W. DERDA[*], J. SIWKA[*], CZ. NOWOSIELSKI[**]

CONTROLLING OF THE NITROGEN CONTENT DURING EAF – TECHNOLOGY AND CONTINUOUS CASTING OF STEEL

KONTROLA ZAWARTOŚCI AZOTU PODCZAS PROCESU TECHNOLOGICZNEGO W PIECU ŁUKOWYM ORAZ CIĄGŁYM ODLEWANIU STALI

One of the main problem of steel melting in EAF technology are excessive contents of nitrogen in a semi steel products. This concerns in peculiarity these grade of steels from which the good plasticity was required or steels designed to production of the wire rod for welding electrode. The object of investigations was the range of changes of the nitrogen concentrations in the liquid steel immediately before tapping from the UHP – EAF's (105 MVA) in dependence of the kind of metallic charge (scrap and other iron sources). Then the changes of nitrogen content were qualified during steel treatment in a ladle furnace and pick up of nitrogen content during continuous casting of rectangular billets was established. The theoretical description of nitrogen absorption during steel tapping and continuous casting was applied. The dependence among the nitrogen concentration in liquid metal and quantity of the carbon oxidized during oxygen injection was determined. The influence of electric parameters (length of electric arc) on the nitrogen absorption into liquid metal was also considered in the investigations.

The influence of different materials bringing carbon into the bath as well as several kinds of scrap on nitrogen content in steel was considered in these investigations. The series of testing heats in the EAF were executed for verification of these settlements. As result of the modification of melting and casting technology, the decrease of the final nitrogen content of about 20 ppm in semi-product was achieved.

Keywords: EAF technology, nitrogen content, carbon boiling, obsolete scrap

Jednym z najważniejszych problemów podczas roztapiania wsadu w piecu łukowym są nadmierne zawartości azotu uzyskiwane w półproduktach stalowych. Dotyczy to szczególnie gatunków stali dla których wymagana jest dobra plastyczność lub stali przeznaczonej na druty elektrod spawalniczych. Badano zmiany zawartości azotu w ciekłej stali bezpośrednio przed spustem z pieca łukowego o dużej mocy (105 MVA), w zależności od źródła materiałów metalicznych (złom lub inne materiały). Zbadano zmiany zawartości azotu podczas obróbki stali w piecokadzi, a także we wlewkach po ciągłym odlaniu stali. Zastosowano teoretyczny opis absorpcji azotu podczas spustu stali oraz procesu ciągłego odlewania. Określono zależność pomiędzy zawartością azotu w ciekłym metalu a ilością utlenianego węgla podczas wdmuchiwania tlenu. Uwzględniono również wpływ parametrów elektrycznych (długość łuku elektrycznego) na absorpcję azotu do ciekłego metalu. Rozpatrywano również wpływ rodzaju materiałów wnoszących węgiel do kąpieli metalowej oraz rodzaju złomu na zawartość azotu w stali. Celem zweryfikowania postawionych tez wykonano serię próbnych wytopów testowych w piecu łukowym. W rezultacie zmodyfikowania technologii roztapiania i odlewania stali uzyskano spadek zawartości azotu w półproduktach stalowych rzędu 20 ppm.

1. Introduction

The significant, presently 43%, share of the electric process in the overall production of steel in Poland indicates an increasingly large field of application of products manufactured from electric steel. The technology of steel smelting in electric arc furnaces (EAF), on the one hand, offers great freedom in the choice of both the type and share of iron-bearing materials between scrap, solid or liquid pig iron, direct reduced iron (DRI/HBI) or iron carbide (Fe_3C), and, on the other hand, enables a wide range of steels of special properties to be manufactured with a productivity comparable to the oxygen converter process. Steels manufactured in the electric process contain most often from 70 to 120 ppm of nitrogen, so considerably higher nitrogen contents compared to converter steels,. Nitrogen is considered an undesirable component in steels which are required to have high

