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Study of the effect of gaseous elements on metal macrostructure during cooling

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Дослідження впливу газоподібних елементів на макроструктуру металу під час охолодження

Abstract. *The article presents a study of the influence of gas elements (oxygen, hydrogen and nitrogen) during metal processing with a mixture of gases (argon, nitrogen) on the macrostructure of the metal after cooling. One of the most common methods of ladle processing of steel is the process of blowing metal with inert gases and its vacuuming. A mathematical model has been developed that allows us to consider the process of gas removal and calculate the quantitative indicators of the removal of dissolved gases from the metal during its processing. Taking into account the thermodynamic and kinetic features of the dissolution of gases in the metal during blowing metal in the ladle with inert gases and during vacuuming allowed us to clarify the physicochemical processes of gas behavior in the metal, which will lead to the possibility of developing a new technology of ladle processing of metal using mixtures of inert gases.*
Key words: *metal, gas mixture, nitrogen, hydrogen, oxygen, macrostructure, ladle-furnace installation.*

Анотація. *У статті представлено дослідження впливу газових елементів (кисню, водню та азоту) під час обробки металу сумішшю газів (аргон, азот) на макроструктуру металу після охолодження. Одним з найпоширеніших методів ковшової обробки сталі є процес продування металу інертними газами та його вакуумування. Розроблено математичну модель, яка дозволяє розглянути процес видалення газів та розрахувати кількісні показники видалення розчинених газів з металу під час його обробки. Врахування термодинамічних та кінетичних особливостей розчинення газів у металі під час продування металу в ковші інертними газами та під час вакуумування дозволило уточнити фізико-хімічні процеси поведінки газів у металі, що призведе до можливості розробки нової технології ковшової обробки металу з використанням сумішей інертних газів.*
Ключові слова: *метал, газова суміш, азот, водень, кисень, макроструктура, ківшово-пічова установка.*

Introduction.

The influence of gaseous elements on the formation of the macrostructure of metals during cooling is a key aspect of modern metallurgy and metal processing technologies. For metallurgical enterprises of Ukraine, an urgent task is to develop a technology for ladle metal processing using cheap gas mixtures that allow reducing the cost of metal. The use of a mixture of gases with an increased nitrogen content will reduce the cost of ladle processing of ordinary steels, low-carbon and steels with an increased nitrogen content. Control of parameters related to the dissolution and removal of gases in liquid metal and metal that is being cooled allows optimizing the properties of metal products for various industrial applications. Due to the expansion of technological capabilities of production, the stability of the composition increases and the quality of the produced steel improves. The use of ladle furnace units and vacuum metal processing allows significantly reducing the content of impurities in steel and obtaining narrow limits of element content. However, despite undeniable achievements in ensuring reproducible quality of metal smelted with modern out-of-furnace processing schemes, there are issues that can only be resolved on the basis of compatible modeling processes and active industrial experimentation.

Literature analysis.

Non-furnace metal processing is a key stage of modern metallurgy, which allows you to regulate the chemical composition and improve the quality of the final metal product. It is aimed at improving the chemical composition, cleaning from non-metallic inclusions, gases, macro- and microstructural improvement. One of the directions is the use of mixtures of technical gases, in particular argon and nitrogen, which are used as a working medium during mixing and cooling of the metal.

Argon is widely used due to its inert properties: it does not react with metal or slag and promotes degassing and mixing. However, due to the high cost of argon, metallurgical enterprises often use it in a mixture with nitrogen.

According to studies [1,2], the introduction of a controlled amount of nitrogen into argon allows you to reduce gas costs while maintaining the efficiency of mixing and degassing. However, excessive saturation with nitrogen can lead to an increase in the nitrogen content in the metal, which is undesirable for low-carbon and structural steels.

