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CHANGES OF SURFACE LAYER
OF NITROGEN-IMPLANTED AISI316L STAINLESS STEEL

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Изменение свойств поверхности нержавеющей стали
марки AISI316L, имплантированной азотом

Выполнены исследования влияния имплантации ионов азота с энергией 125 кэВ и дозами $1 \cdot 10^{17} - 1 \cdot 10^{18}$ ат/см^2 на такие трибологические характеристики нержавеющей стали марки AISI316L, как коэффициент трения, износостойкость и микротвердость. Состав поверхностных слоев стали исследован с помощью методик RBS, XRD, GXRD, SEM и EDX. Коэффициент трения и стойкость против истирания нержавеющей стали измерены в атмосфере воздуха, кислорода, аргона и в вакууме. Проведенные исследования показали увеличение сопротивления истиранию после имплантации изучаемых образцов, однако эти изменения различаются для различных окружающих сред. Наибольшее повышение износостойкости наблюдалось при испытании в воздушной атмосфере, и наибольшее понижение коэффициента трения было получено для всех имплантированных образцов, испытанных в атмосфере аргона. В результате трибологических испытаний увеличилось содержание азота, углерода и кислорода в стертых фрагментах образца по сравнению с их содержанием в поверхностных слоях образцов сразу после имплантации.

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Changes of Surface Layer of Nitrogen-Implanted
AISI316L Stainless Steel

The effects of nitrogen ion implantation into AISI316L stainless steel on friction, wear, and microhardness have been investigated at energy level of 125 keV at fluence of $1 \cdot 10^{17} - 1 \cdot 10^{18}$ N/cm^2. The composition of the surface layer was investigated by RBS, XRD (GXRD), SEM and EDX. The friction coefficient and abrasive wear rate of the stainless steel were measured in atmospheres of air, oxygen, argon, and in vacuum. As follows from the investigations, there is an increase in resistance to frictional wear in the studied samples after implantation; however, these changes are of different characters in various atmospheres. The largest decrease in wear was observed during tests in the air, and the largest reduction in the value of the friction coefficient for all implanted samples was obtained during tests in the argon atmosphere. Tribological tests revealed larger contents of nitrogen, carbon, and oxygen in the products of surface layer wear than in the surface layer itself of the sample directly after implantation.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

INTRODUCTION

Surface modification of stainless steels by nitrogen ion implantation is a well-established process. The possible mechanisms of such a modification are not fully understood, but the formation of new nitride phases in the implanted layers is expected to have a large effect on tribological properties. The microstructure of the implanted layer has attracted much attention because of its important influence on the surface properties of a work piece implanted with nitrogen ions.

In austenitic stainless steels (304, 304L, 316, 316L), ion implantation treatments are able to produce a modified surface layer consisting of metastable phase, known as supersaturated or expanded austenite γ_N [1]. However, the authors of [2] concluded that the ion implantation did not create any new phase and did not influence the crystallographic texture that they observed before the implantation. Implantation at the fluence $6 \cdot 10^{16} - 1.2 \cdot 10^{17}$ N/cm^2 to the steel of types 304 and 316 is responsible for precipitation of CrN [3].

Changes in the surface layer due to nitrogen implantation may be larger than those observed so far. Paper [4] shows that the high-fluence carbon ion implantation modified the microstructure of the steel, as demonstrated by the presence of two amorphous layers separated by a layer of extended austenite. The divergent opinions about the effect of nitrogen implantation on properties of the steel AISI316L inspired us to study the crystalline structure of steel, formation of the compounds Fe–N and Cr–N, as well as change of steel tribological properties after implantation.

As mentioned before, implantation with nitrogen ions is a well-recognized technique of surface modification that improves the tribological properties of machine tools and is frequently used for steels. However, there is lack of information concerning the influence that the type of atmosphere has on the course of development of tribological process of ion-implanted metals. Changes of steel tribological properties after implantation are rarely studied. Paper [5] studied the effect of implantation on the change of steel wear in air and nitrogen atmospheres. Nitrogen implantation at high fluence has been shown to increase microhardness [1], but friction and wear tests show no significant change of the friction coefficient, whatever the relative humidity during the tests; however, an important wear resistance improvement was observed.

