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USE OF SPECTROSCOPY AND COMPUTER SIMULATION TO THE STUDY OF SURFACES MODIFIED BY IONIC IMPLANTATION

Using X-ray Photoelectron Spectroscopy (XPS) and energy dispersion spectrometry, the phase and elemental compositions of the nanoscale surface layer of implants are studied. The method of determination of the optimal mode of nanoscale modification of the surfaces of metals and alloys by means of the ionic implantation is presented. The problem of processing the curved surfaces with mathematical calculations and a computer simulation is solved. The proposed technique is tested on synthesized implants. The sample hardness was taken as a criterion.

Keywords: XPS, energy dispersion spectrometry, implant, nanoscale surface modification, ionic implantation, computer simulation, hardness.

1. Introduction

There are many methods for improving the physical, chemical, and mechanical properties of metals and alloys, among which the most common are: thermal treatment, metal treatment, curing, and plasma processing. Among the most promising techniques is the ion-beam surface treatment, in particular the technology of ionic implantation [1–15].

The technology of ionic implantation as a method of influence on the properties of materials has several advantages, the main among which are the absence of a mechanical and temperature deformation of the sample (the heating of the sample does not exceed 100 °C); a small amount of consumable materials; a significant change in the characteristics of the surface layer up to 1 μm in thickness, only; clean conditions for the process; high bond strength of the base material and the deposited layer of doping components.

In order to improve the characteristics of various details, in particular, curvilinear forms (shafts, *etc.*), ionic implantation technology can be recommended.

But there is a certain shortcoming of the ionic implantation method. When the bombarding of complex surfaces takes place, ion jets fall into areas of the curvilinear detail at various angles. As a result, the dose of ions deposited on different places of the surface can be significantly different after the treatment.

Two possible ways to solve this problem exist: the implantation from several sides simultaneously or the realization of implantation process by several times (stepwise), with the shaft rotating at a certain angle

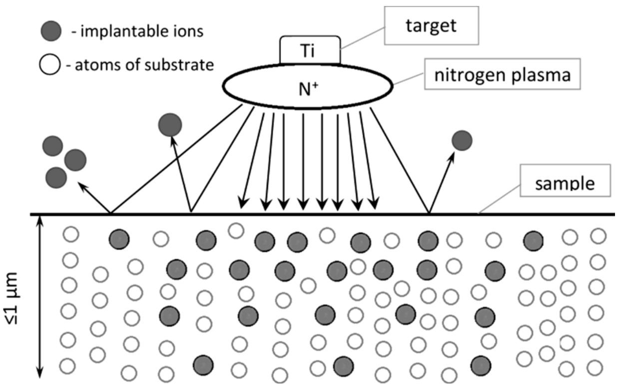


Fig. 1. Ionic implantation scheme

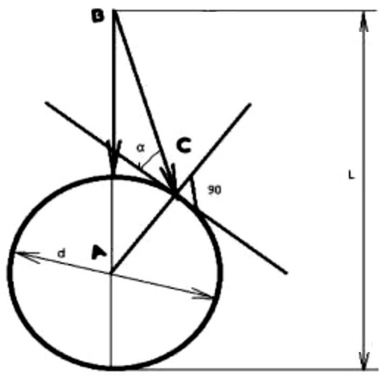


Fig. 2. A scheme for calculating the boundary angle

after each treatment. Unlike the first method, which requires additional complex equipment (such as in the patent [16]), the second method is easier. But then the question about the number of revolutions of the shaft required to achieve the optimal concentration of ions arises. The amount of impurity (implanted) ions in the treated material is very small, and they don't form crystalline compounds. Thus, it is impossible to identify these metals or their compounds by traditional methods such as XRD [17–20].

The main aim of the work is related to the investigation of the surface of implants, the determination of the optimal parameters of ionic implantation of a curvilinear surface by a shaft example and the practical verification of the obtained results.

As a result, it is necessary to solve the following tasks: to determine of the optimal concentration of ions of the surface brush implant, to determine of the limiting angle of rotation of the shaft using a computer simulation, to realize of shafts of different grades of steels, to study of elemental and phase compositions of the sample surface layer, to determine of the hardness of the modified surface of the implants.