The use of an argon-nitrogen mixture has shown positive results in the production of ordinary steels [3] and nitride-forming steels. [4] note that when alloying with titanium or aluminum, a moderate presence of

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nitrogen can be useful, since nitrides are formed, which increase the tensile strength of the steel, but the authors of [3] found out that it is necessary to clearly select the amount of alloying elements to avoid discontinuity of the workpiece. At the same time, [5] emphasizes that in the production of bearing or spring steel, it is important to avoid excessive nitriding, since this reduces the viscosity of the metal. In such cases, it is recommended to maintain the nitrogen content no higher than 0.008%.

Optimization of the composition of the gas mixture and its supply mode is an urgent task. The authors [6, 7] showed that when using an Ar–N_2 mixture with a variable concentration (from 5% to 30% N_2), the degassing efficiency remains high up to the level of 20% N_2, after which the level of dissolved nitrogen in the steel increases noticeably. It was also found that under conditions of low-temperature out-of-furnace processing (1500–1570 °C), especially under vacuum, the addition of nitrogen has almost no effect on the overall level of gas saturation of the metal, while under atmospheric conditions precise adjustment of the parameters is necessary [8].

Among the impurities that have a significant effect on the properties of the metal, gaseous ones — nitrogen and hydrogen — occupy a special place. Their excessive presence can cause brittleness, porosity, reduced plasticity and other defects.

Nitrogen enters the metal mainly from the atmosphere or from process gases during melting and pouring. Excessive nitrogen concentration in steel leads to the appearance of “aging” of the metal, a decrease in impact strength and problems during deformation forming. According to research [9,10], effective removal of nitrogen is possible when using vacuum arc treatment or an inert atmosphere (argon), as well as using modifiers that form stable compounds with nitrogen. Hydrogen in liquid metal causes the appearance of pores in the cast metal, the development of “flocs” and contributes to brittleness. It enters the metal from moisture, oils and other sources. According to [11, 12], the most effective degassing methods are argon treatment with bubbling, vacuum degassing and the use of powder additives that promote bubble coagulation.

The main difficulties in removing nitrogen and hydrogen are associated with the thermodynamics and kinetics of the dissolution and removal processes, because nitrogen requires a very low partial concentration for the degassing process to be effective, and hydrogen has the ability to easily redistribute between the metal and slag. The degree of turbulence in the metal bath, temperature, and slag composition also play an important role.

Therefore, the main task for non-furnace steel processing is to be able to predict the ratio of argon and nitrogen in the gas mixture under different processing schemes (at atmospheric pressure (ladle-furnace) or under pressure (vacuum machine) for different steel grades, taking into account their cooling and operating conditions for further development of ladle metal processing technology using inert purge gas mixtures, which allow reducing the cost of metal and obtaining high-quality steel.

Among the current research areas are the use of combined methods (vacuum + argon), intelligent degassing process control systems, as well as mathematical modeling of the behavior of gases in liquid metal.

Materials and methods.

When modeling the metal production process, a complex model was used, the algorithm of which includes an assessment of metal degassing indicators at atmospheric pressure, analysis of the behavior of CO bubbles and dissolved gases (hydrogen, nitrogen and oxygen) during metal treatment with inert gases and their mixtures, vacuum, as well as gas evolution during metal cooling [13,14]. The created model allows predicting the results taking into account the chemical composition of the metal and selecting the gas mixture that will be used to purge the metal in the ladle during post-furnace treatment.

The mathematical model is described by the main equations:

removal of dissolved oxygen is carried out due to the decarburization reaction

$$[C] = [O] = \{CO\}, \qquad (1)$$

hydrogen and nitrogen – by releasing it in the form of molecules that form gas bubbles

$$[H] = \frac{1}{2} H_2. \qquad (2)$$

$$[N] = \frac{1}{2} N_2. \qquad (3)$$

oxygen and carbon transfer equations in metal

oxygen in metal $$\frac{\partial [O](x,\tau)}{\partial \tau} = \frac{D_M}{H_M^2} \frac{\partial^2 [O](x,\tau)}{\partial x^2} - \frac{16}{12} V_C + \frac{q_M}{H_M} \quad , \qquad (4)$$

