Ferrous alloys cast under high pressure gas atmosphere

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Abstract
The main objective of this paper is describing the essence of the process of introducing nitrogen to the melt of ferrous alloys by application of overpressure above the metal bath. The problem was discussed in terms of both theory (the thermodynamic aspects of the process) and practice (the technical and technological aspects, safety of the furnace stand operation, and technique of conducting the melt). The novel technique of melting under high pressure of the gas atmosphere (up to 5 MPa) has not been used so far in the domestic industry, mainly because of the lack of proper equipment satisfying the requirements of safe operation. Owing to cooperation undertaken with a partner from Bulgaria, a more detailed investigation of this technology has become possible and melting of selected ferrous alloys was conducted under the gas atmosphere at a pressure of about 3,5 MPa.

Keywords: Innovative foundry materials and technologies, metallurgical process conducted under high pressure of gas atmosphere, nitrogen solubility, ferrous alloys, high-nitrogen steels

1. Introduction

The concept of metallurgy under gas pressure was created to provide some means for production of high-quality nitrided chromium steels. Nitrogen in ferrous alloys has been up to now regarded as a harmful admixture. At present, it is considered the alloying element highly desired, specially in high-chromium steels. There is more than one reason to account for this fact. It promotes the stabilisation of austenite, increases the steel mechanical properties, delays the formation of harmful precipitates, improves the resistance to corrosion, assists the favourable distribution of alloying elements, specially that of chromium, between the phases α and γ. In spite of all these advantages, only very few, highly specialised foundries feel capable of undertaking the task of making castings in ferrous alloys containing nitrogen, specially when content of this element exceeds 0,3%. This is due to the great difficulties that introducing of nitrogen to a metal bath usually causes. The difficulties result from a low solubility of this element in ferrous alloys. The solubility depends, on one hand, on the content of other elements in molten iron, while - on the other - and more important even, it depends on the value of partial pressure of nitrogen above the metal bath. The first factor (the chemical composition) is adjustable to some extent by introducing a large volume of, often expensive, additions, like chromium, molybdenum, or manganese. The second factor (high pressure of N₂ above the bath) – is definitely much more difficult as regards experimental verification of the theoretical assumptions and practical application of the obtained results. It requires designing of very
expensive and failure-free equipment, satisfying - moreover - very stringent ecological requirements.

At the Foundry Research Institute in Krakow, Poland, the problems of making high-alloy cast steel with additions of nitrogen have been studied by Dr Eng. Zenon Pirowski and a team of his co-workers (numerous reference publications, patent PL 168867 B1). By melting in induction furnace in the atmosphere of air, applying proper metallurgical treatment, sound castings (free from gas inclusions) were made from chromium-nickel-molybdenum steel with nitrogen content of up to 0.5%. Testing the corrosion wear behaviour of these castings has revealed a definitely better resistance of these alloys than the resistance obtained in materials used so far for elements operating in corrosive media.

2. Solubility of nitrogen in ferrous alloys under high pressure atmosphere in furnace chamber

The equilibrium constant of the reaction of nitrogen dissolving in the metal bath of liquid ferrous alloys in the presence of various alloying additions obeys the following equation:

\[
\text{Fe}_X + \frac{1}{2} \text{N}_2 \leftrightarrow [\text{N}]_{\text{Fe}X}
\]  

and depends not only on the chemical composition of alloy \( f_N \), but also (and to a great degree) on the partial pressure of nitrogen above the metal bath \( p_{N_2} \). In the presence of element \( X \), the equilibrium constant of this reaction is:

\[
K = \frac{[\%N]}{(p_{N_2})^{1/2} f_N}, \tag{2}
\]

The former of the above mentioned factors (the activity coefficient) can be controlled in certain range of values by increasing the content of elements, like chromium, molybdenum, or manganese. The latter - by creation of a high nitrogen overpressure above the melt [1, 29].

As we can see there is no place here for the use of vacuum process, except - possibly - the preparation of basic charge for proper melting (deoxidising, decarburisation). The activity coefficient \( f_N \) is described by the following equation:

\[
\log f_N = -0.048[\%Cr_{eq}] + 3.5 \cdot 10^{-4}[\%Cr_{eq}]^2 + 0.13[\%N] \tag{4}
\]

where: [\%Cr_{eq}] is the equivalent alloying additions interaction referred to chromium interaction. For example, this coefficient is for nickel–0.22, and for molybdenum +0.27 [1].

The effect of nitrogen pressure in furnace chamber on the solubility of this element in different phases of Fe-N alloys is shown in Figure 1.

![Fig. 1. Increased solubility of nitrogen in Fe-N alloys due to increased partial pressure of N₂](image)

From the curve plotted above it follows that raising nitrogen pressure in furnace chamber from one to two bars makes its content increase quite notably in the individual phases of Fe-N system. Nevertheless, the solubility of this element is considerably lower in the solid phases than it is in the liquid. This is specially true in the case of ferrite.