2. Nanoscale Layer Formation

The synthesis of implants was carried out by the ionic implantation with a preliminary surface preparation by means of the cleaning in an ultrasonic device by the following algorithm.

In a vacuum chamber, using an electromagnetic field inside the source, a nitrogen plasma (Fig. 1) was created, and its ions bombard the target. The metal ions (Ti) emitted by the target are directed from the target to the treated surface.

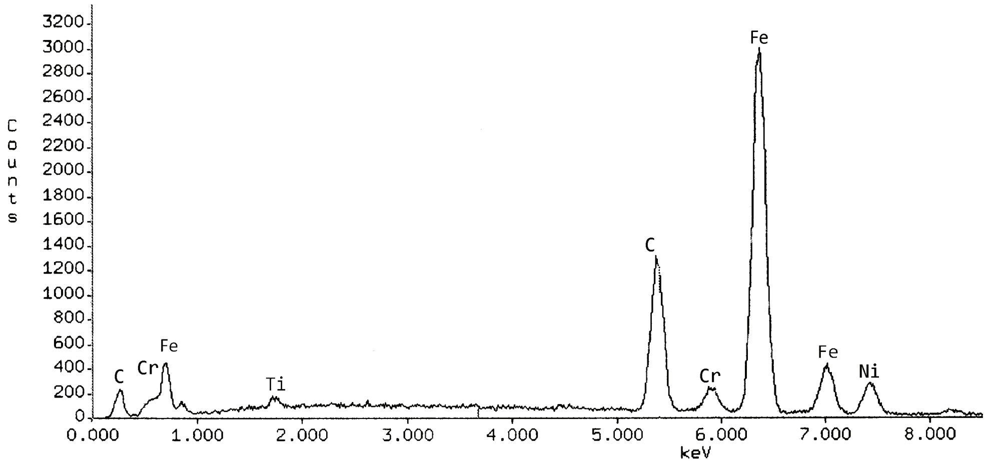
The process was carried out in vacuum at a voltage of about 20 kV between the source of ions and an implant. The analysis of the literature data [6–8] showed that the optimal fluence (dose of implantation), by which the physical and mechanical characteristics are maximally improved, is equal to 10^{17}–10^{18} ions/cm^2. Therefore, for the treatment of samples, a dose equal to 5×10^{17} ions/cm^2 and an hourly synthesis time were used.

3. Research Methodology

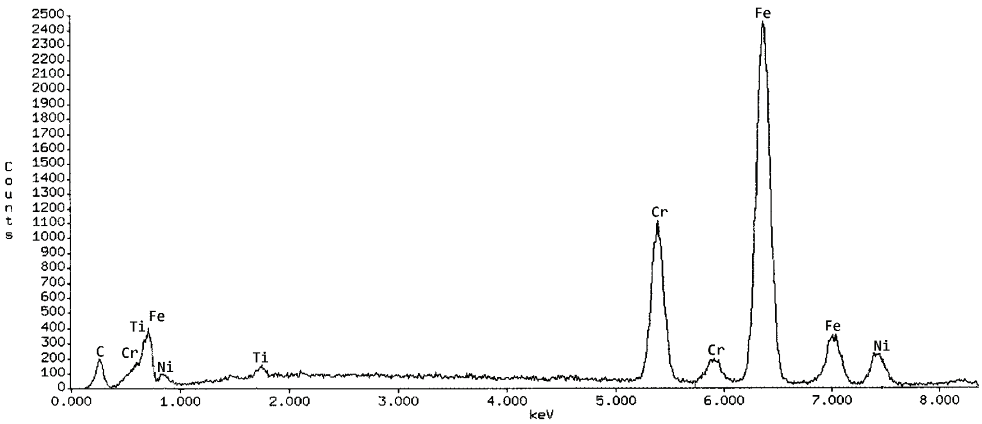
The research of samples by the X-ray photoelectron spectroscopy was carried out using a spectrometer equipped with a hemispherical analyzer (SES R 4000, GammadataScienta). The effective depth calculated for the carbon matrix was 1.0÷1.2 nm. These values cover 95% of photoelectrons leaving the surface. The accuracy of the quantitative XPS analysis is approximately 3%. The spectra were analyzed and calculated using the CasaXPS 2.3.10 software.