carbon in metal

$$\frac{\partial [C](x,\tau)}{\partial \tau} = \frac{D_M}{H_M^2} \frac{\partial^2 [C](x,\tau)}{\partial x^2} - V_C \quad , \qquad (5)$$

where [O] and [C] are the concentrations of oxygen and carbon in the metal, kg/m^3; D_M - s the effective (turbulent) diffusion coefficient in the metal, m^2/s; H_M - the thickness of the metal layer, m; q_M - he source term that takes into account the possibility of blowing oxygen into the metal during the vacuum process, kg/(m^2·s); V_C - is the source term describing the oxygen and carbon consumption for the reaction (carbon oxidation rate), kg/(m^3·s); x - he dimensionless coordinate; τ - the time, s.

The carbon oxidation rate will be

$$V_C = K_V\ f(S)\ [C](x,\tau)\ \{[O](x,\tau) - [O]_r(x,\tau)\}\ , \qquad (6)$$

where K_V - rate constant of carbon oxidation reaction for large-scale level; *f*(S) - the function depending on the surface area of bubbles as they float.

In turn, the frequency of bubble formation is related to the number of active centers of their nucleation and the frequency of formation on one active center $\nu = \nu_S n$, where ν_S - frequency of bubble formation at one active site, 1/s; *n* - amount of active centers, 1/m^2.

The mass transfer process in the metal occurs at the metal-bubble interface. The flows of nitrogen, hydrogen, and oxygen with carbon required for the formation of CO and argon bubbles can be represented by the following expressions:

$$j_N = \beta_N([N] - [N]_r), \quad (7)$$

$$j_H = \beta_H([H] - [H]_r), \quad (8)$$

$$j_{CO} = 1{,}75([O] - [O]_r). \quad (9)$$

Masses of nitrogen, hydrogen and CO diffusing into the volume of the bubble

$$m_N = \int_0^\tau \beta_N([N] - [N]_r) S_N d\tau, \quad (10)$$

$$m_H = \int_0^\tau \beta_H([H] - [H]_r) S_H d\tau, \quad (11)$$

$$m_{CO} = 1{,}75 \int_0^\tau \beta_O([O] - [O]_r) S_{OC} d\tau, \quad (12)$$

where □ □ - bubble rise time. The total mass of gases removed in argon bubbles is obtained in this case by multiplying by the frequency of their formation – □ $_P$, concentrations of substances expressed in kg /m^3.

The surface area of a bubble is determined by its volume.

$$V = \frac{1000m}{28}\frac{RT}{P_{MAX} - \rho_M g H_M x}, \quad (13)$$

where $P_{MAX} = P_{AT} + \rho_M g H_M + \rho_Ш g H_Ш + 2\sigma / r$ - maximum pressure, Pa.

The partial pressures of individual gases in bubbles are described by the expression

$$P_i = \frac{(m_i/M_i)P}{\sum(m_i/M_i)}, \quad (14)$$

where M_i - molecular mass of the gas, *P* - total pressure, equal to the sum of all pressures acting on the bubble, taking into account the height of the metal layer - *h* when the bubble rises.

When cooling the metal, the equations describe the processes of the metal cooling rate, the thickness of the solid metal crust, and the speed of the bubble movement in height.

Objectives of this work.