In this paper, friction tests in various atmospheres — air, oxygen, argon, and vacuum — show a considerable influence of the atmospheric environment on the rate and character of wear, which indicates the importance of the modified ion-implanted layer and its reaction with the environment. The aim of the experiments was to test the changes in tribological properties caused by various kinds of atmospheres in which the friction process takes place.

1. EXPERIMENTAL DETAILS

AISI316L stainless steel samples were used in this study. The chemical composition of the samples was: (wt %) (0.1% C, 0.16% Al, 0.29% Si, 0.52% S, 17.58% Cr, 10.32% Ni, 0.36% Cu, Fe = balance). The specimens were the discs of 25 mm diameter and 4 mm thickness, mechanically polished to a mirror finish to obtain a roughness parameter $R_a = 0.08$ μm.

The subsequent implantation with 125 keV N^+ ions was carried out using the standard ion accelerator. The beam current density was 3 μA/cm^2. The samples were implanted over the fluence range from $1 \cdot 10^{17}$ to $1 \cdot 10^{18}$ N/cm^2. Depth profiles of the nitrogen distribution were measured at the JINR, Dubna via the RBS technique, using a He beam with the 2.04 MeV energy scattered at the angle of 170°.

The X-ray diffraction (XRD) experiments were performed using a CuK$_\alpha$ source (0.15406 nm) over the 2θ range from 20 to 100°. Grazing incidence X-ray diffraction (GXRD) was performed for 1 and 5° incidence angles.

Friction and wear testing for the stainless steel samples were performed on a ball-on-disc tribotester, using a tungsten carbide ball of 0.5 mm diameter at the indentation load of 491 mN and velocity of about 56 mm/s. The friction measurements for the stainless steel samples were carried out under the technically dry friction. The environment temperature was about 20°C and relative humidity 25–30%; the atmospheric pressure value was about 1000 hPa.

A hermetic cover was used over the measurement area to produce a controlled atmosphere for friction tests. A vacuum pump was used to obtain pressures of 10^{-4} Pa in the bench measurement chamber and various gases could also be admitted to produce a test environment at normal atmosphere.

Energy dispersive X-ray spectroscopy has been obtained with electron microscope (Vega 5135 with X-ray detector Link 300 ISIS Oxford Instruments) to measure chemical composition of the surface layers.

2. RESULTS AND DISCUSSION

The depth distribution profiles of the implanted nitrogen atoms, evaluated from the Rutherford Backscattering Spectrometry (RBS) measurements at different fluences, are presented in Fig. 1. The figure also shows the predicted distribution of nitrogen atoms calculated by means of the program SATVAL [6]. As follows from RBS measurements with the increase of the implanted ions fluence, more nitrogen atoms are found in farther layers of the sample than predicted from the theoretical distribution. However, after implantation of the fluence of $5 \cdot 10^{17}$ N/cm^2, their amount diminishes significantly in the surface layer.
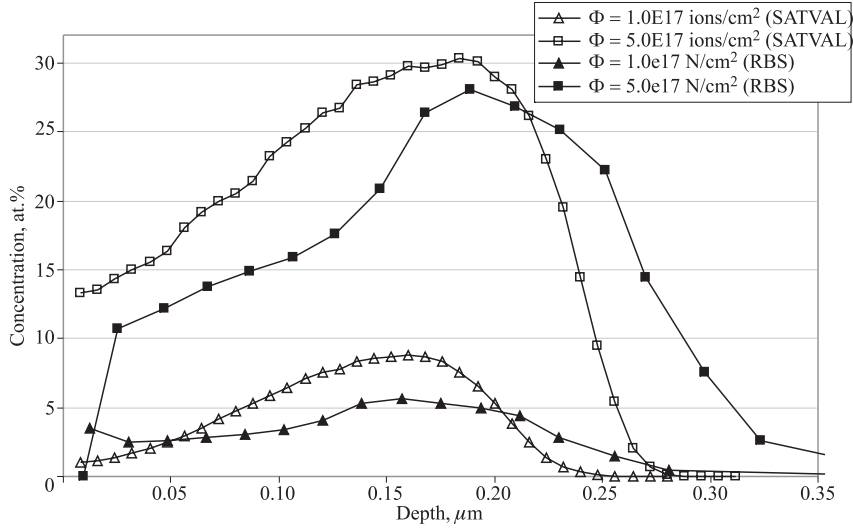
Fig. 1. RBS and simulated by SATVAL code depth profiles for AISI316L stainless steel implanted with nitrogen at energy 125 keV

This situation is attributable to the two factors — diffusion of nitrogen atoms, both deep down into the sample and towards the surface, as well as sputtering of the sample surface layer during implantation. With the increase of the fluence, the thickness of the sputtered layer containing larger nitrogen atoms concentration increases. Diffusion of atoms inside the sample (also deep down) is probably attributable to strong repulsion forces between the first and second nearest neighbours of nitrogen atoms in the face-centered cubic (fcc) austenite structure [7].

