A COMPARATIVE STUDY OF NITROGEN STRUCTURAL STEEL PRODUCED ACCORDING TO ELECTROSLAG REMELTING UNDER PRESSURE

Hristo Argirov, Yavor Lukarski

Institute of Metal Science, Equipment and Technology
“Acad. A. Balevski” with Centre of Hydro Aerodynamics,
Bulgarian Academy of Sciences, 77 Shipchenski Prohod,
1574 Sofia, Bulgaria
E-mail: h.argirov@ims.bas.bg; lukarski@ims.bas.bg

ABSTRACT

The specificities of the electroslag remelting process and the structural characteristics of the blocks, manufactured according to the electroslag remelting method, are studied together with the advantages of electroslag remelting (under pressure), as compared to the conventional methods of producing structural steels. Nitrogen solubility in 30Cr2Ni2MoNV steel has been investigated by the levitation melting method. A technology (technological scheme) has been developed for producing 30Cr2Ni2MoNV nitrogen steel on the basis of the diagrams of estimated nitrogen concentration in the liquid state, at a given temperature and pressure. A block of 30Cr2Ni2MoNV steel had been produced using the methods of metallurgy under pressure and its structural parameters: macrostructure, density of dendritic structure, volume fraction of dendrites, were studied. Higher density and homogeneity, as well as a trend towards increasing the volume fraction of dendrites and density of dendritic structure, have been established for the nitrogen steel block.

Keywords: levitation melting method, microscopy, steel, electroslag remelting under pressure, structure.

INTRODUCTION

Electroslag remelting (ESR) belongs to the methods of special electrometallurgy that have proven advantages over the classical steel production methods. The steels, manufactured according to these methods, are used for responsible elements in mechanical engineering and in special production.

Electroslag remelting is a secondary melting of electrodes, preliminarily prepared in classical steelmaking aggregates or in machines operating on the counter-pressure casting principle (nitrogen and high-nitrogen electrodes). The furnace is indirectly heated. Melting is realized due to the heat released as a result of the electric current through the slag bath (Joule effect).

The essence of the ESR method consists in the following: the remelted electrode is immersed in a layer of an electrically conductive flux, placed in a water-cooled crystallizer. The alternating electrical current flowing through the electrode and the flux keeps the flux in the liquid state at a temperature of 1850 - 2300 K. Part of the heat released in the slag bath is transmitted to the electrode, which starts melting. The regime of melting is maintained automatically by the control system by immersing the electrode in the slag bath. The metal droplets running down the electrode surface pass through the chemically active slag, being refined as a result of the contact with it, and then go to the crystallizer. The crystallizing block is with a homogeneous structure, with crystal axes perpendicular to the front of crystallization. The sealing of the installation in casing under pressure allows operation under high nitrogen pressure to produce nitrogen and high-nitrogen steels-electroslag remelting under pressure (ESRP) [1].

The aim of this work is the comparative study of the influence of nitrogen, as an alloying element, and the technological factors, on the structural changes of the 30Cr2Ni2MoNV nitrogen construction steel, manufactured according to the methods and in installations of metallurgy under pressure.
ADVANTAGES OF THE STEELS PRODUCED ACCORDING TO ESR (ESRP)

The main advantage of ESR is the manufacturing of dense blocks without defects of liquation and crystallization origin, with minimal development of chemical and physical heterogeneity. The overall purity of the metal increases considerably, the content of harmful impurities and gases decreases, and the content of non-metallic inclusions is significantly reduced. The metal is characterized by high homogeneity of structure and properties. A typical feature of the ESR process is the oriented crystallization of the metal, which is realized under conditions of continuous heat input from above (from the electrode metal and the slag bath), with simultaneous removal of heat to the block and crystallizer wall. The formation of a slag crust between the block and crystallizer wall, which reduces heat transfer in horizontal direction, also contributes to the oriented crystallization of the block. The slag crust ensures also the smooth surface of the blocks [2]. The high quality of the metal after electroslag remelting, makes it possible to use it for products intended for responsible purposes. It has been established that the quality of the cast electrically remelted metal is not inferior to the quality of the conventional forged metal, and even exceeds it in some parameters. The electroslag steel deformed by rolling or forging differs from the conventional steel by its substantially higher quality of structure. This determines the significant increase in the general level of the physical and mechanical characteristics and their isotropy, as well as in service-operation properties, such as reliability and durability of the products.

