Conception of Low Nitrogen Steel Production Technology
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In the production of transport metal: low carbon steel for auto sheets and high carbon steel for steel cord, nitrogen, undoubtedly, is a detrimental additive. Its content in the finished steel for the above products should be minimized and be within the range up to 50 ppm (mass portion % x 10^4) at best.

Contrary to other gases (oxygen, hydrogen) nitrogen is low active in relation to iron that is why to achieve its low as well as high concentration is a very complicated and complex task.

This work investigates the behaviour of nitrogen in steel melts with a wide range of carbon content in oxygen converters and electric furnace production. It determines the main ideas of low nitrogen steel technology.

1. Thermodynamics and kinetics of nitrogen absorption and extraction.

Solubility of nitrogen in iron is subject to Sivert’s law:

\[ [N] = K_N \sqrt{P_{N_2}} \]

where \([N]\) – solubility of nitrogen, %

\(P_{N_2}\) – partial pressure of nitrogen, atm.

K – equilibrium constant of the reaction of nitrogen dissolution in iron, % x atm\(^{-1/2}\)

Measurement of nitrogen solubility in molten iron executed by professor A. G. Svyazhin [1] allowed to get the equalization for the constant of solubility of nitrogen in iron.

\[ \text{Lg } K_N = - \frac{850}{T} - 0.905 \]

At present solubility of nitrogen in iron at 1600 °C has been determined rather accurately and it equals to 440 ± 10 ppm.

2. Some matters of the kinetics of nitrogen sorption.

The kinetics of nitrogen adsorption and extraction from a melt is studied to a lesser degree than its thermodynamic behaviour, and the data available are rather contradictory. In general dissolution of nitrogen goes through several stages:
1. Convectional transfer in a gas phase.
2. Molecular transfer in a gas phase through a diffusion boundary layer.
3. Surface chemical reaction including adsorption and desorption of nitrogen molecules and the transfer of the adsorbed atoms of nitrogen into the solution.
4. Molecular transfer in a metal through the diffusion boundary layer.
5. Convectional transfer in the volume of the metal.
Solubility kinetics (sorption) of nitrogen in real melts was studied by melting in a suspension state in an electromagnetic field [2]. In real steel making processes dissolution of nitrogen proceeds parallel to oxidizing processes, consequently air was used as a gas. Interaction of the gas with pure iron, iron-carbon melt, and steel 3SP and 15 GUT was examined (table 1) with the air consumption of 0.25; 0.5; 1.0; 10 l/min, which corresponds to the rate of a flood running over the drop surface equal to 0.016; 0.032; 0.065; 0.650 m/s. Temperature of a drop was measured with a colour pyrometer and kinetic curves of gas and basic elements content change in time were taken.

Table 1

Initial data of the metal examined

<table>
<thead>
<tr>
<th>Metal</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ti</th>
<th>Al</th>
<th>P</th>
<th>S</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.007</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.001</td>
<td>0.01</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe-C</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.002</td>
<td>0.002</td>
<td>0.0004</td>
</tr>
<tr>
<td>3SP</td>
<td>0.16</td>
<td>0.61</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
<td>0.030</td>
<td>0.017</td>
<td>0.002</td>
<td>0.005</td>
</tr>
<tr>
<td>15GUT</td>
<td>0.16</td>
<td>1.43</td>
<td>0.32</td>
<td>0.17</td>
<td>0.18</td>
<td>0.024</td>
<td>0.026</td>
<td>0.002</td>
<td>0.0062</td>
</tr>
</tbody>
</table>

Characteristic kinetic curves for steel 3SP are shown in fig. 1. It was established that in pure iron nitrogen absorption is insignificant and the higher the air flood rate is the less the absorption is, because the rate of nitrogen dissolution increases here; after the saturation of metal with oxygen nitrogen sorption ceases, though its concentration in the metal is low.
With air blasting ($u = 0.016$ m/s).

Discontinuation of the nitrogen adsorption under the conditions of these experiments speaks in favour of the assumption of a continuous oxide film formation on the metal surface slowing down the nitrogen intake. Nitrogen behaviour in Fe-C alloy and in steels 3sp and 15GUT is similar to that in pure iron and is determined by the rate of the saturation of the metal with oxygen. With the increase of the flood rate oxygen adsorption rate increases as well, nitrogen adsorption ceases earlier, and its concentration attained herewith becomes less. When the maximum concentration of oxygen in metal is achieved nitrogen adsorption ends and metal temperature starts to decrease evidencing in favour of a continuous oxide film formation or its continuous formation along the entire drop surface top and tickling down. From the initial first order model data nitrogen dissolution rate was determined by the graphical differentiation. Mass transfer apparent factors or to be exact constants of the first order reaction speed were calculated on the base of the dissolution rates and the corresponding mean nitrogen concentrations. Values obtained are given in fig. 2 dependent upon the value of $[O]+0.5[S]$ together with the data on nitrogen dissolution from the atmosphere of nitrogen.