In addition, the study of the surface of samples was carried out using a Philips CM 200 energy dispersion spectrometer, which permits one to determine the elemental composition of the surface layer on the depth up to 1 μm.

Theoretical determination of the concentration of ion implants on the sample was executed using the program "RIO" [21]. The RIO program has a number of important advantages: it accounts for the actual composition of components, their diffusion, and allows one to predict the concentration profiles and the depth of penetration of the treated surface and associated ions with regard for the sequence of their penetration. The calculation was based on the Linhard–Scarf–Shiotte model, and the shielding parameter was taken according to the Thomas–Fermi model.



a



b

Fig. 3. Results of the analysis on an energy dispersion spectrometer: initial steel (*a*), steel with implanted titanium (*b*)

The limiting angle of the curvilinear sample (shaft) during the implantation was determined using mathematical calculations.

Since the implantation results depend essentially on the angle at which the ions fall into the surface, geometric calculations can be used (Fig. 2).

In Fig. 2, directions BA and BC are separated ion flow jets, falling at 90° and α angles to the surface, respectively. The angle α is the marginal angle for processing conditions.

Given the angle α, the number of shaft revolutions during the implantation can be calculated as

$$n = \frac{180^\circ}{90^\circ - \alpha - \arcsin\left(\left(\frac{d}{2}\cos\alpha\right)/\left(L - \frac{d}{2}\right)\right)}. \quad (1)$$

The obtained results were checked by measuring the hardness of the surface layer by the Vickers method with the help of the combined hardness meter "NOVOTEST T-UD" and with translation of values on the Brinell scale.

4. Data Processing and Discussion of Results

The results of microanalyses of the samples based on steel 12Cr18Ni10Ti by means of an energy dispersion spectrometer show that the surface composition of the initial sample of the carrier corresponds to its nominal composition (Fig. 3, *a*).

The implantation of titanium accompanied by an increase of the intensity of the Ti $K\beta$ line and leads

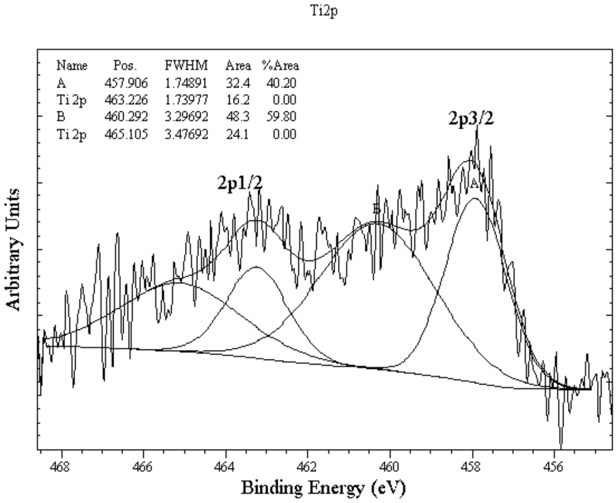


Fig. 4. XPS spectra of the steel with titanium

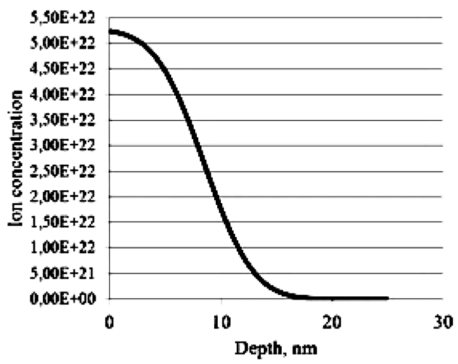


Fig. 5. Distribution of ions over depth

to the appearance of a new $L\alpha$ line at 0.74 keV (Fig. 3, *b*), which confirms the fact of the titanium introduction in the support (steel) and predictes that the titanium introduced onto the surface can exist in other compounds than that of the original sample.