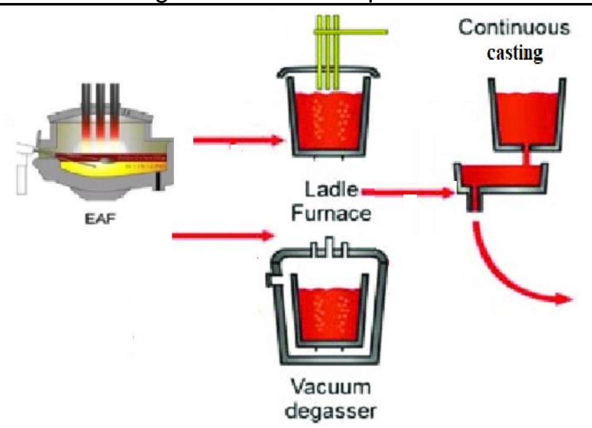
One of the main tasks of extra-furnace treatment is to reduce the content of dissolved gases in steel - oxygen, hydrogen, nitrogen. Argon is most often used as an agent that assimilates gases from steel and mixes it during vacuuming and averaging blowing.

The advantages of argon are the lack of interaction with the metal and the low partial pressure of oxygen, hydrogen, nitrogen, which ensures their effective removal. The content of argon in the air is low, which predetermines the high cost of its production in oxygen shops, where large quantities of nitrogen are formed along the way, the cost of which is four times less.

In a number of cases, nitrogen blowing led to an increase in its content in the metal, which in most cases leads to deterioration in the properties of steel and is unacceptable [15]. At the same time, there is information about the successful use of such treatment [16, 17]. Therefore, to substantiate the possibility and assess the limitations of the applicability of nitrogen instead of argon, it is necessary to comprehensively assess the physicochemical conditions of the main reactions, which can be done using a mathematical model of steel degassing during extra-furnace treatment, the adaptation of which was carried out according to real experimental data.

The adequacy of the complex model was checked based on the results of experimental determinations of the nitrogen content given in Table 1 using three schemes for organizing extra-furnace treatment.

Table 1 - Total gas content in the pilot melt

	Processing scheme	nitrogen content, ppm
		азот
	EAF-LF-VD	70
	EAF -VD- LF	69
	EAF - LF	84

The initial data on the content of carbon (C=0.85%), oxygen (O=0.005%), nitrogen (N=0.008% -), hydrogen (H=0.0015%), the proportion of open surface of 20%, argon purging (q – 0.2 m^3/min), obtained a result that is in good agreement with the production data (Figure 1).

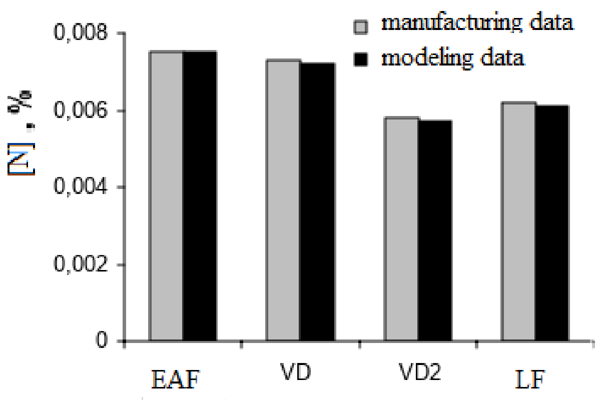


Figure 1. Nitrogen content in steel production

The error in calculating the mathematical model does not exceed 1%.

The model assessed the possibility of using nitrogen as a gas for blowing metal during ladle processing of steel, as well as a mixture of nitrogen and argon (Figure 2).

