

# Structural and phase transformations in cast irons when implanted into the surface layers of nitrogen ions

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**Abstract.** The results of the Mossbauer studies of graphite cast iron implanted with nitrogen ions are represented. We study the influence of the shape of graphite inclusions and modes of nitrogen ion implantation on the formation of in the surface layers of new phases and changes in the properties of cast iron.

## 1. Introduction

Ion implantation method, based on the implementation of the accelerated ions of different elements into the surface layers of solids, is quite effective, modern way to influence the properties of the materials. By means of ion implantation may be substantially changed the composition and structure of the near surface areas of irradiated materials that allows you to modify almost all properties of solids controlled by the state of the surface [1, 2]. Originally an ion implantation developed as technology to control the properties of semiconductor materials for microelectronics. Recently there has been a growing interest in studying the possibilities of ion implantation for the modification of surface-sensitive properties of metals and alloys. This was the basis for the formation of a new in ion-beam technology area - implant metallurgy. Compared with traditional methods of surface treatment of metal products (diffusion saturation, spraying, CTP), ion implantation has several advantages: a sharp reduction in the duration of the treatment process; increasing the solubility limits in the solid state and the independence of the formation of surface alloys from diffusion constants; no adhesion problems, as there is not a distinct boundary between the modified layer and the volume of the material; very little change in size of the part; opportunity to carry out selective processing of individual sections of it, and others. [3].

Progress in the field of implant metallurgy associated primarily with the development of fundamental ideas concerning the interaction of accelerated ions with the surface layers of complex metal systems. Of great importance are studies of structural phase transformations and mechanisms of the specific metallic materials properties change under ion irradiation. As for cast iron, it is the material relating to the category of highly complex, heterogeneous metal systems, as for the ion-beam modification prospects they are hardly been studied.

## 2. Object and methods of study

The object of study in this paper is graphite cast iron, whose surface is bombarded with nitrogen ions. The original structure of the samples was a ferrite-pearlite metal matrix with graphite inclusions of flake, vermicular and spherical shape. To assess the effect of the shape of graphite inclusions to the processes in the irradiated layers, samples for series of the experiments were chosen so that their chemical composition, the amount of graphite inclusions of graphite and density of distribution in the



metal matrix were as close as possible. In this case the main variable factor is the total surface area of graphite inclusions per unit of the material volume, ie, density of graphite borders - minimal for cast iron with compact-spherical shape of graphite inclusions and higher for vermicular and flake graphite.

Irradiation of cast iron was carried out in accelerator IRA-3 by the stream of singly charged nitrogen ions with an energy of 40 keV in a dose range from 1 to  $5 \cdot 10^{17} \cdot 10^{17}$  ions / cm<sup>2</sup>, the ion current density of 50 mA / cm<sup>2</sup>. The choice of irradiation modes is made based on the analysis of data from works [3, 10, 11, 12, 13 and others.] devoted to the study of the effect of nitrogen ion implantation on the mechanical and tribological properties of iron and iron-carbon alloys. Before and after cast iron irradiation the durability of samples was measured, and the microhardness of the surface layers also.

For registration of changes in structural and phase composition of the irradiated surface layers was used the nuclear gamma resonance (Mössbauer) spectroscopy (NGR spectroscopy). Mössbauer spectra were obtained in backscattering geometry by means of registration of internal conversion electrons and secondary characteristic X-rays. The choice of methods for measuring the spectra due to the fact that the samples studied cast irons are opaque to the Mössbauer gamma radiation and the traditional method of measuring of Mössbauer spectra of "with X-ray" for these objects is unacceptable. In case of registration of internal conversion electrons thickness of the probed layer (the escape electrons depth) is comparable to the average depth of the run of implanted in material nitrogen ions. Upon registration of the secondary X-ray a thickness of the probed layer by two orders of magnitude greater. This allows selective according to the depth researches - to receive information directly about the implanted layer and its adjacent layers with the registration of changes in the structure and phase composition [8, 9]. The possibility of a conventional X-ray analysis for solving such problems are severely limited, since the formation of the X-ray diffraction pattern the surface layer is involved, considerably exceeding in the thickness an area of intense radiation-induced phase formation.