[*] CZĘSTOCHOWA UNIVERSITY OF TECHNOLOGY, 42-200 CZĘSTOCHOWA, ARMII KRAJOWEJ 19 AV., POLAND

[**] CMC ZAWIERCIE S.A., POLAND

plasticity (e.g. deep-drawing steels), in steels for welding wires, or in high-purity steels, such as those of the IF (Interstitial-Free) group. At the same time, in many contemporary steelmaking technologies, nitrogen plays the role of an important alloying element that imparts a number of unique properties to special-purpose steels. For steels with a limited nitrogen content, their production in a technological process, which consists of EAF smelting, ladle-furnace (LF) treatment and continuous casting, is accomplished so as to fully control the nitrogen concentration increment in liquid metal during these process stages. While the reduction of liquid metal nitrogen content in relation to the condition after complete charge melting may take place during relevant treatments in the process of EAF smelting as well as during secondary processes (mainly by vacuum treatment), what is left to be done in continuous steel casting is only to more or less effectively protect the liquid steel against nitrogen adsorption from the gaseous phase. Notwithstanding numerous experiments, many scientific and research centres or, directly, steelworks smelting steel in EAFs continue conducting research work on improving the capability of reducing the nitrogen content in products manufactured. These problems are also addressed in the present work.

2. Nitrogen removal during steel smelting in the EAF

The reduction of nitrogen content in steel in individual technology stages, i.e. during EAF smelting, ladle-furnace treatment and continuous casting, is accomplished in different ways, depending on the local conditions and the technological capabilities of the steelworks. As regards the EAF steel smelting technology, except for the injection feeding of powdered iron carbide (Fe_3C) to the liquid bath, which yields the best nitrogen removal results, the remaining methods bring about a variable final effect which is not always satisfactory, due to the complexity and multitude of factors of thermodynamic and kinetic nature, that determine the final nitrogen contents in steel. Therefore, if the aim is to smelt steel with a nitrogen content of approx. 80 ppm or less, then the objective necessity will in many cases be to employ several different methods simultaneously, which reduce the nitrogen content in liquid steel.

It is known from steelmaking practice that the vacuum degassing of liquid steel, depending on the chemical composition of the steel and on condition of maintaining high air-tightness of the vacuum chamber ($p_{tot.}$¡1Tr), allows the nitrogen content to be reduced by approx. 10÷20%. If electric arc furnaces are equipped with a bottom stirring system, then it will be possible to apply

metal bath blowing using argon or CO_2. Literature descriptions [1] suggest that this method enables the reduction of nitrogen concentration in steel down to 30% of the original value. It should be borne in mind, however, that as a result of blowing with CO_2, the decomposition of this carbon dioxide results also in an increase in the concentration of both oxide and carbon in the steel. It is considered effective to remove nitrogen from liquid steel using a slag phase with a special chemical composition, including chemical compounds, such as BaO, ZrO_2, TiO_2, BaF_2, CaF_2 and others [2, 3]. The nitrogen bonding efficiency is dependent on the nitride capacity value of the slag at its given chemical composition and temperature, and on a number of other conditions, and in the most favourable case it may reach a value of approx. 40% of the original nitrogen content [3]. The consequence of using slags containing the above-mentioned chemical compounds is a possibility of undesirable metals passing to the metal phase, and, in addition, this is a costly method due to the high prices of the special slag components. The effective influence of slag on nitrogen absorption from liquid steel is often joined with extensions of the melting time what state a problem for the modern technology at the EAFs. A method worthy of application to modern EAF steel melting technologies, and still being improved, which allows the reduction of nitrogen content at relatively low costs, is the implementation of so called carbon boiling. The release of CO bubbles as a result of the oxidation of carbon in the bulk of the liquid metal phase can be initiated and intensified in several ways, e.g. by injection, simultaneous feeding of carbon carriers and gaseous oxygen, or blowing in fine forms of iron ore or directly reduced iron. This method was applied in the tests described in the present paper.