To the determination of the nature of compounds which can be present on the surface of aa nano-dimensional layer of the synthesized composite, the analysis [9] of the surface composition was performed by means of XPS (Fig. 4).

The XPS spectra of titanium for the implant demonstrate the presence of two doublets with peaks from $2s3/2$- and $2p1/2$-electrons (Fig. 4). The binding energy of the $2p3/2$ electrons of the first of the peaks (457.9 eV) and the splitting energy constant (5.3 eV) are characteristic of the surface groups of titanium nitride bound to oxygen [22] or titanium oxynitride. (The splitting constants of TiO_2 and TiN are equal to 5.7 eV and 4.8 eV, respectively). For the second peak, the BE of Ti $2p3/2$ electrons which is equal to 460.3 eV and splitting constant – 4.8 eV correspond to the presence of titanium nitride. The ratio of the intensities of the peaks permits us to determine that, on the surface of the synthesised sample, 40% of titanium oxynitride and 60% of titanium nitride are present. The formation of titanium oxynitride is confirmed by the presence of a low-energy peak (400.2 eV) in the spectrum of O 1s-electrons and a high-energy peak (527.6 eV) in the spectrum of N 1p-electrons, which shows the electron density transfer $N \to O$.

As mentioned earlier, it is necessary to control the concentration of titanium ions on the surface, which is achieved using the boundary angle of implantation.

In order to find the boundary angle, the required concentration of ions from the target on she surface has been determined. Using the program "RIO" [21], the concentrations of ions for the fluence were determined to be 5×10^{17} ions/cm^2 (Fig. 5).

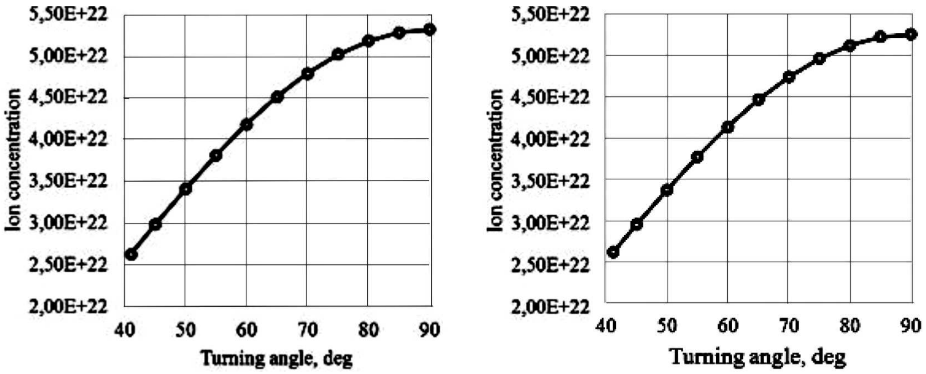
Therefore, when machining, it is necessary to rotate the shaft in such a way that the concentration of the target metal ions ($4{\div}5 \times 10^{22}$ ions/cm^2) is not less than at a depth of 0 nm.

Then the research for different angles of the ion fall, base materials and various target metals were used (Fig. 6).

It was taken into account that, during the rotation, a part of the surface will be implanted twice, that is, the surface will receive the double number of ions. Therefore, the boundaries of the site must receive ions at one time so that their concentration is not less than a half of that observed at 90°.

It was established that, regardless of the main material (steel 50, CrNi3A steel, *etc.*), the character of the ion penetration is the same. In this case, the steel composition almost does not affect the numerical values of the dependence of the ion concentrations on the angle of rotation. This is probably due to the fact that the penetration of ions is mainly influenced by iron, which is the basis of all steels. In particular, for 50 and CrNi3A steels (Fig. 6), the half concentration is observed at an angle of 41° and 41.5°, respectively.