### 3. Experimental results and discussion

Analyzing the results of Mössbauer studies, it may be noted that the Mössbauer spectra of all samples in the initial state are virtually identical and are representing a typical for the solid solutions of substitution based on  $\alpha$ -iron superposition of sextets corresponding to atomic configurations with different numbers of impurity atoms of silicon in the immediate vicinity of Fe<sup>57</sup>. The ratio of the intensities of lines in subspectra correlates with the chemical composition of the cast iron. In all spectra in addition to the dominant ferrite component it is also observed less intense lines sextet which is characteristic for cementite. In general, the nature of the Mössbauer spectra is in good agreement with the concept of the original structure, chemical and phase composition of the investigated cast iron [6, 7].

Irradiation of cast iron by nitrogen ions leads to a marked reduction in the relative intensity of the spectrum components, due to the presence in the ferrite silicon atoms. To the greatest extent this effect is seen in cast iron with flake and vermicular graphite at doses  $D \geq 2 \cdot 10^{17}$  ions/cm<sup>2</sup>. This phenomenon may be due to the following processes in irradiated irons. The bombardment of the surface layers of accelerated ions leads to the formation in the material the cascades of atomic displacements and accumulation along the trajectories of the implantable particles a large number of point radiation defects. In conditions of high radiation doses typical for such studies, the disordering processes (accumulation of defects) are compensated by their annealing processes (dynamic interstage and volumetric heat, due to local heating of the target). A significant part of the point radiation defects leaves the area of their generation and are sent to places of the effective capture (drain), ie to the grain boundaries, the free surfaces, etc. [4, 5]. As is known, the defects flow can entrain the impurity atoms having an atomic radius smaller than atoms of the solvent [3, 4]. This leads to a phenomenon of radiation-induced segregation, i.e. accumulation of impurity atoms in the drains. Obviously, in graphite cast iron the most efficient drain of radiation-induced defects are the boundaries of graphite inclusions, which may involve atoms of the dissolved in the ferrite silicon and implemented nitrogen atoms also. Since the density of drains (graphite borders) in cast iron with vermicular flaked graphite

and higher than in nodular cast iron, then these processes occur here more effectively. Another reason for the decline of the silicon content in the ferrite can be its selective spraying under the influence of the ion beam.

Starting with dose of cast iron irradiation  $2 \cdot 10^{17}$  ions/cm<sup>2</sup> in their Mössbauer spectra obtained by the registration of internal conversion electrons, there are additional components that can be explained by the appearance of new phases in the alloys. In the spectra of the same samples, but obtained by the registration of the secondary characteristic X-rays, the additional components are not observed. This suggests that intensive phase formation caused by the implantation of nitrogen ions into the cast iron occurs primarily in the surface layers of a thickness from several tens to hundreds nanometers [6].

