreover, the measurable presence of nitrogen in the oxygen used within the BOF and Q-BOP also reflects on its contribution to higher nitrogen level. There is also probability of higher nitrogen content due to additional blowing (correction of chemistry before tapping). Since this is a complex function, it necessary to control the level of nitrogen in various steps of the heat.

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MATERIAL AND METHODS

The significant fraction of nitrogen content in the oxygen converter comes in the hot metal. Much attention was attracted to the relation between nitrogen content in the hot metal versus both chemical composition and other metallurgical factors of blast furnace (BF) process, [1-3]. The available information are mostly contradicting where the fact of discrepancy between measured values (lower values) in comparison with expected theoretical equilibrium values was confirmed. It was shown in the reference [1] that average value of nitrogen content in the hot metal at tapping depends on its temperature, chemical composition (carbon, silicon), but there wasn´t found any influence of titanium in the range (0,02 to 0,11) wt% Ti. Maybe one of the greatest sources of nitrogen is an absorption of nitrogen from the atmosphere, which can be performed by entrapping of

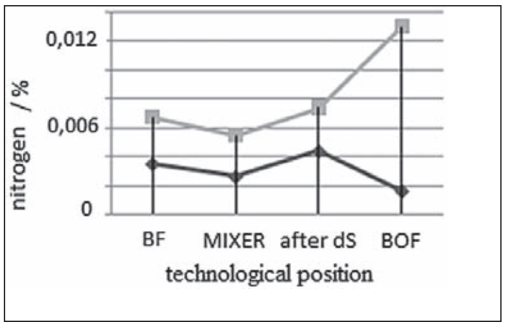

Figure 1 The change in the nitrogen level in the production cycle BF – BOF

gas bubbles (air) during tapping, by uncovered metal surface during agitation using argon or by any other form of interaction between liquid steel and nitrogen from atmosphere [4]. Theoretically, denitrogenation requires larger phase interface gas-metal that is not occupied with surface-active elements like oxygen and sulphur. Similar conditions are achieved just at oxygen converter (BOF) processes and partly at vacuum decarburisation process.

The process of nitrogen absorption is preferentially happening during the technological operations such as tapping, secondary refining, steel casting. There is no progress in the denitrogenation within the steels with nitrogen content lower than 25 ppm even if there´s conditions of vacuum decarburisation. Therefore the strategy of low-nitrogen steel grades production must be based on the achievement of minimal possible nitrogen level within the semi-product (before tapping) and also on the prevention of nitrogen „input“ in all of the subsequent stages of technological cycle. The change in a nitrogen content with metal transport in the individual technological positions is illustrated on the Figure 1.

The dissolution of gaseous diatomic nitrogen in the liquid metal is happening through the dissociation of diatomic nitrogen into monoatomic form. In the conditions of thermodynamical equilibrium between nitrogen in the gas and in the metal, this phenomenon could be described with the chemical equation:

$$1/2\{N_2\} = [N] \qquad (1)$$

with the equilibrium constant:

$$K_N = \frac{[\%N]\cdot f_N}{p_{N_2}^{1/2}} \qquad (2)$$

Impurities present in the metal increase or decrease dissolution of nitrogen in the liquid metal (within the given temperature). Other impurities act more neutrally. For example: sulphur and oxygen [5]. The relationship among nitrogen dissolution, temperature, chemical composition and pressure can be described using an equation:

$$\log\,[\%N] = 0{,}5 \cdot \log P_{N2} - \log K_N - \log f_N \qquad (3)$$

In the case of iron-based systems, following equation can be used [6]:

$$\log\,[\%N] = 0{,}5 \cdot \log P_{N2} - 664\,/\,T - 0{,}999 - \log f_N \qquad (4)$$

The calculation of the nitrogen dissolution in the liquid steel or in the iron-based alloys, within the wide range scatter of chemical composition for various temperatures and parcial pressures of nitrogen, could be done thanks to knowledge of interaction coefficients of first and second degree (using Table 1) and thanks to equation (5), [1].

$$\log f_N = \sum_i e_N^i\,/i/ + \sum_i r_N^i\,/i/^2 + \sum_i\sum_{ij} r_N^{ij}\,/i/\cdot/j/ + \qquad (5)$$

Table 1 **The interaction coefficients of nitrogen in the liquid iron [1, 7]**

i	$e_N^i = \frac{A}{T} + B$		r_N^i	i, j	r_N^{ij}
	A	B			
C	90	0,047	60/T-0,022	C, Si	0,01
Si	35	0,03	0,0008	Si, Mn	-0,0009
Mn	-5	0,006	-0,0004	Mn, C	0,02
P	148	-0,034			
S	23	-0,0053			
Cr	-164	0,0415	0,00036		
V	-316	0,053			
Ti	-4835	2,04			
Al	-332,2	0,04			