Phenomenon of dissolving of diatomic gaseous nitrogen particles in liquid iron is preceded by its dissociation to the atom form or in some cases by atom ionization. This phenomenon, under condition of the thermodynamic equilibrium between nitrogen in the gas phase and in the metallic solution is given by chemical reaction:
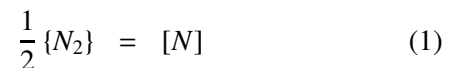
$$\frac{1}{2}\{N_2\} = [N] \tag{1}$$

At the equilibrium state the chemical potentials of nitrogen in both phases are equal, so

$$\frac{1}{2}\mu_{N_2} = \mu_N \tag{2}$$

It is assumed as first approximation, that in liquid metallic solution nitrogen exist in atomic form. Expressing concentration in wt.%, for general case of reaction (1), the equilibrium constant can be expressed as follows:

$$K_{N\,(Me)} = \frac{[\%N] \cdot f_N}{P_{N_2}^{1/2}} \qquad (3)$$
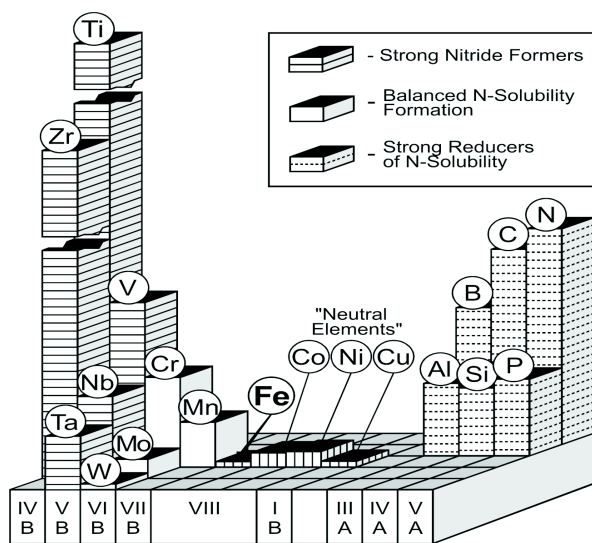

Fig. 1. represents influence of the respective elements on solubility of nitrogen in steel

As follows from Figure 1, steel components are divided into those which strongly increase nitrogen solubility in steel, and those which decrease this solubility. There are also such steel components that behave neutrally in this respect. It should be added that, as works [5,6] indicate, also sulphur and oxygen can be numbered among neutral components. Very important information is the fact of decreasing nitrogen solubility by nitrogen itself. The thermodynamic characteristics of nitrogen – nitrogen interaction with regard to liquid iron are described in detail in work [7] and presented in an abbreviated form, e.g. in work [8]. For system of liquid metal – nitrogen-containing gaseous phase, the following general functional relationship is valid:

$$\lg\,[\%N]_{P_{N_2}} = 0.5 \cdot \lg P_{N_2} - \lg K_{(Me)} - \lg f_N \qquad (4)$$

In the case of the system with liquid iron, Equation (4) has the following form, enabling the calculation of nitrogen solubility, depending on of temperature and nitrogen partial pressure in the reaction space:

$$\lg\,[\%N]_{P_{N_2},T} = 0.5 \cdot \lg P_{N_2} - \frac{664}{T} - 0.999-$$
$$-\left(\frac{386}{T} - 0.158\right) \cdot [\%N] \qquad (5)$$

It follows from relationship (5) that at a temperature of 1873K and under a gaseous phase nitrogen partial pressure of $p_{N_2}= 0.1$ MPa, nitrogen solubility in liquid iron is 441 ppm, while under $p_{N_2}= 0.078$ MPa the limiting nitrogen concentration is 390 ppm. The Fe-C system is the basis of steel metallurgy. The majority of steels contain carbon, hence detailed data on nitrogen solubility are essential in order to precisely predict the solubility of nitrogen in more complex alloys, all the more so because carbon strongly influence the activity of nitrogen in liquid iron. As shown in work [9], the variation of the nitrogen activity coefficient under the influence of carbon can be calculated using the following relationship:

$$\lg f_N = \frac{280}{T} \cdot [\%C] + \left(-\frac{74}{T}\right) \cdot [\%C]^2 \qquad (6)$$

The calculation of nitrogen solubility in liquid steel of arbitrary chemical composition, within a wide range of nitrogen partial pressure and temperature, is possible with the use of the thermodynamic model and the database provided in work [10]. This model, using Lupis' methodology for the determination of the nitrogen activity coefficient, *TRIALRESTRICTION*, in the iron alloy, allows for all the essential parameters of interaction between nitrogen and components, as well as nitrogen self-interaction parameters, including the nitrogen – nitrogen self-interaction parameter. An important influence on the progress of the nitrogen absorption – desorption reaction between the gaseous phase and the metal under industrial conditions is exerted primarily by factors of a kinetic nature.