The high chemical homogeneity of the electroslag metal is favorably combined with its high structural homogeneity, determined by the specific conditions of crystallization of the electroslag block. The qualitative base of the structure of steel as construction material is formed as early as in the period of crystallization. The results of the ongoing physico-chemical and thermal-physical processes are fixed in the solidifying metal, in the form of structural, physical and chemical heterogeneity. It is known that the macrostructure of blocks, produced according to the conventional steel-making methods, consists of a surface zone with small randomly oriented crystals, a trans-crystalline zone, a transitional zone with oriented and randomly oriented crystals, a zone of large crystals with equal axes and finally - a deposition (precipitation) zone of single crystals, forming a “cone” in the bottom part of the block. Each of the mentioned zones reflects certain changes in the thermo-physical conditions of steel crystallization. Four such changes take place during the solidifying of a conventional block. The crystal composition of the electroslag blocks is more uniform. Their macrostructure is characterized by oriented trans-crystallization, which reflects the high stability of the thermo-physical conditions of metal solidification. Only in the case of large electroslag blocks with diameters exceeding 500 mm, two zones are observed - a peripheral area of columnar crystals and a central area of crystals with equal axes. The analysis of the dendritic structure proves, that the high crystallization rates and the temperature gradient at the crystallization front of the electroslag metal provide favorable conditions for the growth of relatively thinner crystals. The distance between characteristic second-order dendritic axes (dispersity of structure) in a cast electroslag remelted metal is with 20% smaller than the conventionally produced metal.

According to [3] the heterogeneity in the size, shape and distribution sites of the crystals in the block volume, is a major problem for producing a quality block. This problem is successfully solved by the ESR (ESRP) method. The physical heterogeneity of the conventionally produced blocks, excluding the casting defects, is expressed in the presence of gas pores of different sizes and holes. The gas pores are situated mainly in the transitional zone and in the zone of the crystals with equal axes, while the holes are found in the axial part of the blocks. The occurrence of such density disturbances in the metal is provoked by hampered or lacking feeding with molten metal at the front of solidification. Therefore, a conventionally cast block cannot be used directly to produce an element and is subjected to obligatory hot deformation not only to change its shape but also to weld the internal defects. The rate of deformation along the section during block rolling is not less than 6 and during forging - not less than 3. The welding of the gas pores contributes to certain increase in the specific density of the deformed metal. The porosity of the metal matrix of conventionally produced blocks is also due to the separation of nonmetallic inclusions. The size of such pores may reach 500 μm in some cases. In the process of metal rolling and forging such pores do not disappear.
and are not welded - they only change their shape in the form of protracted continuous or discontinuous rows.

The electroslag block differs from the conventionally produced one by its significantly higher physical homogeneity. In fact, the sequential solidification of the metal in upwards direction under conditions of unobstructed feeding with molten metal at the front of crystallization, hampers the occurrence of physical inhomogeneity in the form of gas pores and holes. This is confirmed by the fact that hot deformation of electroslag metal virtually exerts no effect on its specific density. The total area of the pores, formed by the nonmetallic inclusions, is several times smaller than that of conventional steel and the size of the single pores does not exceed 30 μm. For this reason, the specific density of cast electroslag steel is higher than the specific density of deformed conventionally produced steel. The high physical homogeneity of the electroslag blocks provides the possibility of using them in the cast state for the manufacture of various products. Because of that, both the cast and the deformed electroslag steel possess, under equal other conditions higher plastic properties and toughness. The macrostructure of electroslag blocks is characterized by uniform distribution of the main and alloying elements as well as of the impurities - sulphur, phosphorus, oxygen and nonmetallic inclusions. The macrostructure of the deformed metal is with high density and homogeneity. The enhanced structural, physical and chemical homogeneity of the metal by ESR (ESRP) is hereditary transmitted to the deformed metal, in the form of rolled, forged or stamped products.