According to [8], the close correspondence within the comparison of real and equilibrium nitrogen contents in many BF plants during tapping, in the torpedo car and in the iron ladle was found. This means that the nitrogen concentration value was indicated more by thermodynamical conditions of processes and technological factors affects more the scatter of acquired data. From the results of circa 200 measurements, the following relationship can be expressed:

$$[N]_{real} = (\,0{,}0015 \pm 0{,}0007) + (0{,}48 \pm 0{,}1)\,[N]_{equilib.} \qquad (6)$$

According to [8], the equation (6) enables to achieve sufficiently exact information about nitrogen level in the hot metal poured into the BOF in the beginning of the heat. Within the hot metal pre-treatment in the iron ladle, depending on used caring media, the nitrogen concentration can rise or decline [9].

The amount of nitrogen passing from the gas phase to the bath is dependent not only on the nitrogen dissolution but on the dissolution rate as well. The real nitrogen level in the steel is a function of 2 processes: a) mechanism and kinetics of dissolution, b) mechanism and kinetics of removal from the bath. The kinetics of absorption and desorption of nitrogen in the liquid iron was studied by a number of researchers in the past [3,10]. The kinetics of nitrogen change in the metal can be described by the equation:

$$d[N]/d\tau = v_N^{dissolved} - v_N^{removed} \qquad (7)$$

The nitrogen transport during the steelmaking process at the presence of liquid phase is controlled by mass transfer J_N and by chemical kinetics. The nitrogen transfer can be expressed by the relation (8), [11]:

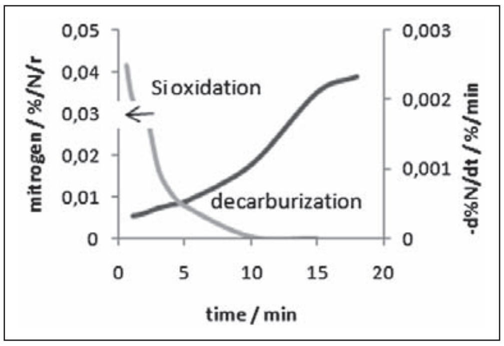

Figure 2 The process of denitrogenation and nitrogen dissolution during the oxygen blowing

$$J_N = \frac{m + p}{100}[\%N^B - \%N^5] \quad (8)$$

where, *m - mass transfer coefficient (m/s)*
ρ – *steel density (kg/m³)*
$\%N^B$, $\%N^S$ – nitrogen concentration in the volume and on the phase interface

The rate of denitrogenation of metal bath (using [11, 12]) and the process of nitrogen dissolution during the steel refining are illustrated in the Figure 2. It shows that there is no nitrogen removal during the beginning of the blow, since the desiliconisation is the primary reaction. The rate of nitrogen removal changes abruptly as soon as decarburisation process starts, due to removal of nitrides and carbonitrides of titanium. To the end of the heat, the generation of CO a the kinetics of denitrogenation slows down as a consequnece of decline of level of dissolved carbon and decline of decarburisation rate. The noteworthy fact is that the nitrogen dissolution in the steel rises with decline of carbon content.

Figure 3 describes the favourable conditions for the formation of TiN in the hot metal, comparing thermodynamic conditions with the contents of these elements in the samples from the blast furnace.

In the dependence on the concentration of surface-active elements, such as oxygen and sulphur, the rate of the nitrogen-liquid iron reaction is affected by various rates in the individual steps. At lower concentrations of these elements, the extent of nitrogen absorption in the liquid metal is governed mainly by the mass transfer in the liquid phase. At higher concentrations of sulphur and oxygen, the extent of nitrogen absorption in the liquid metal is governed mainly by the chemical kinetics. The rate of the secondary step, with the view of nitrogen level in the melt and the rate of supervisory step of nitrogen molecules dissociation on the liquid surface of the metal. At the average level of oxygen and sulphur, the rate is limited both by chemical kinetics and by mass transfer in the liquid phase as well.

