Researches on the Diffusion Phenomena in the Thermo-Chemical Treatment of Oxy-nitrocarburizing of Some Grey Cast Irons

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The thermo-chemical treatment of oxy-nitrocarburizing consists in the enrichment of materials in C, N and O in order to improve the physico-mechanical properties and the use of the materials. This leads to the increase in exploitation life, the increase of wear resistance, galling, corrosion, and slight erosion. The research presented in this article followed the study of the application of this treatment and the results obtained on pearlitic grey cast iron with different chemical compositions, domain in which there are few experimental results published. The results obtained on a number of 10 samples, presented in the article, highlighted the good compatibility of these materials with the thermo-chemical treatment of oxy-nitrocarburizing, obtaining on the surface some white layers which give good anti-corrosive properties, similar to those obtained on steel. There was no correlation between the depth of the white layer and the chemical composition of the studied cast iron. It was also emphasized that the depth of nitrogen diffusion is influenced by the chemical composition of the studied materials which is directly proportional to carbon equivalent ($C_{eq}$) of cast iron.

Keywords: oxy-nitro-carburizing, pearlitic grey cast iron, white layer

The study of the oxy-nitrocarburizing process applied to cast iron represents a novelty, there is not enough data described in the bibliographic papers studied. In this context, it is considered that the experimental research and the processing of the results obtained in a batch of 10 grey cast iron samples that have been subjected to oxy-nitrocarburizing treatment make a particular contribution to the development of this type of treatment for new applications.

For this study a large number of experimental determinations were performed, which were analyzed with laboratory techniques and finally the results were interpreted to establish correlations between the different sizes studied.

Experimental part

Oxy-nitrocarburizing is an enrichment treatment in C, N and O [4, 9] applied to materials in which the growth of exploitation life [1], the growth of wear resistance, galling [11], corrosion, gentle erosion are sought. It is also sought to reduce technological consumption and replace salt baths, and even galvanic baths. Because the duration of the process is very low (4 to 8 h), oxy-nitrocarburizing is recommended instead of normal nitration in natural gas [10]. At temperatures of 570 - 600 °C in the case of oxy-nitrocarburizing (Fe - N - C system), the phase domain ε (which confers corrosion resistance) [4] is wider than with the usual nitration (Fe - N system) [4], it is possible to obtain this phase in lower temperature conditions and nitrogen concentration as compared to the Fe - N system, the layer obtained may consist of one or more phases [5], depending on the N concentrations and temperature, the chemical composition of steel or cast iron.

The research published in technical literature demonstrated the existence of complex phases of the type α, with a compact crystalline network which, depending on the cementing environment, may be nitrides, nitrocarbides or oxy-nitro-carbides[4, 8].

On the surface of oxy-nitrocarburized parts a white layer [14] is formed, which has a fine structure, resembling a lot to the chemically deposited layer made of vapors, presented as a continuous amorphous layer. It has anti-corrosive properties.

The active elements that diffuse in the superficial layer are nitrogen, oxygen and carbon. Due to the fact that the nitrocarburizing process takes place at low temperature, the two main elements, nitrogen and carbon, behave differently from the point of view of interaction with the superficial layer. Nitrogen diffuses inside the superficial layer, while carbon, unable to enter the diffusion layer, remains in the maximum concentration in the compound layer [6].

For this study, 10 samples of grey cast iron with the chemical composition shown in table 1 were used.

| Sample No. | Sample Code | C [%] | Si [%] | Mn [%] | P [%] | $C_{eq}$ [%] |
|------------|-------------|------|-------|-------|------|-------------|
| 1          | OCN1365     | 3.03 | 1.97  | 0.58  | 0.12 | 3.73        |
| 2          | OCN1375     | 3.05 | 2.15  | 0.58  | 0.13 | 3.81        |
| 3          | OCN1584     | 2.80 | 1.54  | 0.53  | 0.10 | 3.35        |
| 4          | OCN1600     | 2.91 | 1.81  | 0.56  | 0.096| 3.55        |
| 5          | OCN2933     | 3.12 | 1.94  | 0.68  | 0.088| 3.8         |
| 6          | OCN3142     | 2.93 | 1.70  | 0.53  | 0.034| 3.31        |
| 7          | OCN3150     | 3.42 | 2.26  | 0.52  | 0.087| 4.2         |
| 8          | OCN3241     | 3.20 | 2.10  | 0.63  | 0.07 | 3.92        |
| 9          | OCN3437     | 3.46 | 2.27  | 0.37  | 0.019| 4.26        |
| 10         | OCN3446     | 2.94 | 1.83  | 0.65  | 0.075| 3.58        |

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Table 1

CHEMICAL COMPOSITION [%] OF SAMPLES USED
Parameters of the thermo-chemical treatment of oxy-nitrocarburizing [5, 12] applied are shown in table 2.

