

PHYSICS
OF NANOSTRUCTURES

Formation of Nanosized Surface Layers of 03Kh17N12M2 Stainless Steel by Implantation of N⁺ Ions

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Abstract—Accumulation of nitrogen in nanosized surface layers of 03Kh17N12M2 stainless steel has been detected upon N⁺ ion implantation up to 14 at % together with metal nitrides, mainly of chromium nitride CrN and interstitial solid solution. It has been demonstrated that N⁺ ion implantation accompanied by preliminary irradiation by Ar⁺ and O⁺ ions decreases maximum nitrogen concentration by at least two times. It is assumed that this is stipulated by segregation to surface layers of iron atoms upon irradiation by Ar⁺ ions as well as formation of chromium oxide Cr₂O₃ and chromium hydroxide CrOOH upon irradiation by O⁺ ions.

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INTRODUCTION

Performance properties of metals and alloys (wear resistance, cyclic fatigue, and others) are determined by structural and phase state of surface layers, they can be significantly improved by surface modification. As is known, surface treatment of metals and alloys is executed by ion implantation [1–3]. A peculiar feature of this method in comparison with other ionic vacuum treatments is minimum variations of geometrical sizes of items and the possibility of low temperature treatment, which in most cases eliminates item shrinkage. However, despite numerous studies in this field, formation of nanosized surface layers of metals upon ion implantation is not studied in detail. In particular, the influence of alloy components on accumulation of implanted elements and formation of chemical compounds upon ion implantation remains unclear.

In this regard this study is aimed at comparative studies of influence of N⁺ ion implantation, consecutive Ar⁺ and N⁺ ion implantation, and consecutive O⁺ and N⁺ ion implantation on accumulation of nitrogen atoms and formation of chemical compounds in nanosized surface layers of 03Kh17N12M2T stainless steel.

EXPERIMENTAL

Plates of 03Kh17N12M2T stainless steel with a length of 30 mm and cross section of 8 × 2 mm were cut out of an as-delivered sheet by spark cutting. The composition of the initial samples was as follows: Fe, base; C, 0.03%; Cr, 17%; Ni, 12%; Mo, 2%; Mn, 1%; and Ti, 0.6%. The samples were mechanically polished using polishing pastes and cleaned in organic

solvents. Recrystallization annealing of the samples was carried out at 750°C for 30 min in vacuum ~10⁻⁴ Pa.

Ar⁺ or N⁺ ion implantation and consecutive Ar⁺ and N⁺ or O⁺ and N⁺ ion implantation was performed using pulse vacuum arc in pulse periodic mode ($f = 100$ Hz, $t = 1$ ms) with a binding energy of 30 keV, radiation dosage of 10¹⁸ ion/cm², and pulse current density of 3 mA/cm².

Chemical composition of nanosized surface layers before and after irradiation was studied by X-ray photoelectron spectroscopy (XPS) using SPECS and ES-2401 spectrometers with MgK_α excitation of photoelectron spectrum ($E = 1253.6$ eV). X-ray photoelectron spectra Fe 2p_{3/2}, Ni 2p_{3/2}, Cr 2p, Mo 3d, Ti 2p, N 1s, O 1s, and C 1s were recorded. Spectral data were processed by Casa XPS software. The first processing stage was smoothing, which increases signal to noise ratio; then, the background was subtracted by the Shirley method and integral intensity of the component was determined (area under curve). Based on integral intensity of photoelectron peaks the composition of the considered alloy was determined as follows:

$$C = \frac{C_a/S_a}{\Sigma(C_i/S_i)},$$

where C is the concentration, C_a is the signal integral intensity of the photoelectron line, S_a is the factor of relative sensitivity in XPS for the given substance, $\Sigma(C_i/S_i)$ is the sum of ratios of integral intensities to factors of relative sensitivity for all elements in the solid composition. The relative error of determination of element concentration was ±3 at %. Layer by layer