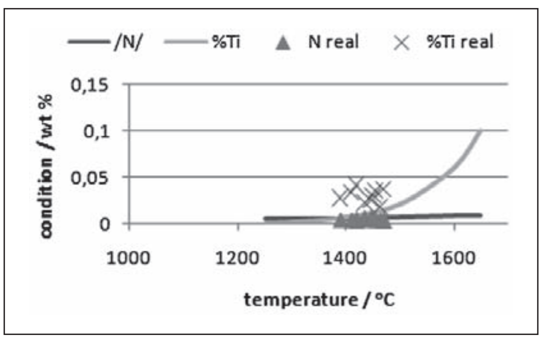

Figure 3 The comparison of thermodynamic and real conditions for TiN formation in hot metal

RESULTS AND DISCUSSION

The possibilities enabling modification of nitrogen content in the steel during the heat are complicated and they depend on thermodynamic and kinetic factors that are specific for each particular type of process. Therefore, if there is a need of low-nitrogen steel production, then the variability of different methods must be employed in order to decrease the nitrogen level in the liquid metal.

The nitrogen enters the metal bath in the BOF within the oxygen jet, but it removes by generation of CO bubbles. The deciding factor is a thermodynamic equilibrium between blowing and nitrogen content in the steel. This is significantly dependent on the ratio of rate of absorption of the nitrogen from the oxygen jet and from the BOF atmosphere and of nitrogen desorption by CO bubbles / [1, 13-15].

The CO generation during the intense refining of the metal bath is a very effective „tool" in the technological cycles of BOFs –Figure 4, Figure 5.

Steel scrap and its properties are considered as recognized source of nitrogen. Increasing proportion of scrap in the charge results in rising of nitrogen in the steel melt. It can be seen from the Figure 6 that in the end of refining period the nitrogen level is greatly affected by the scrap quality. The selectivity No.1 represents the highest quality scrap (Figure 6).

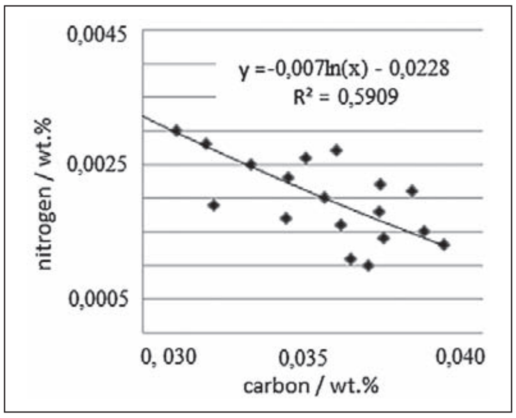

Figure 4 The dependence of nitrogen level in the steel (after refining) on carbon content in the pre-sampling.

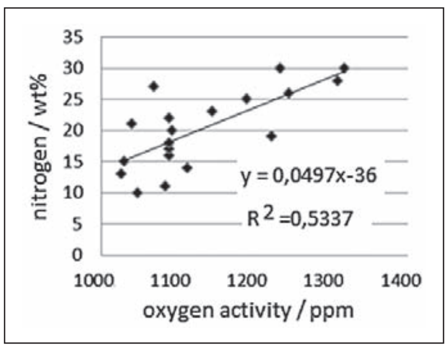

Figure 5 The dependence of nitrogen level (pre-sampling) on the oxygen activity

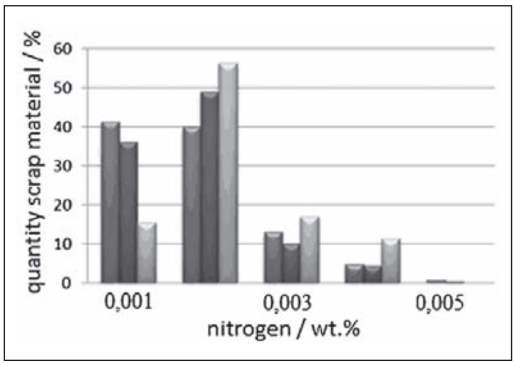

Figure 6 The dependence of nitrogen level (pre-sampling) on the steel scrap quality

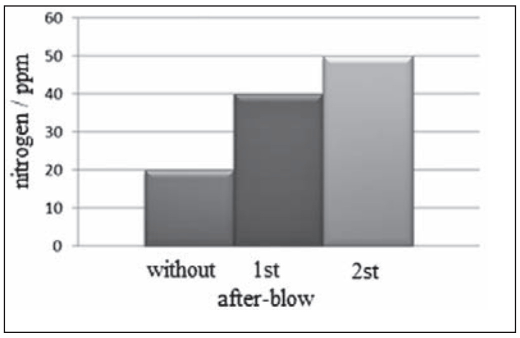

Figure 7 The influence of additional blowing on the rise of N level in the metal

Except of strong effect of additional blowing (see Figure 7), there are also other metallurgical factors affecting the nitrogen level in the steel: rate and mode of oxygen blowing, the level of the jet, lime charging methods, refractory wear.