As described in detail in monograph [11], as possible controlling stages, only the stages of surface reaction and nitrogen transfer in liquid metal can be considered. In that case, the generalized equation for controlled process rate in these two stages (the mixed model of reaction) has the following form:

$$\frac{dC}{dt} = \frac{S}{V} \cdot \{\beta \cdot \left(\frac{\beta^2}{4k^2} + \frac{\beta}{k} \cdot C + C_e^2\right)^{\frac{1}{2}} - \frac{\beta^2}{2k} - \beta \cdot C \} \qquad (7)$$

where: C – nitrogen concentration in bulk of metal, wt.%, C_e – nitrogen equilibrium concentration in bulk of metal, wt.%, β – mass transfer coefficient of nitrogen in metal phase, m s^{-1} k – effective rate constant of surface chemical reaction, m s^{-1} %$^{-1}$; S – effective interphase free surface area, m^2; V – volume of metal, m^3.

Usually, for example as in works [12, 13] it is take into account that nitrogen absorption proceed on the surface free of SAE (Surface Active Elements), mainly oxygen and sulphur. From here, the rate of reaction constant is proportional to the area of non – coated surface Θ by sulphur and oxygen e.g. $k = f(1 - \Theta)$. As described in monograph [11], value of constant kcan be calculated using Eq. (8):

$$k = 9,23 \cdot 10^6 \exp\left(-\frac{40000 \pm 20000}{T}\right)\frac{1}{1 + 3350\left([O] + 0,5[S]\right)^{1,2}} \tag{8}$$

The interaction of SAE on the kinetics of nitrogen mass exchange with liquid metal is more complex than is usually believed. SAEs have an influence on both the surface reaction rate and the mass transfer rate in liquid metal. Depending on the extent of participation of SAEs themselves in mass exchange, they can either speed up or slow down a given process, and either stabilize the phase boundary or cause its turbulence. With either mechanism, the influence of SAEs involves their adsorption on the surface, therefore experimental data for some SAE concentration ranges satisfy the ideal Gibbs and Langmuir adsorption models. Probably the most physically-determined mechanism of SAE influence on interfacial mass exchange can be established by solving the hydrodynamic problems for the gas – metal interface.

As regards the EAF technology, a lot of interesting core information on the nitrogen absorption - desorption mechanism is contained in work [14]. It states the following: (Citation): "*The two major methods of reducing nitrogen in steels are by carbon oxidation and the use of direct reduced iron (DRI) such as Midrex DRI, HBI and iron carbide. For carbon oxidation the CO picks up nitrogen from the metal and protects the metal from the atmosphere. Direct iron dilutes the nitrogen from the scrap, forms an early and larger slag layer for protection and produces CO from the reaction of unreduced iron oxide and carbon in the pellets*"

3. Experimental results and discussion

The subject of investigation were low-carbon steels smelted in an electric arc furnace of a UHP class, of a nominal capacity of 140 Mg. In order to establish the current condition for the technologies presently used in the steelworks, a detailed analysis of variations of nitrogen content in steel was performed in the principal stages of the technological process, an particularly:

- immediately before steel tapping from the EAF,
- at the beginning of the process in the ladle furnace (LF),
- before the completion of the ladle furnace process,
- during continuous steel casting, after casting of about 40 Mg of steel (samples from the tundish),
- after casting of about 80 Mg of steel (samples from the tundish), and
- from the final semi-finished products (a square cross-section billet).

Nitrogen concentration variations were determined in several steel grades, including steels intended for welding electrode wire rod, round plain wire rod (C – 0.07%, Mn – 0.38%, S – 0.009%) – steel "a", for ribbed reinforcement bars (C – 0,17%, Mn – 0,65%, S – 0,026%) – steel "b" in Fig. 1, for microalloyed steel (Nb, Ti), etc.