![Fig. 2. Influence of oxygen and sulphur concentration in metal on the constant of nitrogen dissolution rate (cm/s).](image-url)
Range of values of $K_1$ for the iron - oxygen alloys at 1600 °C according to the literary data generalized in [3] is cross - hatched. Our results for the atmosphere of pure nitrogen are in concord with the literary data. Air data show significant diversity, however not connected with the influence of the metal content and the air flow rate. Rate constant $K_1$ depends on temperature. Temperature dependence of $K_1$ with constant value of $[O]+0.5[S]$ was determined separately for different methods of actual temperature measurement (brightness-temperature and colour pyrometers) because there are differences between them in the period of nitrogen dissolution. The so obtained activation energy values (200-400 kJ/mole), considering their accuracy, fit very well the data [3] for nitrogen dissolution with iron – oxygen melt from nitrogen atmosphere.

High value of the activation energy and strong dependence of dissolution rate on oxygen and sulphur allows to assume that absorption of nitrogen from the air is limited by the reaction on the metal surface. This does not exclude the use of the first order rate equation as the reactions going on the surface have different order, besides, nitrogen dissolution data are low sensitive to the order of the rate equation.

3. Nitrogen behaviour in various melting units.

3.1. Basic oxygen process.

Nitrogen content in the converter metal is determined by:
1. The content in cast iron and other grey materials.
2. The state of equilibrium between gaseous metal and slag phases in the total converter capacity.
3. The difference of the rate of transfer from gas phase into metal and its discharge into the gas phase together with bubbles of carbon oxide.

Undoubtedly, purity of oxygen has a paramount significance in the conditions of the converter process. To obtain low nitrogen content (less than 40 ppm) purity of oxygen should be not lower than 99.5%.

Besides, when tapping a smelt from the converter, deoxidizing in the ladle, and casting as a rule, the content of nitrogen in the metal increases, that is why one of the conditions for obtaining a low content of nitrogen in steel is reaching its extremely low concentration before tapping a smelt from the converter.

The research was carried out with 350 t converters of Karaganda metallurgical integrated works.

Nitrogen content change in every technological stage was evaluated: during pouring cast iron from a ladle into a converter, in the process of a heat soaking with the converter being turned down, during blowing and a final blow.

It was determined that when pouring cast iron into a converter an intensive removal of nitrogen from a liquid part of the charge material takes place (at the average 0.007 – 0.006% to 0.004 – 0.003%). During first minutes of blowing a significant decrease of nitrogen content in metal is also registered. Consequently nitrogen concentration stabilizes and practically remains constant during the entire blowing. At the end of the blowing period with a low carbon content concentration
of nitrogen in the metal increases. During final blow an intensive absorption of nitrogen by metal takes place (at the average by 0.0015 – 0.0007%). During soaking when the converter is turned down the concentration of nitrogen does not change. This dynamic change of the nitrogen content in the course of a converter melting is explained by the thermodynamic facilitation of nitrogen extraction from the melt with bubbles of CO at the very beginning of blowing, and the rate of this process is much higher than the rate of the nitrogen inflow from the converter atmosphere and melting scrap. With carbon content decrease the rate of nitrogen intake and removal from the metal equalize. The end of the period of blowing is characterized by the low intensity of the bath rimming and the rate of nitrogen intake into the metal becomes prevailing. With the decrease of the amount of effluent gas the bath level falls, air suction raises, facilitating its ejection with an oxygen stream into the reaction zone. Before the final blow with the converter being turned down the bath is killed, blowing is carried out in the unburied mode, and here favourable conditions for metal saturation with nitrogen are created.

To reduce nitrogen content increase in steel during final blow it was suggested to foam slag at the beginning of final blow by adding 0.5 – 1.0 t of limestone. This quantity of limestone provided slag foaming and the transfer of blowing into the buried mode, thus preventing nitrogen ejection into the metal.