The parameters of the hyperfine structure (HFS) of additional components of the NGR spectra allow to connect them with nitrides  $\epsilon\text{-Fe}_3\text{N}$  и  $\gamma'\text{-Fe}_4\text{N}$ . Cast iron with flaked graphite at a dose of  $2 \cdot 10^{17}$  ion/cm<sup>2</sup> shares of subspectra  $\epsilon$ -phase and  $\gamma$ -phase in the resulting spectrum is 6% and 12%, and at a dose of implantation  $5 \cdot 10^{17}$  ion/cm<sup>2</sup> - 17% and 8% respectively. Shares of subspectra  $\epsilon$ -phase and  $\gamma$ -phase in vermicular graphite iron at a dose of  $2 \cdot 10^{17}$  ion/cm<sup>2</sup> are 16% and 7%, and at a dose of  $5 \cdot 10^{17}$  ion/cm<sup>2</sup> - 18% and 12%. In nodular cast iron only at a dose implantation  $5 \cdot 10^{17}$  ion/cm<sup>2</sup> are observed subspectra  $\epsilon$ - and  $\gamma$ -phases and their proportions are 14% and 5%, and at a dose of  $2 \cdot 10^{17}$  ion/cm<sup>2</sup> changes in the NGR spectrum are minor. Mathematical treatment of NGR spectra of cast iron with flaked and vermicular graphite also indicates the presence in the spectra of the paramagnetic and magnetic component with parameters HFS, distributed in a fairly wide range of values. The proportion of these components in alloys with flaked graphite with implantation at a dose of  $5 \cdot 10^{17}$  ions/cm<sup>2</sup> is 18%, and in alloys with vermicular graphite - 13%. HFS parameters of these components allow you to associate them with the hexagonal  $\epsilon$ -carbides and carbonitrides. Metastable  $\epsilon$ -carbides in the ion bombardment conditions can be formed in atomic displacement cascades by the mechanism of atomic mixing [3, 4]. The most likely place for the formation of such carbides in the cast iron is obviously the border area of graphite and metal matrix. Regarding nitride  $\epsilon\text{-Fe}_{2+x}\text{N}$ , then nitrogen and carbon are interchangeable in this compound and the concentration of these elements can vary here within wide limits ( $0 < x < 3.2$ ). Changing the content of nitrogen and carbon in the carbonitride  $\epsilon\text{-Fe}_{2+x}(\text{N}, \text{C})$  leads to a continuous change of HFS parameters of the corresponding subspectra HFS. For  $x \leq 0,3$  magnetic  $\epsilon$ -phase turns into a paramagnetic.

The results of measurements of microhardness and wear resistance of irradiated specimens correlate with the data of Mossbauer spectroscopy. The greatest effect of increasing the wear resistance and microhardness is observed in cast iron with flaked form of graphite inclusions, and the lowest - in nodular cast iron. In this case, the microhardness retained increased for all samples to a depth of not less than 50 microns, which is about two orders of magnitude greater than the thickness of the implanted layer [6, 7].

#### 4. Conclusions

Analyzing the results and comparing them with data from the literature we can make the following assumptions:

1. Free carbon graphite of cast irons promotes caused by nitrogen ion implantation the formation process of secondary nitride and carbonitride phases as the relative proportion of these phases in the irradiated cast irons is higher than in pure iron and carbon steels with similar modes of implantation [10, 11].
2. Predominant phases formed in the cast iron by implanting nitrogen ions are nitrides, carbides and carbonitrides of  $\epsilon$ -type. These phases have a hexagonal crystal lattice, similar to graphite lattice, and dissolved nitrogen and carbon in a wide range, which are used interchangeably herein. Apparently, under nonequilibrium conditions of ion implantation and in the presence of free carbon the formation of such phases is preferred in the kinetic and thermodynamic points of view. Leading role in the mechanism of phase formation processes may play a radiation-enhanced diffusion processes of impurity atoms to grain boundaries and ion mixing effect.

3. The formation of new phases takes place predominantly at the boundaries of graphite inclusions. These boundaries during irradiation cast irons by nitrogen ions play the role of effective drains (traps) of point radiation defects. Flow defects to drains entrains implanted into iron nitrogen atoms, which increases the likelihood of formation here of secondary nitrogen phases. Higher density of graphite boundaries in flake graphite cast iron causes a great number of secondary phases in these alloys. Density of graphite borders in nodular cast iron is the smallest, so the phase formation processes take place here less intensively.

4. The main reason for increasing the cast iron wear resistance and microhardness is the loss in the irradiated surface layers of nitride and carbonitride secondary phases. The greatest effect of improving the wear resistance and microhardness is observed in a flake graphite cast iron, and is accompanied by a higher content of said phases in the surface layers of the material. Another mechanism to improve the microhardness of cast iron may be an increase in the irradiated layers the density of point radiation defects that with the growth of its concentration in the are combined into three-dimensional clusters and dislocation loops, reinforcing the material. Increased microhardness of the samples at depths much greater than the value of average path of nitrogen ions in cast iron, can be explained by the phenomenon of radiation-enhanced diffusion of implanted atoms and radiation defects in the bulk of the sample.

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