**THEORY**

The determination of the dependence of the equilibrium nitrogen concentration on temperature and pressure for a given alloy composition is very important for the development of the technological parameters of steel production by the counter-pressure casting. Regardless of the significant progress achieved in the theory of solutions, there is still no precise methodology for calculating the coefficients of activity depending on the components. For this reason, the experiment remains an essential tool to determine solubility. Since solubility grows with increasing the partial pressure in the gas phase, the possibility appears to obtain higher nitrogen concentrations in steel. Pressure is one of the three thermodynamic parameters with values that may rise several times and even within an order of magnitude.

The knowledge of the parameters of interaction, indicating the effect of the concentration of components on activity, and their temperature dependence in the “Fe-N-alloying element” systems, is relevant to the determination of the thermodynamic characteristics of nitrogen solubility in complex alloyed melts. The impact of the alloying element on nitrogen solubility depends on the ratio of the chemical interaction forces between the atoms of Fe, alloying element and nitrogen. A number of equations have been proposed on the base of experimentally determined parameters of the “nitrogen-alloying element” interaction to find the nitrogen activity coefficient in steels and iron-based alloys [4 - 7].

Iron forms solutions with Cr, Ni, Mn and Mo close to the ideal ones, and alloying exerts an insignificant effect on nitrogen behavior. The absence of pronounced chemical interaction between nitrogen and the alloying elements contributes to increasing its activity.

It is known [8], that the equilibrium between nitrogen in the gaseous phase and nitrogen dissolved in the melt is described by the expression:

\[
\{1/2 N_2\} \leftrightarrow [\%N]_{alloy} \tag{1}
\]

The behavior of nitrogen in the alloyed steel may be expressed in terms of the activity \(a_N\).

\[
a_N = [\%N] \cdot f_{Fe}^N \tag{2}
\]

where: \([\%N]\) - nitrogen content; \(f_{Fe}^N\) - activity coefficient (in atomic parts).

The activity represents corrected concentration of the substance taking into account the deviation from the ideal state. The activity coefficient depends on temperature, concentration of nitrogen and alloying elements. If the concentrations are measured in mass percents and if the assumed standard is nitrogen solution in pure iron corresponding to Sieverts law, then the equation of the activity coefficient can be written in the form:

\[
[\%N]_{Fe} \cdot f_{Fe}^N = [\%N]_{alloy} \cdot f_{alloy}^N \tag{3}
\]

where: \(f_{alloy}^N\) - activity coefficient of the alloy.

The equilibrium constant of reaction (1) is expressed as:

\[
K_{Fe}^N = \frac{a_N}{\sqrt{P_{N2}}} = \frac{[\%N]_{Fe} \cdot f_{Fe}^N}{\sqrt{P_{N2}}} \tag{4}
\]
It is obtained from (3.3) and (3.4):

\[
\%N_{\text{alloy}} = \frac{K_{N}^{Fe} \sqrt{P_{N2}}}{f_{N}^{\text{alloy}}}
\]

and the logarithm is:

\[
\log(\%N_{\text{alloy}}) = \log K_{N}^{Fe} - \log f_{N}^{\text{alloy}} + \frac{1}{2} \log P_{N2}
\]

In case that the dependence of the activity coefficient on concentration is not explicitly known, the expansion of \(\log f_{N}^{\text{alloy}}\) in Taylor series is usually applied. The following is obtained using the general equation for the activity coefficient logarithm of nitrogen, dissolved in the multicomponent melt, as derived by Wagner [4 - 8] on the basis of decomposing \(\log f_{N}^{\text{alloy}}\) in Taylor series in the vicinity of a point corresponding to the pure solvent:

\[
\log f_{N}^{\text{alloy}} = \sum_{j} e_{j}^{N}[\%J] + \sum_{j} r_{j}^{N}[\%J]^{2} + \ldots \quad (7)
\]

The derivatives of \(\log f_{N}^{\text{alloy}}\) are called parameters of interaction of first- \(e_{j}^{N}\), second- \(r_{j}^{N}\) and third order. They are obtained from experimentally determined activity coefficients and the activity coefficients of all main components of steel and slag.