An important effect of pressure on the solubility of nitrogen in liquid Fe-Cr alloy was illustrated in Figure 2.
Figure 3 illustrates the role of nitrogen pressure above the metal bath in the process of crystallisation and solidification of Fe-18Cr-8Ni-2Mo-N alloy.

From the curves plotted above it follows that an increase in partial pressure of nitrogen above the metal bath definitely improves the solubility of this element in steel. At a pressure of 7 bars, the solubility of nitrogen in Fe-18Cr-8Ni-2Mo-N alloy is increasing in continuous mode along with the decreasing temperature. The stable solubility during solid phase crystallisation from the liquid enables manufacture of these alloys in condition free from the gas-related defects caused by inclusions of N\textsubscript{2} particles evolving from liquid due to the reduced solubility of nitrogen in the solid phase formed in alloy at a lower partial pressure.

3. Melting under pressure

Unfortunately, only few countries conduct studies on the development of technology to fabricate high-nitrogen steels under high gas pressure. The reason is mainly high cost of the installations as well as safety aspects. Installations of this type usually comprise several production posts where the operations of nitriding of ferroalloys, remelting of steel ingots to introduce nitrogen to alloy, or final melting to produce shaped castings are carried out. For this purpose, various types of specially designed furnaces are used (e.g. induction, electroslag, and plasma furnaces). The overpressure of N\textsubscript{2} in furnace chamber may reach even 10 MPa. On the schematic diagrams shown below some selected designs of such installations are shown.
Fabrication of high-nitrogen steel by electroslag remelting under pressure

Fig. 5. Schematic diagram of electroslag furnace for production of high-nitrogen steel ingots by the technique of nitrogen carrier powders [7]: 1. gas inlet, 2. frame under pressure, 3. melting electrode holder, 4. electrode, 5. mould, 6. metal bath, 7. cooling water, 8. ingot, 9. slag, 10. container for nitrogen carrier powders, 11. gas outlet

Fig. 6. Schematic diagram of electroslag process of high-nitrogen steel ingots production by the technique of composite electrodes [7]: 1. electrode core – nitrided ferrochromium, 2. electrode casing – tube from remelted steel, 3. metal film, 4. pressure 2MPa, 5. metal drop, 6. slag, 7. metal bath, 8. high-nitrogen steel ingot

Fig. 7. Distribution of nitrogen and chromium content in ingots obtained by electroslag remelting [7]: a) nitrogen introduced in nitrided powders 1. mean value – target, 2 and 3. true distribution of N and Cr, b) nitrogen introduced in composite electrode 1. mean value – target consistent with the line of true distribution.

Casting with counterpressure

Fig. 8. Schematic diagram of installation for fabrication of high-nitrogen steel in the process of casting with counterpressure [7]: 1. autoclave for induction furnace, 2. overflow pipe, 3. container
with working gas, 4. ingot mould, 5. solidification chamber, $P_1$ – working pressure, $P_2$ – counterpressure

Fig. 9. Stages of casting manufacture from high-nitrogen steel under the conditions of casting with counterpressure [7]. a. melting, b. pouring, c. squeezing

4. Test melting

In Poland, no installations are available to carry out wide-scale trials on the process of melting and casting under gas pressure. Owing to a cooperation established with one of the leading research centres working on this subject, which is Bulgarian Academy of Sciences, it has been possible to investigate this subject under a commissioned research project currently in execution.

Trials were conducted in a laboratory IFP 001 pressure induction furnace. The ingots prepared in Poland were next remelted under a pressure of 3.5 MPa.

The research material were two grades of steel, two grades of cast iron, three aluminium alloys, one nickel alloy, and one composite material. Each of the examined materials was melted in the atmosphere of nitrogen (the first series of melts) and of argon (the second series). The melt was held at a preset overheating temperature for a time of about 15 minutes to let the gas present in furnace chamber dissolve in melt. The metal was next tapped to small ingot moulds and was held in them for the next 15 minutes until solidification. After the lapse of this time, the pressure was equalised and the solidified ingots were taken out from the respective ingot moulds.

Examples of melts are shown as photographs in Figure 10.

Fig. 10. Photographs of trial melting under gas pressure

5. Summary

The preliminary trials of remelting of the selected alloys under gas pressure, conducted within this study, confirmed the applicability in this task of the melting post

The alloys manufactured at the Bulgarian Academy of Sciences were brought to Poland.

Examples of ingots are shown in Figure 11.

Fig. 11. Examples of ingots produced in trial melting under gas pressure

The design and photograph of the small ingot mould for casting of iron and nickel alloys are shown in Figure 12.
Cast materials will make the research samples and as such will be used in further investigations. A wide range of the material-related studies is anticipated for the future.

At the present stage of research, the effectiveness of the technology of melting under high pressure gas atmosphere created above the melt has been proved for ferrous alloys. Applying this technology, high-nitrogen chromium-nickel and chromium-manganese cast steels were produced. The content of nitrogen in cast ingots exceeded 1%. The content of nitrogen so high in cast ferrous alloys cannot be obtained by the conventional melting techniques.

Fig. 12. Small ingot mould for casting under gas pressure of ingots in iron and nickel alloys

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