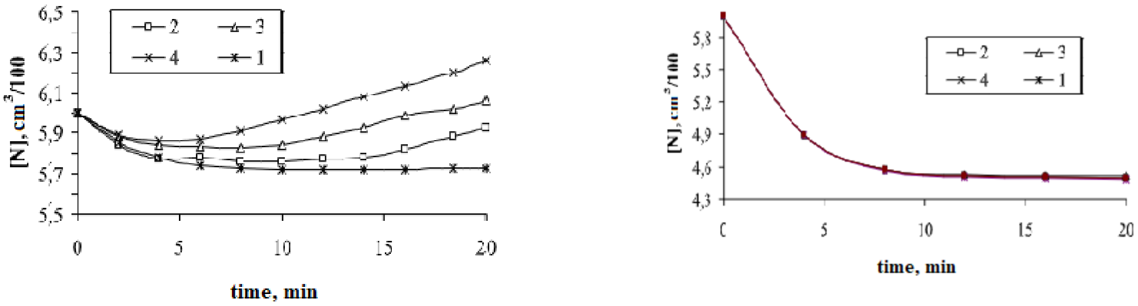


Figure 2. Change in nitrogen concentration in metal at different ratios of argon and nitrogen in the blowing mixture: 1 - argon 0, nitrogen 0.2; 2 - argon 0.1, nitrogen 0.1; 3 - argon 0.2, nitrogen 0 m^3/min.

Modeling has shown that during ladle metal processing, in the first 4-6 minutes of blowing, when maximum removal of CO bubbles occurs, the nitrogen content in the metal decreases. Then, due to the presence of an open blowing spot, nitrogen accumulates in the metal, and when blowing with pure nitrogen and mixtures of argon and nitrogen, the nitrogen content in the metal increases, the value of which depends on the proportion of nitrogen in the mixture.

During vacuuming, the nitrogen content in the metal depends little on the composition of the blowing mixture and the metal can be blown even with pure nitrogen. During vacuuming, a decrease in the nitrogen content against the initial one was achieved in all cases, which indicates effective removal of gases during processing.

A numerical experiment on a mathematical model showed the possibility of using pure nitrogen as a blowing gas during vacuuming, and when processing at the LF, its mixture with argon in a ratio of 1:1

Results and discussion.

Experimental studies of steel that was melted in a chipboard with an acceptable nitrogen content and purged with pure nitrogen in a ladle-furnace installation with subsequent cooling on a continuous casting machine were conducted, which showed that the concentration of dissolved nitrogen increased in the metal, which led to the production of a poor-quality workpiece after its cooling. The macrostructure is presented in Figure 3.

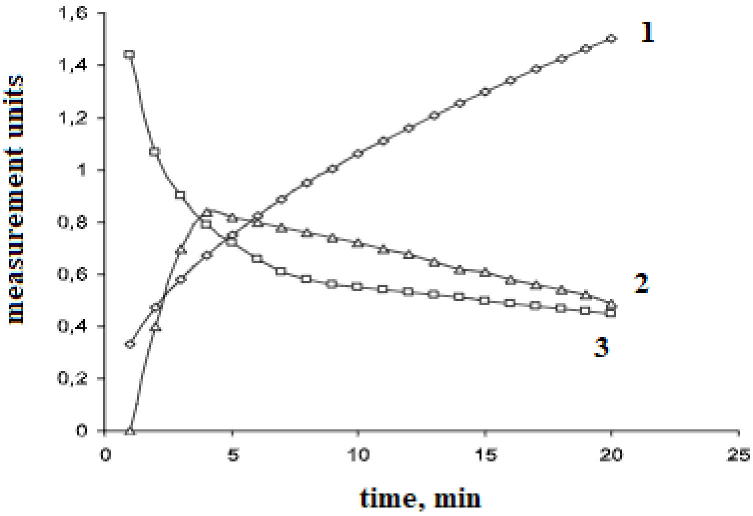
The thickness of the bubble-free zone was 1 mm, and the radius of the pore for bubble formation was about 0.5 mm, the maximum length of the gas pore was 1.5 cm.. The conducted modeling studies showed adequate results and are presented in Figure 4.

It was also found that the formation of the bubble begins in the upper horizons of the crystallizer and continues at a depth of 1.2 m. At this depth, two processes occur almost simultaneously: a decrease in the pressure in the bubble relative to the partial and ferrostatic; and an excess of the crystallization rate over the bubble growth rate. With further cooling, the partial pressure in the bubble becomes less than the partial pressure over the metal, which leads to the cessation of gas pore growth.

When studying the workpiece with an acceptable nitrogen content during smelting in a chipboard and during vacuum processing, purging with pure nitrogen, no changes associated with the occurrence of the day were detected in the macrostructures, which also confirms the model data.