The concentrations of nitrogen in the modeled alloys are determined using eq. (6).

Absorption (Sieverts method) and hardening methods are applied to study the solubility of gases in liquid metals and alloys. When determining the solubility in gases and liquid metals and alloys it is desirable to entirely eliminate the interaction of the investigated metal with the refractory crucible, since solubility is especially sensitive to metal purity.

**EXPERIMENTAL**

The present study of nitrogen solubility under pressure of nitrogen atmosphere from 0.1 to 4.3 MPa has been carried out using the unique installation (Fig. 1), developed in the Institute of Metal Science, Equipment and Technology “Acad. A. Balevski” with Center for Hydro- and Aerodynamic, Bulgarian Academy of Sciences (BAS). Based on the results obtained, diagrams are plotted for determination of nitrogen concentration, as depending on composition, pressure and temperature. The investigation of nitrogen solubility in the 30Cr2Ni2MoNV liquid steel is realized for three model compositions for normal and higher partial pressures of nitrogen in the gaseous phase (0.1; 0.4; 0.9; 1.6; 2.5; 3.6 and 4.3 MPa) within

---

*Fig. 1. Scheme of the apparatus for levitation melting: 1-stand for pure gases; 2-gas cleaner; 3-circulation pump; 4-direct current motor; 5 and 6-gas fittings; 7-manometer; 8-prism; 9-optical pyrometer; 10-work chamber; 11-potentiometric recorder; 12-fore-vacuum; 13-vacuum pump; 14-tiristor regulator.*
the temperature range from 1898 to 2023 K.

The kinetic investigations conducted by us for a partial pressure of 2.5 MPa and 1898 K prove that the temperature equilibrium, as well as the equilibrium nitrogen content in the drop is achieved for 40 - 60 s. The equilibrium amount of nitrogen under the conditions of each particular test is fixed by hardening in copper wedge mould. No changes in chemical composition have been observed during the tests. The solubility of nitrogen, in the model steels studied, slightly increases with raising the temperature.

RESULTS AND DISCUSSION

The results of the study are given in [9]. They are statistically processed using the BMDP mathematical package, the 1R program. The geometrical interpretation of the model is shown in Figs. 2 - 4. When calculating nitrogen solubility from thermodynamic data, good agreement is observed with experimental data to nitrogen concentration of up to 0.3%. At higher nitrogen concentrations the experimental results are lower from the calculated ones and this difference grows with increas-

Fig. 2. Geometric interpretation of the model; 30Cr2Ni2MoNV steel - composition 1.

Fig. 3. Geometric interpretation of the model; 30Cr2Ni2MoNV steel - composition 2.
ing of the nitrogen content, while it does not depend on the type and quantity of the alloying elements and the temperature.

The plotted diagrams allow the graphical determination of nitrogen concentration in the liquid state for a given temperature and pressure. On the basis of the diagrams of the estimated nitrogen concentration in the liquid state for a given temperature and pressure, a technology (technological scheme) had been developed for producing the 30Cr2Ni2MoNV nitrogen steel.