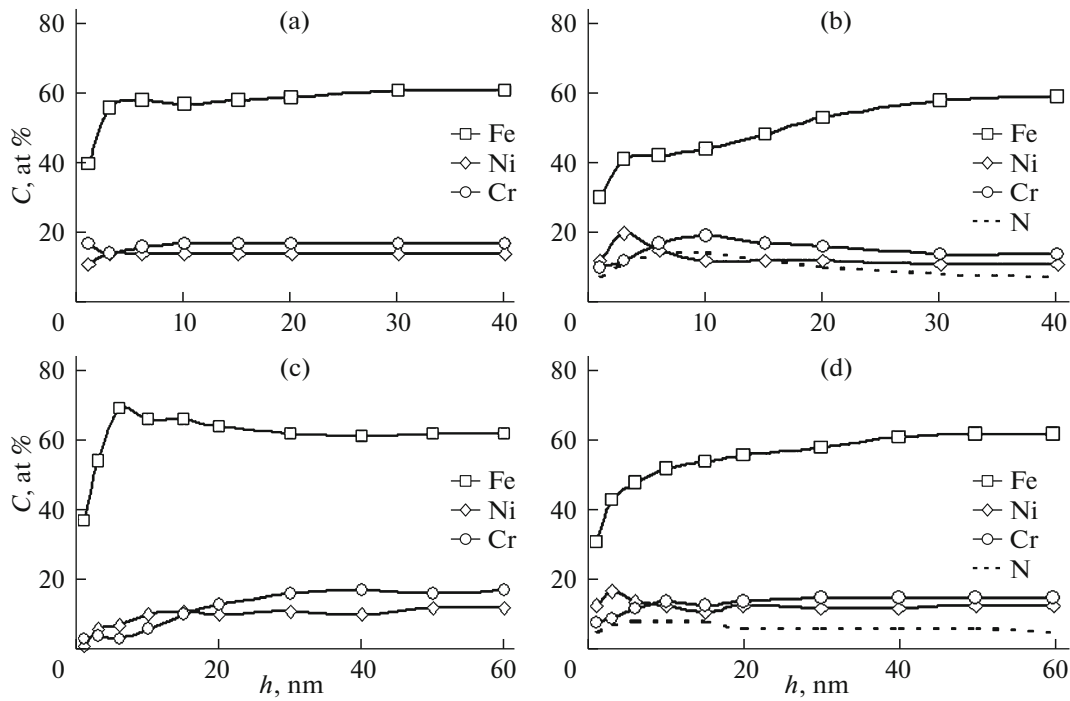


Fig. 1. Concentration profiles of element depth distribution in 03Kh17N12M2T stainless steel in initial state (a), after irradiation by N^+ ions (b), after irradiation by Ar^+ ions (c), and after consecutive irradiation by Ar^+ and N^+ ions (d).

XPS analysis was performed using surface dispersion by argon ions at a surface etching rate of ~ 1 nm/min using reference data [4–6].

RESULTS AND DISCUSSION

XPS studies of the initial sample revealed that starting from a depth of ~ 6 nm the concentrations of iron atoms reach 60 at %, nickel atoms, 14 at %, and chromium atoms, 17 at %, and remains steady with variation in depth (Fig. 1a). In addition, molybdenum and titanium atoms of 2 at % were revealed on the surface of the initial sample together with 1 at % of manganese (Table 1).

N^+ ion implantation leads to accumulation of nitrogen atoms in surface layers of stainless steel up to

14 at % and rearrangement of iron atoms as well as of major dopants (Fig. 1b). An extra thin surface layer with a depth of less than 10 nm is enriched with nickel atoms to the maximum concentration of 20 at % and depleted with iron atoms. Distribution of chromium atoms in surface layers is characterized by a dome shape with the maximum concentration of 20 at %, its distribution pattern corresponds to that of nitrogen atoms (Fig. 1b). It is assumed that segregation of nickel atoms into an extra thin surface layer is stipulated by the fact that nitrogen atoms penetrating surface layers chemically interacts with chromium generating chromium nitrides in the form of atomic clusters or nanosized phases, which displace nickel atoms to the surface. This assumption is confirmed below. It should be mentioned that irradiation by N^+ ions and

Table 1. Relative concentration of elements in surface layers of 03Kh17N12M2T stainless steel in the initial state

h , nm	Fe, at %	Ni, at %	Cr, at %	Mo, at %	Ti, at %	Mn, at %	O, at %	C, at %
1	40	11	17	1	1	0	26	2
3	56	14	14	2	2	1	7	3
6	58	14	16	2	2	1	4	3
10	57	14	17	2	2	1	4	2
15	58	14	17	2	2	1	3	3
20	59	14	17	2	2	1	2	2
30	61	14	17	2	2	1	1	1
40	61	14	17	2	2	1	1	1

Table 2. Relative concentration of elements in surface layers of 03Kh17N12M2T stainless steel after irradiation by N^+ ions

<i>h</i> , nm	Fe, at %	Ni, at %	Cr, at %	Mo, at %	Ti, at %	Mn, at %	O, at %	C, at %	N, at %
1	30	12	10	1	0	0	31	8	7
3	41	20	12	1	1	0	6	6	11
6	42	15	17	1	1	0	4	4	14
10	44	12	19	1	1	0	3	3	14
15	48	12	17	1	1	1	3	3	12
20	53	12	16	1	1	1	2	2	10
30	58	11	14	1	1	1	2	2	8
40	59	11	14	1	1	1	2	2	7

by other ions used in this study does not lead to segregation of additional dopants, such as molybdenum, titanium, and manganese, into surface layers (Table 2). The data in the table for a sample in the initial state and after irradiation by N^+ ions demonstrate that N^+ ion implantation does not lead to segregation of minor dopants and we will not pay attention to this fact in this study.