As it results both from the plant experience and also from the studies of various researchers, the production of steels with regulated nitrogen level remands actions in the particular vessel as well as in the whole technological line of production cycle. There were derived many algorithms that involve charge chemistry, blowing practice, slag formation practice. These algorithms enable the production of low-nitrogen steels. However, the real nitrogen concentration is mainly affected by technology, raw materials for pig iron production, pre-treatment of hot metal, portion and quality of steel scrap [16].

Some amount (10 – 20%) of nitrogen can be removed by vacuum utilization. The nitride capacity of the slags is also very important issue, especially within the slags containing BaO, ZrO_2, TiO_2, BaF_2, CaF_2. In the case of slags with ideal chemical composition and other optimal conditions, the nitrogen level could be decreased up to 40% of its previous level. However, also this way is complicated due to impact of scrap quality, steelmaking technology and due to high cost of individual components as well.

CONCLUSION

Better understanding of the structure of the melts, thermodynamics of solutions of diatomic gases in the iron, mechanism and kinetics of absorption and desorption of nitrogen from the ambient and to the ambient area through the phase interface metal-slag, metal-gas, in combination with technological possibilities of individual production cycles, with the capability to predict the nitrogen level in hot metal, with the possibility of option of proportioning of suitable steel scrap and with the possibility of suitable refining regime enable to produce the steel with desired nitrogen level in the metal.

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REFERENCES

[1] M. A. Poživanov, E.Ch. Šachpazov, A.G Svjažin: Vyplavka stali dlja autolista, Interkontakt Nauka, 2006, 166
[2] N. N. Kuzkina, Ju. V. Kofman, V.K. Batluk: Effect of the converter steelmaking technology on the nitrogen content of steel, Metallurgist, 45 (2001), 3-4,156-157
[3] P. Pribula, Ľ. Dobrovský, J. Kijac: Vplyv technologických faktorov na obsah dusíka v oceli vytavenej v kyslíkových konvertoroch s dúchaním zhora, Hutnícke listy, (1990), 1, 27 – 32
[4] S. Misra, R.J. Fruehan: Nitrogen pickup during taping of liquid steel, AISTech 2004 Conference proceedings, 1057-1069
[5] W. Derda, J. Siwka, CZ. Nowosielski: Controlling of the nitrogen content during EAF – technology and continuous casting of steel, Archives of metallurgy and materials, 53 (2008), 2, 523-529
[6] J. Siwka, A. Hutny: An universal formula for the calculation of nitrogen solubility in liquid nitrogen – alloyed steels, Metalurgija 48 (2009), 1, 23-27
[7] W. Kim, J. Kang, Ch. Park, J. Lee, J. Pak: Thermodynamics of aluminum, nitrogen and AlN formation in liquid iron, ISIJ International, 47 (2007), 7, 945–954
[8] A. G. Svjažin: Azot pri proizvodstve stali. Teorija i technologija, Metallurgija i metallurgi XXI veka, Sbornik trudov, Moskva 2001, 305-320
[9] D. Janke: Stahl und Eisen, (1992), 2, 49-56
[10] T. Nagasaka, R.J. Fruehan, A.W. Cramb: The reaction kinetics of nitrogen with liquid iron containing surface-active species — Is nitrogen in steelmaking an old subject or a modern topic?, ISSTech 2003 Conference Proceedings, 979–991.
[11] R. J. Fruehan: Fundamentals and practice for producing low nitrogen steels, ISIJ International, 36 (1996), Supplement, S58-S61
[12] D. Goldstein: Nitrogen reactions in the EAF and OSM, Ph.D. thesis, Carnegie-Mellon University, 1996, 27
[13] L. Zhang, B.G. Thomas: State of the art in evaluation and control of steel cleanliness, ISIJ International, 43 (2003), 3, 271–291
[14] D. Trotter, D. Varcoe, R. Reeves, S. Anderson: Use of HBI and DRI for nitrogen control in steel products, 2002, SEAISI Quarterly, 31, 2, 39 -50
[15] S. Misra, Y. Li, I. Sohn: Hydrogen and nitrogen control i n steelmaking at U.S. Steel, AISTech 2009, The Iron and Steel Technology Conference and Exposition, St. Louis, 43-52
[16] A. Majerčáková, Š. Majerčák, J. Kijac, Ľ. Mihok, A. Dudinský: Dusík v surovom železe, Zb. DNT 1992, 74-83

Note: The responsible for English language in the lecturer from TU Košice, Slovakia