Statistical equation determining the content increase during blowing looks as follows:

$$\Delta N = -0.72 \cdot [N] + 3.6 \cdot 10^{-7} V_{O_2} - 9.9 \cdot 10^{-7} - J_{O_2} - 1.1 \cdot 10^{-4} G_{CaCO_3}$$

where
- $[N]$ – concentration of nitrogen in metal before a final blow, %
- $V_{O_2}$ – quantity of oxygen for a final blow, $\text{m}^3$
- $J_{O_2}$ – consumption of oxygen, $\text{nm}^3/\text{min}$
- $G_{CaCO_3}$ – mass of limestone added during final blow, t.

The equation shows that the increase of nitrogen content during final blow is considerably influenced by its initial content in metal and by the consumption of oxygen for the final blow. With the increase of the amount of added limestone increase of nitrogen during final blow becomes lower, proving the efficiency of the measure suggested.

### 3.2. Electric steel melting process.

As a rule, average content of nitrogen in a metal melted in an electric furnace is 20-40 ppm higher than in a converter metal.

The reasons for the higher content of nitrogen in an electric steel are thoroughly studied and well known:
- Use of up to 100% of scrap metal;
- Low rate of decarburization (compared to the converter process);
- Deoxidizing atmosphere and local overheating of metal in the area of arcs, dissociation of nitrogen in the arcs.

Behaviour of nitrogen during electric melting was investigated with cord metal.
At Byelorussian Steel Works (BMZ) steel for tire cord is produced in super power 100-t electric arc furnaces operating by one-slag process with the use of “liquid” start method. The furnaces are equipped with a 75 MVA transformer, a system of continuous slag-forming materials and iron-rich pellets, wall gas-oxygen burners and an oriel device for melt tapping.

At the beginning of the period of cord steel production technology familiarization the charge metal base consisted of pellets produced by Oskol electric steel integrated works (80 to 100%). Later an alternative technology of steel making based on the use of a less deficient raw material – “pure scrap” – containing not more than 0,05% of chrome, nickel, and copper was developed and introduced.

Naturally, the type of charge metal used to a great extent determined nitrogen behaviour in the electric arc furnace bath (table 2).

When making steel in EAF with 100% of iron-rich pellets and their continuous charging in the amount of 100-120 t at the rate of 2 t/min conditions for early slag formation and electric arcs shielding are formed.

The peculiarity of this technology: combination of melting process and oxidation of excessive carbon. Average rate of carbon oxidation is within 9-12 kg/min if its content in iron-rich pellets is up to 1,5% and the consumption of blasting oxygen is 6,5-10,5 m³/t.

Table 2

<table>
<thead>
<tr>
<th>Group of heats</th>
<th>Melting technology</th>
<th>Nitrogen content, ppm*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>After melting</td>
</tr>
<tr>
<td>1</td>
<td>100% iron-rich pellets</td>
<td>22-34</td>
</tr>
<tr>
<td>2</td>
<td>35% iron-rich pellets</td>
<td>46-59</td>
</tr>
<tr>
<td>3</td>
<td>Cast iron +scrap metal</td>
<td>46-60</td>
</tr>
<tr>
<td>4</td>
<td>Cast iron +scrap metal + oxidized pellets</td>
<td>45-58</td>
</tr>
</tbody>
</table>

* numerator - min - max; denominator – average value

Under these conditions nitrogen behaviour was characterized as follows (fig.3).
The conception of charge material melting has no physical meaning when continuously charging iron-rich raw material into the furnace. Both solid and liquid phases are constantly present in the furnace. As a result of continuous supply of a solid charge with 1.5% carbon content into the melt the bath is permanently rimming till pellets supply is stopped 10-20 minutes before tapping. As a result, at the beginning of melting the intake of nitrogen from cast iron, coke, furnace atmosphere under the conditions of minimum intensity of carbon oxidation has the biggest importance the whole melting long. With the increase of the temperature and carbon oxidation intensity till the middle of melting concentration of nitrogen somewhat decreases.

The technology of tire cord steel melting with charge material and 100% use of iron-rich pellets was introduced at BMZ in 1987. It ensured not more than 34 ppm nitrogen content before tapping from a furnace (Table 2).