The metallographic structure of the samples after thermo-chemical treatment is shown in figure 1-10; All samples have lamellar graphite in the Pearlite matrix. The Nitrogen diffusion profile (GDOS-S2), as well as the depth of white layer (GDOS-S1) [7] were analyzed with the GD-OES (Glow Discharge - Optical Emission Spectrometry) spectrometer [5, 13]. So, each sample was analyzed with the GD-OES spectrometer (JY 5000RF spectral apparatus), using an exposure time of up to 550 s. Surface spectral analysis by means of GD-OES technique allowed determination of nitrogen diffusion depth and also the determination of the diffusion curve profile, (fig.11-20).

Through the erosion [3] phenomenon there were obtained results on the concentration of chemical elements of interest, carbon and nitrogen, on a depth of up to 36 microns. Since usual depths of white layers are of 2 microns and the diffusion profile tends to zero in the range of 30-50 microns (see the diffusion curve from figure 11-20), the results are considered satisfactory.

![Fig 1. Metallographic structure of sample 1385](image1)

![Fig 2. Metallographic structure of sample 1375](image2)

![Fig 3. Metallographic structure of sample 1384](image3)

![Fig 4. Metallographic structure of sample 1600](image4)

![Fig 5. Metallographic structure of sample 2933](image5)

![Fig 6. Metallographic structure of sample 3142](image6)

![Fig 7. Metallographic structure of sample 3160](image7)

![Fig 8. Metallographic structure of sample 3241](image8)
Fig. 21. The depth of white layer (IAS and GDOS-S1) and Nitrogen diffusion (GDOS-S2)

Table 3
CHEMICAL COMPOSITION [%] OF SAMPLES USED

| Sample Code | Carbon | Silicon | Sulfur | Phosphorus | Other
|-------------|--------|---------|--------|------------|-------|
| OCN 1365   | 1.305  | 1.25    | 4.55   | 25.0       |       |
| OCN 1375   | 0.803  | 0.85    | 3.85   | 33.0       |       |
| OCN 1584   | 1.297  | 1.11    | 3.9    | 22.9       |       |
| OCN 1690   | 0.769  | 0.84    | 5.34   | 21.6       |       |
| OCN 2933   | 0.937  | 0.95    | 4.2    | 34.7       |       |
| OCN 3142   | 0.857  | 0.9     | 3.8    | 26.0       |       |
| OCN 3160   | 1.056  | 1       | 4.5    | 32.3       |       |
| OCN 3241   | 1.09   | 0.95    | 4.1    | 30.1       |       |
| OCN 3437   | 0.35   | 0.4     | 4.1    | 43.4       |       |
| OCN 3446   | 1.801  | 1.8     | 5.85   | 26.7       |       |

The depth of the white layer was measured with the Image Analysis System (IAS) outfitted with Buehler OmniMet Enterprise image analysis software. The results obtained as an average of 25 measurements, are shown in table 3, as well as both GDOS-S1 and GDOS-S2, in order to be compared.

Results and discussions
In order to study the influence of chemical composition in the case of grey cast iron on the depth of the white layer the dependence of these data was graphically represented by histogram in figure 21. The values for the layers are presented in table 3, as well as for the Nitrogen diffusion.

In order to study the influence of the chemical composition in the case of grey cast iron on the total depth of diffusion of nitrogen (GDOS-TOTAL) the dependence of these data was graphically represented by histogram in figure 22.

Conclusions
The conclusions of this experimental research are:
- for grey cast iron non-alloyed with equivalent carbon in the range 3 - 4.5%, the depth of the white layer does not correlate with the chemical composition of these materials.
- for grey cast iron non-alloyed with equivalent carbon in the range 3 - 4.5%, the depth of nitrogen diffusion is directly proportional to the content of carbon equivalent that can be considered linear.
- the spectral analysis allowed a precise assessment of the diffusion profile, concentration based on the diffusion depth, for the chemical elements used to achieve the enrichment of superficial layers on relatively small depths of up to about 100 microns.

The thermo-chemical treatment of oxy-nitrocarburizing contributes to the improvement of surface characteristics [1, 2, 6, 11] of alloys in the Fe-C system. Corrosion resistance increases considerably [2, 8], being directly
proportional to the thickness of the white layer, comparable to the resistance provided by other protection methods such as zinc coating. Experimental determinations on samples made of oxy-nitrocarburized cast iron revealed a very good corrosion resistance, up to 200 hours without corrosion or oxidation up to a maximum of 5-10% [2, 6]. This property is explained by the presence in the superficial layer of magnetite and iron nitride [4, 6].

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