Unimplanted AISI316L stainless steel showed the characteristic diffraction spectra of the face-centered cubic austenite. The diffraction peaks were $43.5°$ (111); $50.6°$ (200); $74.7°$ (220); $90.5°$ (311) and $95.8°$ (222).

After nitrogen implantation with the fluence of $5 \cdot 10^{17}$ N/cm^2, additional peaks were detected, which showed that a new phase arose in the surface layer. It was identified on the basis of the peaks at: $2\theta = 40.7°$ (111); $45.6°$ (200); $81.4°$ (311) and $87.0°$ (222). This phase has been described as the «m» phase [8], S phase [9], or as expanded austenite [10]. The phases of expanded austenite were not observed after implantation with the smallest fluence. Fluence larger than 1×10^{17} N/cm^2 is necessary for its formation in the AISI316L steel. The small peaks at $2\theta = 38.6$; 45.6; 64.3 and $82.7°$ suggest that, in addition to expanded austenite, fcc CrN is present in the surface region.

Unimplanted 316L stainless steel showed the characteristic spectra of face-centred-cubic austenite $a = 0.3601(5)$ nm. After implantation with the fluence of

$1 \cdot 10^{17}$ N/cm^2, the lattice constant increases to reach the value $a = 0.3719(5)$ nm. Implantation with the fluence of $5 \cdot 10^{17}$ N/cm^2 causes to increase up to the value of $0.3887(5)$ nm. Further increase in implanted ions fluence does not result in lattice changes.
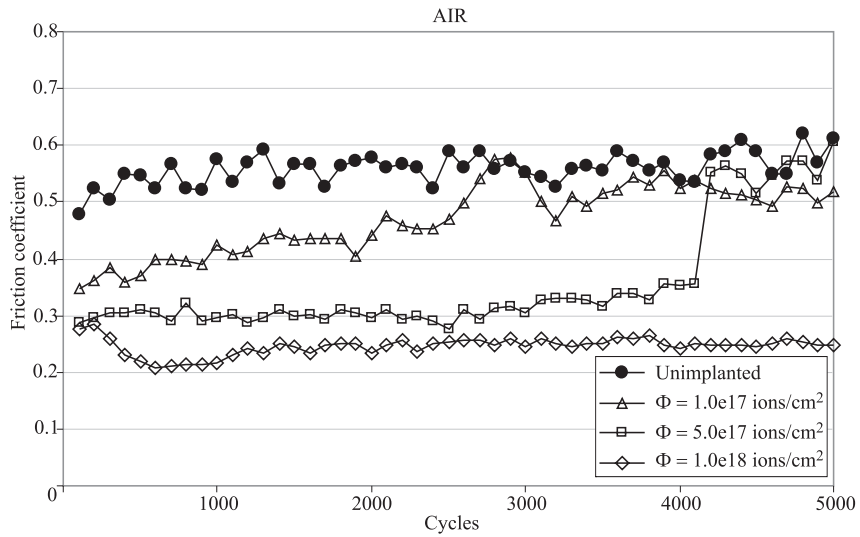