The macrostructure of the metal workpiece during processing with a mixture with argon in a ratio of 1:1 during out-of-furnace processing is shown in Figure 5.

Figure 3. Macrostructure obtained as a result of metal treatment with nitrogen during out-of-furnace processing



1 - thickness of the hardened crust, cm; 2 and 3 - change in the rate of hardening and the rate of bubble growth, mm/s

Figure 4. Model data of the formation of the bubble zone during cooling of the workpiece.

Figure 5. Macrostructure of metal obtained as a result of metal treatment with argon in a ratio of 1:1 during secondary metallurgy.

When analyzing the macrostructure, discontinuities in the solid workpiece were found, which are not associated with an increase in the nitrogen content, since for the formation of a nitrogen bubble during solidification of the workpiece, the pressure in the bubble must be greater than the sum of the partial pressure of nitrogen in the atmosphere and the ferrostatic pressure, and calculations showed that the maximum possible pressure under these conditions of melting and pouring was about 80,000 Pa. Since the partial pressure of nitrogen over the metal is significantly higher than the maximum possible pressure in the bubble, a gas bubble cannot be formed under these conditions. With this pressure ratio, there is only the possibility of nitrogen passing from the atmosphere to the liquid melt during the process of pouring metal. However, for the transition of nitrogen from the atmosphere to the metal, the dissociation of nitrogen molecules into atoms is necessary. This transition is possible at temperatures above 2000 °C, and when pouring metal, the temperature regime does not correspond to this value, therefore nitrogen does not pass from the atmosphere to the metal during pouring. The pouring was carried out without protection of the jet with a submerged pouring glass under a protective slag, which reduces the possibility of nitrogen transition to the metal to a minimum.

In the absence of nitrogen in the purge gas, the nitrogen flow is constantly directed towards the bubble. This circumstance is associated with the high pressure of the metal column, which increases the partial pressure of nitrogen in the gas bubbles.

Further studies on the change in the nitrogen content in the metal at different nitrogen flow rates in the purge gas confirmed that the fraction of nitrogen removal in the CO bubble at the beginning of the process reaches 90% and as oxygen is removed from the metal, it decreases to 40%. Due to this, the fraction of removal through the surface increases accordingly. The fraction of nitrogen removal by the argon bubble is small - about 2 - 3%. Also, with an increase in the nitrogen content in the purge gas, it is interesting to see how this nitrogen is distributed between the metal and the bubbles. It was found that with an increase in the proportion of nitrogen in the purge gas, practically over the entire height of the bubbles rising, the concentration of nitrogen in the metal, in equilibrium with the bubbles, is higher than the actual one. Therefore, there must be a flow of nitrogen from the gas to the metal. To solve this problem, the nitrogen balance from the purge gas was calculated. From the balance, it was found that in the overall balance by the end of the process, about 10% of nitrogen enters the metal, but about 40% is removed into CO bubbles and about 50% is removed through the surface. With an increase in the nitrogen content in the purge gas to 50%, the proportion of nitrogen entering the metal increases to 20%. With a further increase in the proportion of nitrogen in the purge gas to 75 and to 100%, the proportion of nitrogen entering the metal increases to 40% and 60%, respectively.

Conclusions.

Thus, the conducted studies have established that during the process of extra-furnace treatment when purging metal with nitrogen, the metal is saturated to the maximum concentrations. When pouring metal, deviations in the behavior of nitrogen during solidification are possible due to a decrease in temperature. Replacing part of the argon with nitrogen in the purging gas leads to a redistribution of the values and direction of nitrogen flows from the metal to the bubbles of the purging gas. The proportion of nitrogen coming from the purging gas into the metal increases, but the transition of nitrogen from the metal to the CO bubbles and through the surface remains sufficient to ensure a general decrease in the concentration of nitrogen in the metal.

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