During the smelting of those steels, the metallic charge was consisted primarily of steel scrap, and in the casts of steels intended for welding electrode wire rod, the additions of pig iron or HBI were used. A standard addition to the metallic charge was anthracite in amounts not greater than 1500-2000 kg. The furnace was equipped with the EBT bottom tapping system that enabled operation with the hot heel remaining in the furnace. During tapping of steel to the ladle, appropriate alloying additives and deoxidizers were introduced, and the final correction to chemical composition and refining took place in a ladle furnace (LF). Steel was cast on one of the two six-strand CSC machines. Continuous castings of square cross-sections from 105 to 160 mm or of a 145×180 mm rectangular cross-section were cast.

Steels of an aluminium content of approx. 0.02% were cast in ceramic stream shields and using submerged entry nozzles (SEN). A sample distribution of nitrogen concentration variations for two selected steel grades in successive stages of the EAF smelting process, ladle-furnace (LF) treatment, and continuous casting, is shown in Fig. 2. A characteristic feature in Fig. 2 is the higher nitrogen increment for the lower-carbon steel (steel "b") through the whole process.
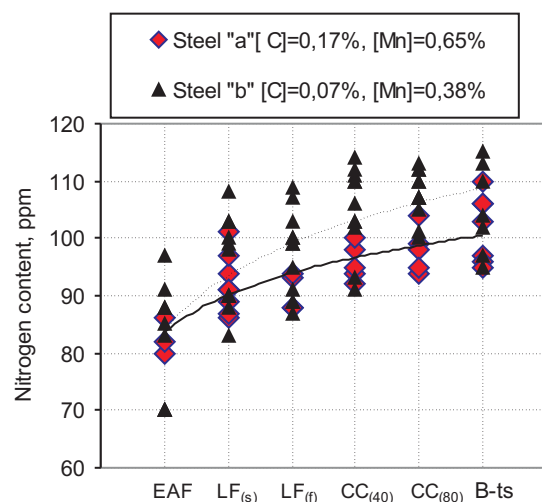

Fig. 2. Comparison of the nitrogen content changes during EAF – LF – CC route for two grades of steel

For a better illustration of the increment of nitrogen concentration in liquid steel in individual stages of the technological process, the variation of the arithmetical mean of nitrogen contents in the melts examined is shown in Fig. 3 for steel "b" with a carbon content of

0.07%. This steel, having an average aluminium content of approx. 0.003% Al, is cast by the open casting method.
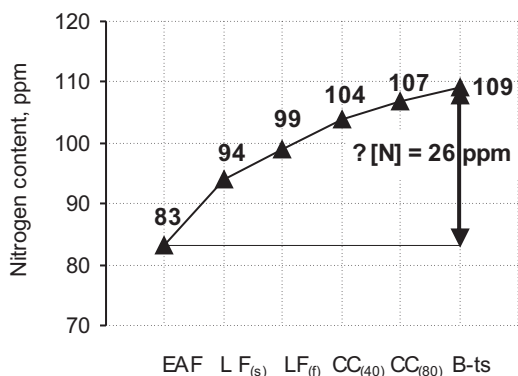

Fig. 3. Change of the nitrogen content during EAF – LF – CC route for steel "b"

Figure 3 indicates that the largest nitrogen content increment, amounting to approx. 11 ppm, takes place during steel tapping. This value consists primarily of the nitrogen absorbed from air by the stream of steel flowing out from the furnace. Fe-Si-Mn and Fe-Si, as well as burnt lime and dolomite lime were added to the ladle during tapping. These ferroalloys, as compared to e.g. the low-carbon Fe-Mn alloy, contain a small amount of nitrogen, which is less than for dolomite lime that usually contains about 140 ppm of nitrogen. The addition of these materials does not, therefore, contribute significantly to the increment in nitrogen concentration in metal being cast. Investigation has shown that the nitrogen concentration increment during tapping is dependent on the condition of the EBT system discharge nozzle. It has been found that, as the nozzle block erodes, increases its dimensions and changes its shape from cylindrical to conical, the melting time shortens approximately by half, i.e. from 270 seconds for a new nozzle to about 137 seconds after making 120 steel casts, on average. Measurements demonstrated that, for longer tapping times, being characteristic of a new nozzle block, nitrogen contents in steel after complete filling of the ladle were by approx. 6 ppm higher compared to steel cast at the end of the campaign foreseen for the ceramic EBT system block.