At the same time, the experience of using the above technology revealed a number of drawbacks. Use of up to 100% of iron-rich pellets in slag is connected with the introduction of a large quantity of waste rock into the furnace. Thus, charging 130 t of pellets per heat up to 6.0 t of silica is put in. To neutralise it and to support basicity at not less than 2.0 the proportion of the pellets and lime weight should be 10:1, so, consumption of lime per heat is 12-13 t. Increase of the slag mass permanently leads to the increase of electric energy consumption. It was determined that for each 50 kg of slag electric energy consumption increases on average by 50 kWt·h/t of steel. Indeed, under BMZ EMS conditions electric power consumption for tire cord steel making on average is 10% higher than for ordinary steel. Lime consumption also increased by 48 percent on average.
The technology of tire cord steel making with the use of “pure” scrap instead of a part of pellets was developed and introduced at BMZ. To increase carbon content in metal after melting pig iron making up 20% of the charge material is used in it.

Modification of burdening essentially changed the melting process and particularly behaviour of nitrogen (fig.3, table 2). Main differences of the melting procedure with the use of iron-rich pellets lie in a hindered slag formation, low melting speed, and carbon oxidation. High nitrogen content in pig iron and scrap metal determines obtaining its high content after melting. Use of iron-rich pellets making up 30-40 % of the charge weight and their addition after scrap melting decreases nitrogen content in metal (fig.3) by attenuation of high-nitrogen melt with the material with a low nitrogen content (nitrogen content in iron-rich pellets is not more than 30 ppm), and by improving a slag mode (first slag after melting has the basicity within 4 - 5).

Making tire cord steel with the use of 100% of scrap nitrogen content before tapping increased 1.6 times compared to melting with 100% of iron-rich pellets, as a result nitrogen content in finished metal rose to maximum allowed values (0.005%), and in some heats went beyond them.

In this situation the task of decreasing nitrogen content was brought to intensification of oxidation processes of the bath admixtures and carbon in the first place. Additives of solid oxidants as rolled scale and oxidized pellets were tested in operation.

Use of the above materials in steel making is always justified because the cost of oxidized pellets and especially scale as iron-containing materials is lower than the costs of iron-rich raw material (DRI, HBI, etc.).

Fig.4 shows the influence of solid oxidants addition on the change of nitrogen content in the oxidizing period of melting with the use of 100% of scrap and pig iron in the charge.
Fig. 4. Influence of solid oxidant additions on nitrogen behavior.

As seen in fig. 4, scale and oxidized pellets addition have various influences on the change of nitrogen contend in the process of melting in EAF. This fact can be explained by different physical properties of these solid oxidants – particle size, specific surface (relation of the outer surface to the mass of the particle).

Thus, scale has a particle size of not more than 3 mm and a highly developed specific surface and dissolves in the upper layers of slag increasing content of (FeO) in slag. Addition of scale during melting allow to improve slag formation decreasing slag melting temperature, improves its reactivity, increases carbon oxidation rate, thus decreasing in its turn the content of harmful admixtures – nitrogen and phosphorus (phosphorus content after charge melting made up 0,003 % an the average).

The size of oxidized pellets particles is more than 5 mm, specific surface is within 0,14-0,30 cm$^2$/g and apparent density is 3,2-3,6 g/cm$^3$, they sink in slag (slag density - 2,0-3,0 g/cm$^3$) and melt at the metal – slag boundary giving possibility of oxygen separation in the form of a separate phase (thin oxide films) and nitrogen absorption decreases appreciably.

Use of oxidized pellets in melting with EAF made it possible to raise the rate of denitration and to get nitrogen content in EAF before tapping not exceeding 0,004%. This technology will be patented in RB, and a positive decision for this work has been obtained.

Interesting data concerning nitrogen behaviour were obtained by BMZ staff together with German and Austrian specialists [5] during development of electric
furnace bottom blowing with an rare gas. It was determined that with a comparatively high concentration of carbon (0.20-0.30%) intensity of decarbonization of metal is high and nitrogen balance has a negative value. But as far as decarbonization intensity decreases, nitrogen balance becomes positive due to its more intensive intake to the melt. During this period without blowing nitrogen content in metal increases by 20 ppm at the average. In account of forced argon blowing with the consumption of 120 l/min equalization of bath rimming power facilitates decrease of nitrogen content in steel by 15 ppm at the average.

**Summary.**

On the basis of laboratory and industrial investigations technological measures allowing to obtain the desired nitrogen content in converter low – carbon autosheet steel made at Karaganda, Novolipetsk, and Cherepovets integrated steel works and in electrical steel with high carbon content used for tire cord production at Byelorussian Steel Works.

**Literature.**

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5. M. P. Gulyaev, V. V. Filippov, V. V. Enders and others. CIS first systems of metal bottom blowing with rare gases in an electric arc furnace. «Ferrous metallurgy» Scientific and technical and economic information bulletin, 2001, No. 8, p.49.