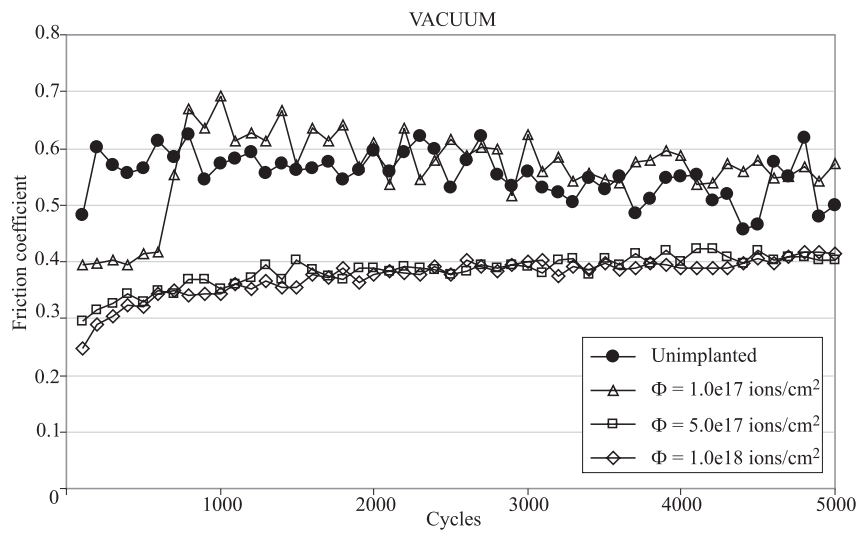Fig. 2. Friction coefficient of studied samples measured in air atmosphere

Fig. 3. Friction coefficient of studied samples measured in vacuum

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The results of friction coefficients measurements are presented in Figs. 2–5. The largest changes after implantation for all implanted doses are observed when the friction node is in the pure argon atmosphere (Fig. 4). There, the friction
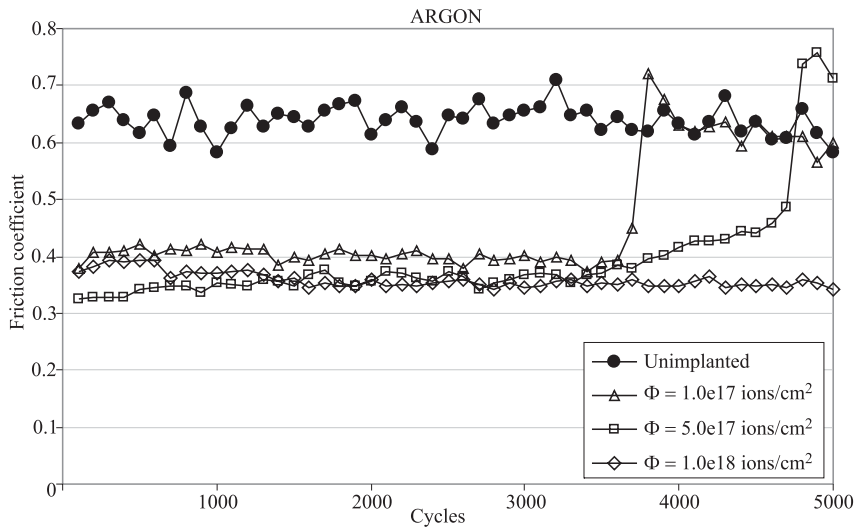

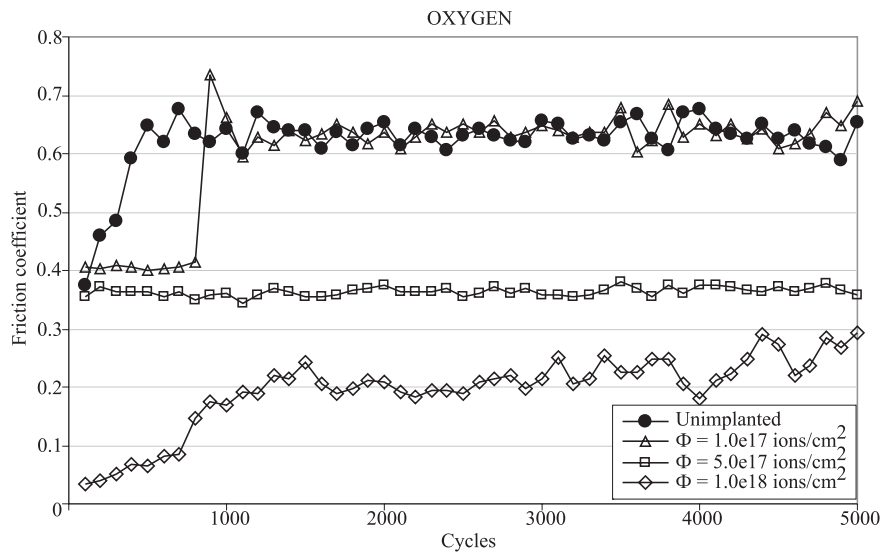Fig. 4. Friction coefficient of studied samples measured in argon atmosphere

Fig. 5. Friction coefficient of studied samples measured in oxygen atmosphere

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coefficient is 0.3–0.4 until the layer modified during implantation is rubbed. In the case of tests carried out in the atmospheres of air (Fig. 2) and pure oxygen (Fig. 5), the friction coefficient decreases significantly with the increasing fluence of implanted ions.