Irradiation by Ar^+ ions causes segregation of Fe atoms into surface layers and depletion with nickel and chromium atoms (Fig. 1c). The concentration profiles of element distribution in nanosized layers consecutively irradiated by Ar^+ and N^+ ions (Fig. 1d) correspond qualitatively to those after irradiation by N^+ ions (Fig. 1b). However, maximum concentration of nitrogen atoms decreases twofold to 7 at %.

XPS analysis of Cr $2p_{3/2}$ spectra is evidence that in nanosized surface layers of the initial sample chromium atoms are in a metallic chemically unbound state corresponding to their position in nodes of crystalline lattice of solid solution (Fig. 2b). This is confirmed by the electron binding energy of 574.2 eV in chromium atoms at the energy level of $2p_{3/2}$ [4, 5]. After N^+ ion implantation, firstly, the maximum electron binding energy at the $2p_{3/2}$ level of chromium atoms is shifted towards higher binding energy of 574.4–574.6 eV and, secondly, the lines of these spectra are expanded, mainly at depths up to 20 nm (Fig. 2a). XPS analysis of the $2p_{3/2}$ spectrum of chromium atoms using spectrum decomposition into constituents made it possible to reveal that this shift can be attributed to formation of chemical compound CrN (Fig. 3a). The electron binding energy at the $2p_{3/2}$ energy level in a chromium atom for this compound is 575.4 eV [4]. Formation of metal nitrides is confirmed also by the existence of a peak with the maximum binding energy of 393.2–393.3 eV in 1s XPS spectrum of nitrogen atoms (Fig. 3b). In the binding energy range from 390 to 397 eV in the 1s spectrum of nitrogen atoms there exists a peak corresponding to electrons at the energy level of $3p_{3/2}$ from molybdenum atoms (Fig. 3b). Analysis of this spectrum shows that molybdenum is only in a metallic state but also in the

form of a chemical compound with nitrogen: Mo–N [4, 5]. This is demonstrated also by chemical shifts in the most intensive lines of molybdenum Mo $3d$, which were used for prediction of relative concentrations; however, this is not focused on much since the molybdenum concentration after irradiation does not exceed 1 at % (Table 2), that is, it is even less than in the initial sample (Table 1). Titanium and manganese are characterized by similar behavior (Tables 1 and 2). In some cases, for instance after consecutive irradiation by Ar^+ and N^+ ions as well as by O^+ and N^+ ions, their concentration is at the level of 0 at %. Thus, it is assumed that generally metal nitride is comprised of chromium and nitrogen atoms. Moreover, it follows from the N 1s spectrum that nitrogen atoms in addition to the chemical state corresponding to nitrides of $3d$ metals are in the state with a binding energy of 398 eV (Fig. 3b). As a rule, this is the state of nitrogen atoms in which they exist in interstitial positions of a crystalline lattice of solid solution [4]. It follows from XPS of the $2p_{3/2}$ spectrum of chromium atoms for a sample irradiated by N^+ ions that not all chromium atoms participate in formation of CrN compound and their main portion is in a metallic chemically unbound state with the binding energy of 574.2 eV (Fig. 3a). In this state chromium atoms are in the nodes of a crystalline lattice of solid solution of this multicomponent system. Iron and nickel atoms are also in a metallic chemically unbound state, moreover, not only in the initial sample but also in irradiated samples. For instance, this is shown by the electron binding energy at $2p_{3/2}$ energy levels for iron and nickel atoms equaling 707 eV and 853 eV, respectively, for a sample irradiated by N^+ ions (Fig. 4). These electron binding energies correspond to iron and nickel atoms located in the nodes of a crystalline lattice of solid solution [4, 5].

Therefore, based on the aforementioned experimental results it is possible to assume that N^+ ion implantation into 03Kh17N12M2T stainless steel is accompanied by formation of metal nitrides, mainly chromium nitride CrN, and nitrogen interstitial solid solution into a crystalline lattice of this multicomponent system.