Given the data obtained, the distance between the ion source and the sample ($L = 1$ m), and the diameter of the shaft ($d = 25$ ma), we calculate the optimal number of turns.



a *b*

Fig. 6. Dependence of the concentration of ions in the surface layer of samples on the angle of incidence of the titanium ions: *a* – in steel 50, *b* – in CrNi3A

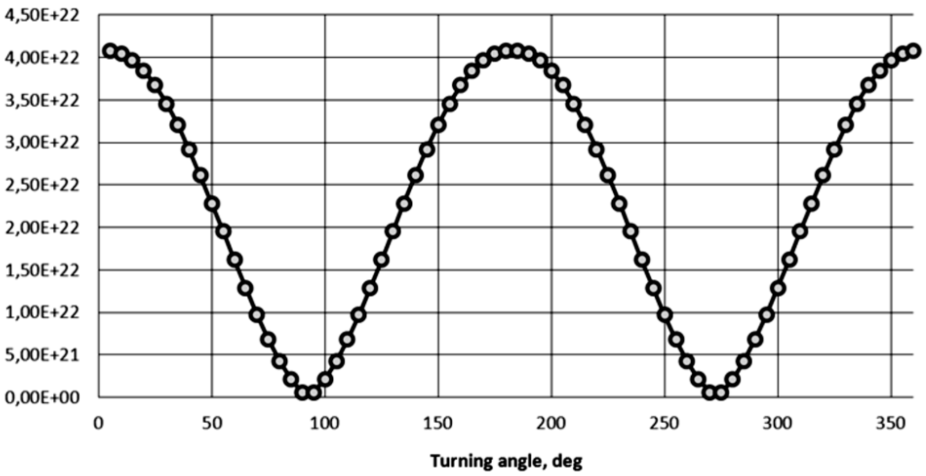


Fig. 7. Dependence of the ion concentration in the surface layer of the sample on the angle of rotation for the double implantation

Thus, the following optimal number of turns of a curvilinear detail of a shaft is obtained: $n = 3.6$–3.7.

Consequently, regardless of the material of the base, the number of turns during the implantation of titanium in order to improve the physical and mechanical characteristics should be 4.

The theoretical verification of the findings is shown in Figs. 7 and 8.

The graph in Fig. 7 shows the lack of a double-sided implantation, since the maximum concentration of ions exceeds the minimum by more than twice.

On the other hand, if you rotate the shaft and implant it four times according to the formula obtained in the study, the result will be perfectly satisfied (Fig. 8). The concentration ratio in this case is approximately 1.25. In this case, the minimum value is equal to the optimal according to fluence.

In order to verify the received technique in practice, implants with titanium ions were synthesized on the basis of Steel 50 and 12Cr18Ni10Ti – steels of two different classes. The implantation was performed three times, that is, at a marginal angle of 60°.

In both implants, the hardness of the resulting nano-sized layer was investigated (Figs. 9 and 10). Hardness measurements did not have a specific starting point. The main condition was the study of the full circumference of the shaft.

According to experimental data, the hardness varies cyclically and has 3 maxima, which corresponds to the theoretical ion concentration profiles.

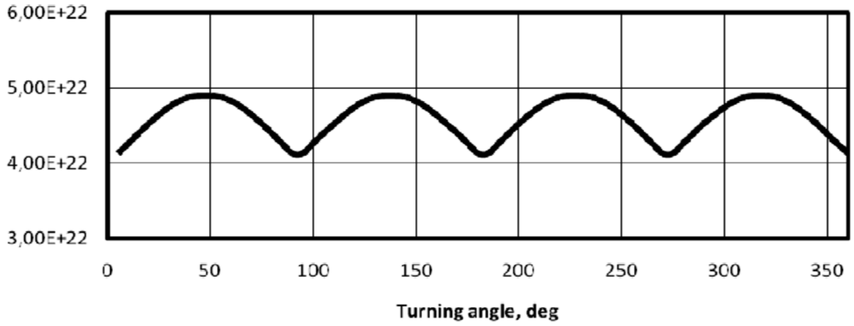


Fig. 8. Dependence of the ion concentration in the surface layer of the sample on the angle of rotation at the four-time implantation