Ball on disc wear tracks were analyzed by means of a Taylor Hobson profilometer. Sets of about 20 profilograms were made for each wear track. One such a track profile formed during friction in air atmosphere is shown in Fig. 6.
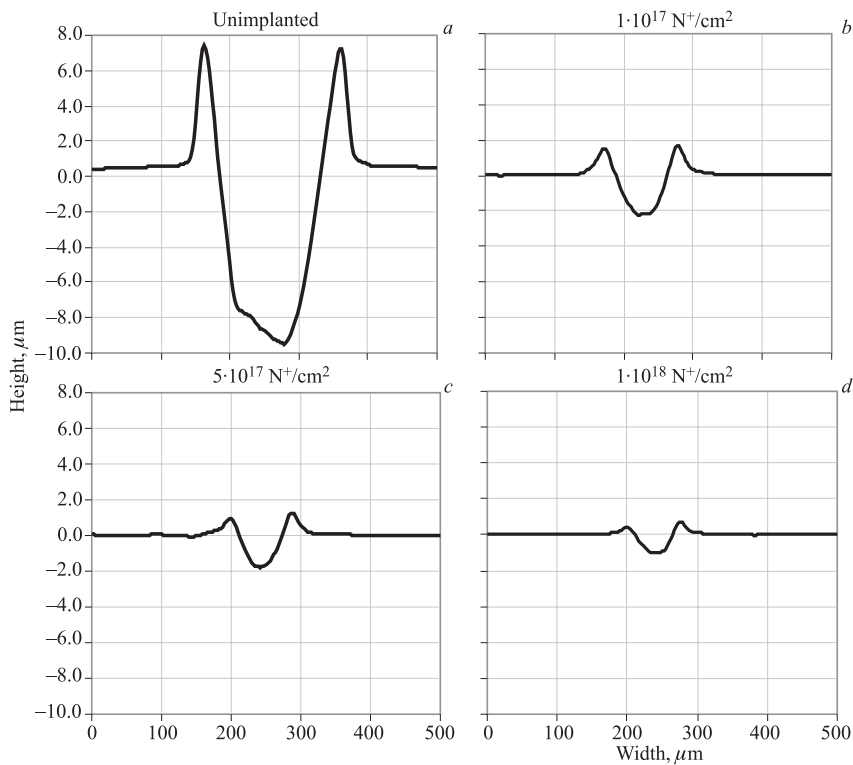

Fig. 6. Profilometer scans of ball-on-disc wear tracks (after the tests in air atmosphere) on the implanted and unimplanted AISI316L stainless steel specimens at energy 125 keV for different nitrogen doses

Oxidizing wear is predominant in the tests made in the air atmosphere. The character of wear does not change practically both for unimplanted and implanted samples. Only its intensity is reduced, which is shown in smaller track width (Fig. 6). Similar changes can be seen in track microphotographs made in the oxygen atmosphere.

The cross sections of these wear profiles under their base lines, defined by the original surface of the sample, were calculated by a special computer program as

explained elsewhere [11]. The results of wear measurements are shown in Fig. 7. It can be stated that implantation of nitrogen to the steel AISI316L increases its resistance to friction wear. This is particularly evident for implantation with the dose of $1 \cdot 10^{18}$ N/cm^2.
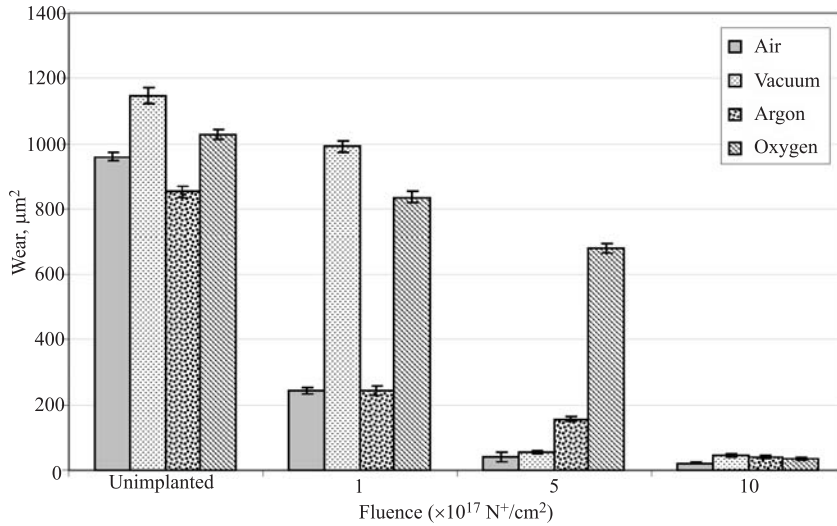