On the basis of these findings it was concluded that efforts should be made in further tests to assure that the nitrogen contents in steel immediately prior to tapping from the EAF be lower than those achieved so far. Emphasis was placed on three basic aspects:

- increase the share of better-quality scrap in the charge, chiefly broken-up scrap,

- assure the proper carbon-bearing additives, mainly pig iron and HBI, in the charge,

and

- modify the power supply of the electric furnace to operate at shorter arcs.

Appreciating the importance of carbon boiling during steel smelting in the EAF and the role of CO bubbles in nitrogen removal, a relationship between the amount of nitrogen removed (i.e. the difference between the nitrogen contents in metal after melting the charge of basket II and immediately before tapping) and the amount of oxidized carbon, expressed as the percentage of metal mass, was established for melts from the ongoing production of different steel grades. The obtained relationship is presented in Fig. 4.

A relationship useful for the local technological practice was statistically described with the equation in a logarithmic form, as follows:

$$\Delta[N], \text{ppm} = 10.34 \cdot \ln(\Delta\%C) + 36.14$$

$$R^2 = 0.4033$$

In the second test series, several variants of charge set-up were used, so as to obtain the proper carbon boiling intensity after melting. With the sheared scrap addition set at about 40% of
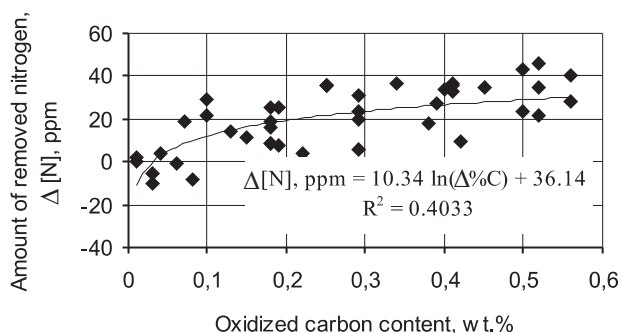

Fig. 4. Amount of the removed nitrogen vs. oxidized carbon content in the bath of EAF

metal charge mass, the pig iron addition was varied in the range from 0 to 17% and HBI from 0 to 10% of metal charge mass. Taking account of the carbon content in the iron-bearing charge materials in the EAF steel smelting process, it was established that the amount of oxidized carbon, in relation to the metallic charge mass, varied in the range from 0.39 to 0.67% C. For the constant quantities of materials added to the charge, such as pig iron, HBI and heavy scrap, it was determined that the nitrogen content assayed in billets is clearly dependent on the mass of obsolete scrap added.
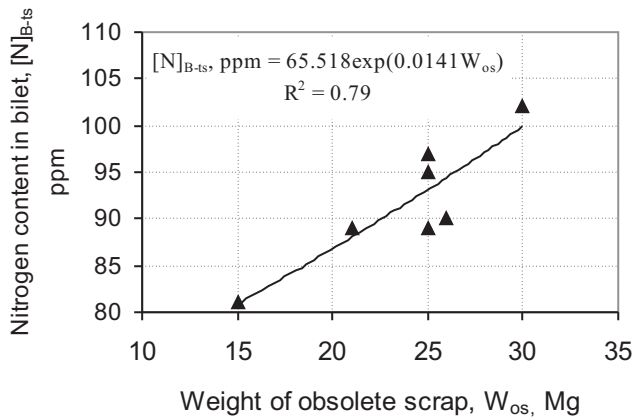
Fig. 5. Dependence of the nitrogen content in billets vs. weight of obsolete scrap in charge

The statistical relationship represented in Fig. 5 indicates that the increase in the obsolete scrap mass from 15 to 30 Mg/melt may cause an increase in the nitrogen content of the finished steel by as much as 20 ppm. This suggests a necessity for reducing the mass of the addition of this type of scrap as the charge material, when a steel with a limited nitrogen content is to be smelted.