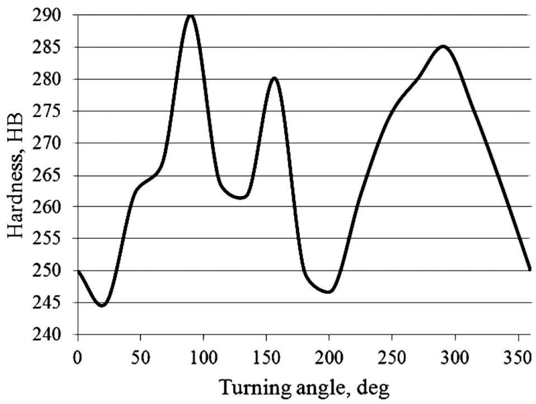


Fig. 9. Dependence of the hardness of the surface layer of steel 12Cr18Ni10Ti on the angle of rotation at the three-time implantation

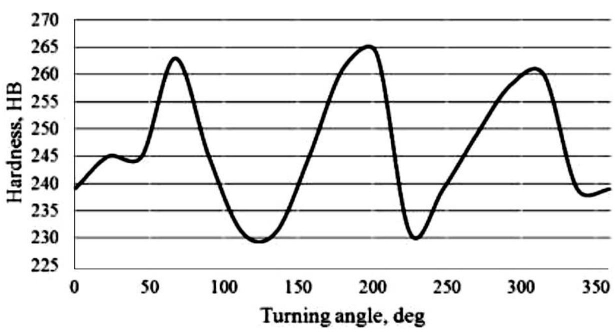


Fig. 10. Dependence of the hardness of the surface layer of steel 50 on the angle of rotation for the three-time implantation

Obviously, the same picture is observed regardless of the steel grade.

However, as it was previously predicted by the formula, three turns are not enough, since there is a significant difference in hardness values over one revolution (for steel – 12Cr18Ni10Ti 290–245 HB, for steel 50 – 265–229 HB). The above indicates the correctness of the calculated assumption that the optimal number of revolutions is four.

5. Conclusion

According to the spectral studies, the presence of titanium ions in the surface layer in various compounds was established. The optimal concentration of ions, which provides the maximum improvement in the physical and mechanical characteristics of the initial steels, was determined. The boundary angle and the minimum number of shaft revolutions that provide the required characteristics are determined. It is shown that these values of the rotation angle for steels 50 steel and CrNi3A steel are not significantly different.

The dependences of the concentration of ions in the surface on the number of shaft rotations are simulated, and the minimum number of treatments is determined.

Implants which are based on various grades of steel were synthesized. It is shown that the hardness values significantly depend on the material of a shaft (steel grade). It was established that the nature of the dependence of the hardnesses of steels 50 and 12Cr18Ni10Ti on the number of turns coincide with the prediction of the model.

Thus, the developed algorithm can be used for various alloys and steels. Moreover, for materials of a similar composition, for example, for steels of the same group, the determination of the optimal mode can be simplified, given the closeness of their boundary angles. The results obtained are relevant in the field of particle technology and promising in terms of optimizing the production of materials with desired properties.

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ВИКОРИСТАННЯ СПЕКТРОСКОПІЇ ТА КОМП'ЮТЕРНОГО МОДЕЛЮВАННЯ ДЛЯ ВИВЧЕННЯ ПОВЕРХОНЬ, МОДИФІКОВАНИХ ІОННОЮ ІМПЛАНТАЦІЄЮ

За допомогою рентгенівської фотоелектронної спектроскопії (X-ray Photoelectron Spectroscopy (XPS)) та енергетично-дисперсійної спектрометрії досліджено фазові та елементарні композиції нанорозмірного поверхневого шару імплантатів. Представлено метод визначення оптимального режиму модифікації нанорозмірних поверхонь металів та сплавів іонною імплантацією. Розглянуто обробку криволінійних поверхонь на основі математичних розрахунків та комп'ютерного моделювання. Запропонований підхід випробовано на синтезованих імплантатах. В якості критерію було взято твердість зразків.

Ключові слова: XPS, енергодисперсійна спектрометрія, імплантат, нанорозмірна модифікація поверхні, іонна імплантація, комп'ютерне моделювання, твердість.