Fig. 7. Sample wear as a function of nitrogen dose at energy 125 keV for the AISI316L steel in addition to the unimplanted sample
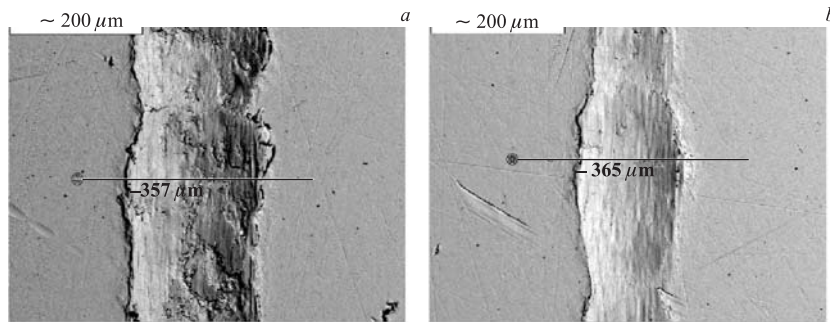

Fig. 8. SEM microphotograph of the track worn on the studied samples by a ball made of WC (tungsten carbide) in the argon atmosphere: a) unimplanted sample, b) the sample implanted with fluence of $1 \cdot 10^{17}$ N/cm^2

Change of wear character after implantation can be observed on the microphotographs taken with a scanning electron microscope (SEM) of the track on the unimplanted samples and that implanted with fluence $\phi = 1 \cdot 10^{17}$ N/cm^2

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during the test in the argon atmosphere (Fig. 8). In the argon atmosphere for an unimplanted sample, adhesive wear is predominant (Fig. 8, a) and after implantation, abrasive wear (Fig. 8, b). The surface layer formed after implantation with the fluence of $1 \cdot 10^{17}$ N/cm^2 in the argon atmosphere possessed greater durability than found in the vacuum because additional convection carried away of heat from the friction node through argon.

Figure 9 presents the results of linear scanning of element contents along a line perpendicular to the friction track. We examined the track obtained during the test in air on the sample implanted with fluence of $1 \cdot 10^{17}$ N/cm^2. Across the track, a line is carried programmatically, along which content elements were measured (diagrams of element distribution are presented at the bottom of the photograph). Dark spots in the photograph indicate the fragments of the worn out sample surface, which press against the track surface (they were not removed during the friction process).
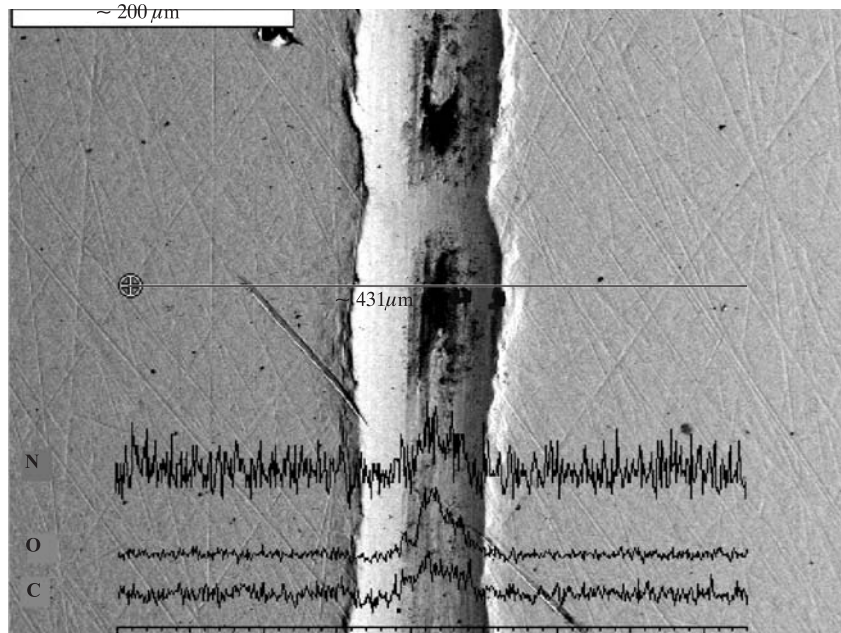