Using the data represented in Fig. 4, the charge components in the modified technology were set up so that the amount of oxidized carbon was not less then 0.3% of charge mass, while reducing the obsolete scrap mass and selecting such a programme of energized furnace operation, so as to obtain the shortest possible arcs. A shorter electric arc column provides, among other things, a smaller surface of contact with the ambient atmosphere, thereby limiting the process of formation of atomic nitrogen and excited molecules, which are much more readily adsorbed on the *metal-gaseous phase* contact surface at electric arc temperatures. The subject of the tests was, among others, the steel of "b" type, which was described in the first series. Twelve melts of this steel were made, assaying the nitrogen content in the liquid steel immediately before tapping from the EBT. The obtained results are shown in Fig. 6.
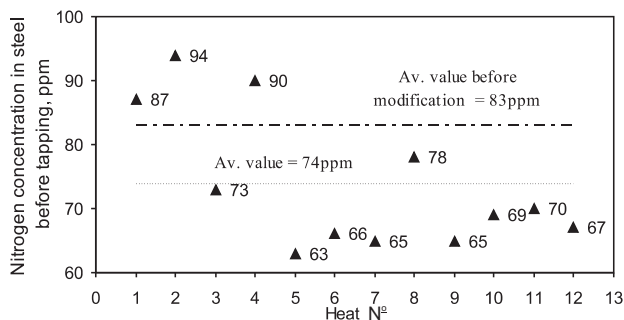

Fig. 6. Comparison of the average value of nitrogen content in steel at EAF before and after modification of technology (steel with 0.07 wt.%C, 0.38 wt.%Mn)

Two lines were also drawn on Fig. 6, one of them mark the average value of nitrogen content in steel before tapping achieved in first series of investigations (Av. value = 83 ppm), and second one which regarded the average value of nitrogen contents from the second series of investigations (Av. value = 74 ppm). Difference between these values is equal 9 ppm, however it should be pointed out that in nine from among twelve heats the nitrogen concentrations in steel before tapping are smaller than 78 ppm. Though using the data represented in Fig. 4, under condition of proper selection of charge components with regard of carbon carried and oxidised it can be expected that this difference should be about 20 ppm, however it must be consider that on the nitrogen content in steel in EAF the influence exerts the lot of different factors.
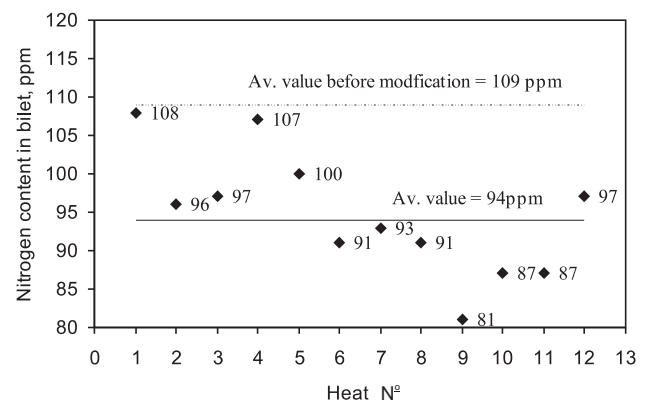

Fig. 7. Comparison of the average value of nitrogen content in billet before and after modification of technology (steel with 0.07 wt.%C, 0.38 wt.%Mn)

To evaluate of how the nitrogen content in the finished steel was effected by this modification of technology, including the applied protection of liquid metal streams during the continuous casting of this series of melts (ceramic tube between the ladle and the tundish and a special protection in the argon stream between the tundish and the mould), comparison of the final nitrogen concentrations obtained in the two series was made. This comparison is shown in Fig. 7, where – similarly as in Fig. 6 – appropriate mean values are designated with horizontal lines. The difference between both mean values is 15 ppm, which can be interpreted in such a manner, that the applied stream protection systems have produced a positive effect, though they require further improvement.