The first block of nitrogen structural steel, brand 30Cr2Ni2MoNV, was produced and investigated. It was manufactured using machines and installations of metallurgy under pressure, namely: the VP 05 machine, operating according to the counter pressure casting (CPC) method and the P951-US installation for electroslag remelting under pressure. These are metallurgical methods and technologies for the production of nitrogen alloyed steels [1]. These methods ensure complete volumetric saturation of steels with nitrogen, providing the possibility, depending on the brand, to reach all nitrogen concentrations necessary for steelmaking. In this way, expensive alloying elements are replaced and steels with improved or new service properties are obtained. Nitrogen alloying is realized by solid nitrided ferroalloys (solid nitrogen carriers). The CPC and ESRP methods possess a number of basic advantages for producing and alloying of steels with nitrogen. The most essential of them are: nitrogen is uniformly distributed along the height and cross-section of the block as it is introduced into the liquid bath, which is intensively stirred and homogenized; nitrogen concentration is precisely regulated; the mould is smoothly and evenly filled with metal. Thus, the original 30Cr2Ni2MoNV brand of nitrogen structural steel [10], intended basically for nuclear power generation, has been developed, together with the technology for its production.

The studied block of the 30Cr2Ni2MoNV nitrogen steel with a diameter of 240 mm was longitudinally cut and a template for macrostructural investigations was prepared from it. The chemical composition of the steel is given in Table 1. The macrostructural analysis was

Table 1. Chemical composition of the block of 30Cr2Ni2MoNV steel.

<table>
<thead>
<tr>
<th>Chemical composition, mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>0,30</td>
</tr>
</tbody>
</table>
carried out according to BDS 12730-75, GOST 10243-75 by development with a standard solution $1\text{H}_2\text{SO}_4 : 6\text{HCl} : 3\text{H}_2\text{O}$, temperature of 80°C, time 30 - 40 min. The macrostructure of the electroslag remelted block under pressure is shown in Fig. 5. It has been established that the metal is with dense structure, with well outlined cone of crystallization and an angle of crystallization typical for the classical ESR-block (30 - 40°).

CONCLUSIONS

After investigating the specificities of the electroslag remelting method and of the structural characteristics of the electroslag remelted blocks, a trend towards increasing of dendrite density along the block height is established as a result of the analysis of the dendrite density and volumetric percent of dendrites. Better shaped dendrites are observed in the center, while the dendrite needles at the surface are longer and with less typical axes of the second-order. This is due to the specificities of the crystallization process in electroslag remelting. The comparison between the dendritic structure of the nitrogen steel and the nitrogen-free analogue exhibits a trend towards increasing of the volumetric percent of dendrites and of dendritic structure density. The dendrites in the block of the 30Cr2Ni2MoNV nitrogen construction steel are smaller and better shaped. This is explained by the specificities of the electroslag remelting process, namely-conducting the process under high pressure. The established macrostructure, after electroslag remelting under pressure, is dense and without defects, which proves also the effectiveness of the technology for producing nitrogen construction steels developed by us. The new nitrogen construction steel is with higher strength and plastic characteristics, compared to the conventional nitrogen-free analogue and in contrast to the conventional nitrogen-free analogues, it does not require expensive antiflack thermal treatment.
of the blocks produced by ESR (under pressure), the advantages of the electroslag remelting method (under pressure), compared to the conventional methods for construction steel production such as physical homogeneity, density and macrostructure have been determined.

The solubility of nitrogen in the 30Cr2Ni2MoNV steel was investigated by the levitation melting method. On the basis of the diagrams of the estimated nitrogen concentration in the liquid state at a given temperature and pressure, a technology (technological scheme) for producing the 30Cr2Ni2MoNV nitrogen steel has been developed.

A block of the 30Cr2Ni2MoNV steel has been produced, according to the methods of metallurgy under pressure, and its structure has been studied.

The following structural parameters have been determined: macrostructure, density of the dendritic structure, volumetric percent of dendrites in four (five) horizons (cross sections along the height from block bottom to face) and three (two) zones-surface, ½ radius and center.
Fig. 7. Dendritic structure in five horizons of a block of a nitrogen-free analogue: a) surface; b) center.
A permanent trend towards increasing the volumetric percent of dendrites and dendrite structure density has been established.

Higher density and homogeneity of the nitrogen steel block have been determined.

REFERENCES