Fig. 9. Microphotograph of the track worn in the air atmosphere in the implanted sample $\phi = 1 \cdot 10^{17}$ N/cm^2. The bottom insert shows relative changes in the nitrogen, oxygen and iron contents along the line marked in microphotograph

As can be seen, the relative contents of nitrogen and oxygen as well as carbon increase in worn out fragments of the sample compared to the portion surrounding the track. No changes were observed in the contents of these elements on the pure

surface of the track, or on the sample surface. However, an insignificant drop in chromium content on the track surface was observed. Before the tribological test, content on the sample surface was 15.93(2)%. When the test was over, this content inside the track diminished to 15.69(2)%.

The carbon content also increased on the track surface from 0.10(2) to 0.14(2)%. The character of changes in the relative contents of elements in question in other atmospheres was similar. After the tests made in the argon atmosphere and in vacuum, there was a lack of oxygen in the wear products and on the sample surface. The wear products formed in other atmosphere contain oxygen.

The large friction coefficients in the vacuum for the unimplanted sample and for that implanted with the smallest fluence is probably a result of local welding with the countersample owing to the Fe–C bonds. A small amount of carbon ($\sim 0.1\%$) is contained in the sample material and the rest comes from the countersample (WC). This interaction leads to significant wear of these samples in vacuum (Fig. 4). This mechanism confirms the increase of oxygen content on the track surface by 0.04(2)%.

In the studies of wear products formed during friction, larger amounts of nitrogen, carbon, and chromium were observed compared to their contents in the track and in the surface layer of the sample. This means that, owing to local increases in temperature in the contact area of the rubbing elements, they acquire energy that is used for dislocation of material towards the surface that is removed in the wear process. These changes are more distinct for nitrogen owing to the larger repulsion between nitrogen atoms. Increased amounts of chromium in the wear products is the evidence for its mobility. At temperatures lower than about 450°C, the chromium diffusion is reduced [12] and formation of chromium nitrides is usually inhibited [13].

SUMMARY

The depth distribution of nitrogen implanted into the steel AISI316L departs from that predicted theoretically because of diffusion. Probably diffusion is promoted by strong repulsion forces between the first and second nearest neighbour nitrogen atoms in the expanded austenite. Nitrogen implantation leads to a change of crystalline structure and chemical changes in the surface layer. The new phase — expanded austenite CrN inserts — as well as crystalline lattice defects formed during implantation improve the steel's tribological properties.

The lower wear rate after implantation is a result of the lower coefficient of friction, which, in turn, is probably ascribable to the increase in surface hardness, leading to a smaller contact area and possibly to the change in the mode of wear, from adhesive (unimplanted) to abrasive (after implantation).

The largest decrease of friction coefficient for all implanted samples was observed in the argon atmosphere. When the modified surface layer was rubbed off, the friction coefficient has a value characteristic of the unimplanted sample. Oxidizing wear found in the oxygen and air atmospheres does not occur in the argon atmosphere. Moreover, tribocorrosion caused by water vapour occurs in air.

The large friction coefficient in the vacuum for the unimplanted sample and that implanted with the smallest fluence is probably attributable to local tacking with the countersample owing to the Fe–C bonds.

The wear products contain larger contents of nitrogen, carbon, and chromium than do the surface layer of the sample.

Finally, one can conclude that:

- Implantation of nitrogen into AISI316L stainless steel forms the new phase — expanded austenite, precipitation of CrN, and increase of lattice constant by $\sim 8\%$.

- Increase of sample temperature during implantation and formation of the phase γ_N are responsible for large nitrogen mobility.

- Nitrogen implantation improves tribological properties of the steel AISI 316L and changes the character of wear. Adhesive wear decreases and abrasive wear increases. Mild oxidizing wear remains one of a kind of wear in the air and oxygen atmospheres.

- Local increase of temperature during friction promotes mobility of nitrogen, chromium, and carbon.

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