4. Conclusions

The requirements of steel product purchasers, limiting the nitrogen content in EAF smelted steels, have forced search for methods that would enable the reduc-

tion of nitrogen increment during individual technological stages. It has been shown that the reduction of nitrogen content in steel may take place during both the smelting and continuous casting of steel. The present work has found that the limiting of the mass of obsolete scrap in the metallic charge contributes markedly to the reduction of nitrogen content during smelting. Of particular importance to the process of bubble nitrogen removal from the liquid metal bath is the generation of sufficiently large amounts of carbon monoxide. Such a state is achieved, if at least 0.3 wt% of carbon relative to the metallic charge mass is oxidized out of the liquid metal phase. Therefore, in order to meet this condition, the carbon-bearing materials (pig iron, DRI/HBI, cast iron scrap, etc.) must be selected in a manner that assures the appropriate content of this element after the charge has been melted. With the proper metallic charge set-up, if the oxidized amount of coal was contained in the range from 0.39 to 0.67 wt% C, the obtained nitrogen content in the metal prior to tapping ranged from 63 to 70 ppm. After obtaining metal of such nitrogen contents, the careful protection of the steel streams against the absorption of nitrogen from the gaseous phase during continuous casting gains particular importance. This way, the increment in the nitrogen content of steel can be reduced by approx. 15 ppm.

REFERENCES

[1] J. Pal, S. Ghosh, M. C. Goswami, D. P. Singh, M. Kumar, R. K. Minj, A. K. Upadhyay, Role of Direct Reduced Iron Fines in Nitrogen Removal from Electric Arc Furnace Steel, Steel Research International **78**, 8, p.588 (2007).

[2] H. Sakai, H. Suito, Nitride Capacities in the CaO-base Ternary Slags at 1873K, ISIJ Intern. **36**, 2, p. 143 (1996).

[3] R. Yamanaka, K. Ogawa, H. Iritani, S. Koyama, Denitrogenization Mechanizm from Molten Steel by Flux Treatment, ISIJ Intern. **32**, 1, p. 136 (1992).

[4] H. K. Feichtinger, G. Stein, Melting of High Nitrogen Steels, Materials Science Forum **318-320**, p. 261 (1999).

[5] R. D. Pehlke, J. F. Elliott, Solubility of Nitrogen in Liquid Iron Alloys. I Thermodynamics, Trans. Met. Soc. AIME **218**, 12, p. 1088 (1960).

[6] T. Fuwa, Sh. Ban-ya, F. Ishii, Effect of oxygen, sulphur and tellurium on the solubility of nitrogen in liquid iron, Tetsu-to-Hagane **51**, 12, p. 1834 (1965).

[7] J. Siwka, D.Sc. Thessis, Diss. TUCz, serie Metallurgy, Częstochowa, 8 (1999).

[8] J. Siwka, Nitrogen Solubility in Liquid Binary Alloys with Chromium, Manganese, Molybdenum, Nickel, Vanadium, Silicon and Carbon, [In:] HNS High Nitrogen Steels, ed. M. O. Speidel, C. Kowanda, M. Diener, vdf Hochschuleverlag AG an der ETH Zurich, 2003, p. 91.

[9] J. Siwka, "Solubility of Nitrogen in Liquid Iron Alloys with Carbon and Silicon in hyperbaric conditions", Transactions of the Indian Institute of Metals **55**, 4 (Part A), p.177 (2002).

[10] J. Siwka, Equilibrium Constants and Nitrogen Activity in Liquid Metals and Iron Alloys, ISIJ International, (2008) 4, in print.

[11] J. Siwka, A. G. Svjazin, Nitrogen in Liquid Iron Alloys, Częstochowa University of Technology, Serie Monography 117, (2006), pp. 136 [in polish].

[12] M. Inouye, I. Choh, Rate of absorption of nitrogen in liquid iron and iron alloys, Transaction ISIJ **8**, 3, p. 134 (1968).

[13] G. R. Belton, How Fast Can We Go? The Status of Our Knowledge of the Rates of Gas-Liquid Metal Reactions, Metallurgical Transaction **24B**, 4, p. 241 (1993).

[14] R. J. Fruehan, Fundamentals and Practice for Producing Low Nitrogen Steels, ISIJ International **36** Supp., p. S58 (1996).