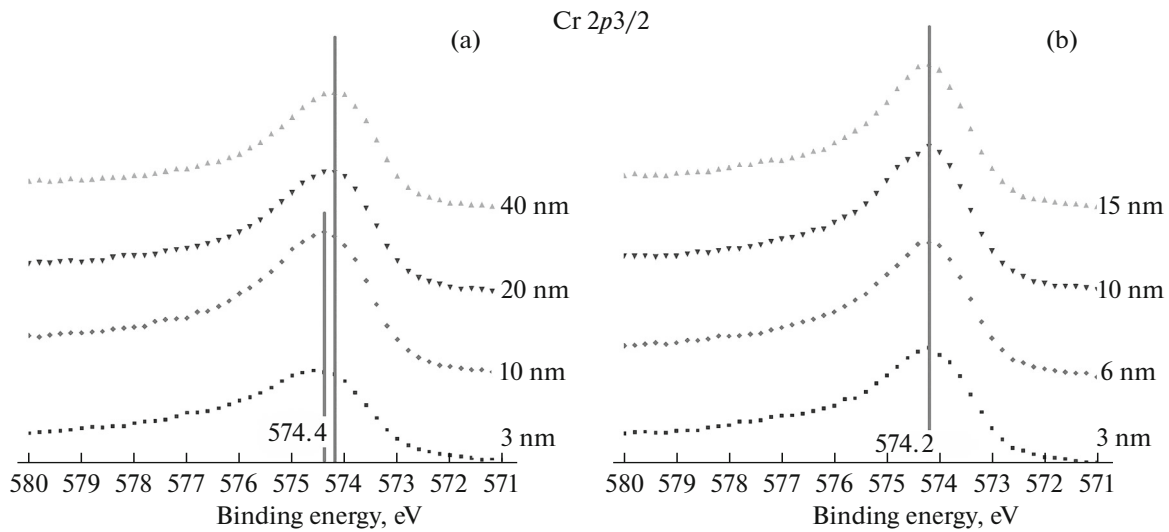


Fig. 2. Cr $2p_{3/2}$ XPS spectra from surface layers of stainless steel after irradiation by N^+ ions (a) and in the initial state (b).

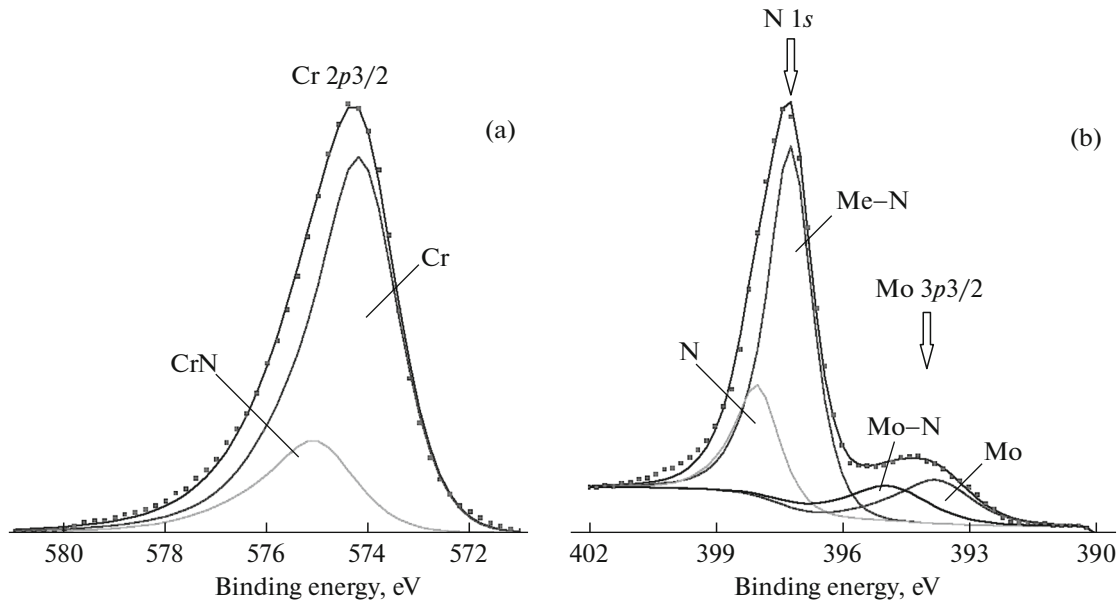


Fig. 3. Cr $2p_{3/2}$, N $1s$, and Mo $3p_{3/2}$, XPS spectrum acquired at a depth of 10 nm in a sample irradiated by N^+ ions.

As a consequence of preliminary treatment by Ar^+ ions the maximum nitrogen concentration in surface layers of stainless steel upon subsequent N^+ ion implantation with parameters similar to N^+ ion implantation without ionic preliminary treatment decreases twofold to 7 at % (Fig. 5a). Probably, this could be attributed to the fact that upon irradiation by Ar^+ ions iron atoms segregate to the surface (Fig. 5b). It is assumed that iron atoms characterized by lower chemical activity to nitrogen atoms in comparison with chromium atoms act as a barrier for nitrogen accumulation upon subsequent N^+ ion implantation.

A similar result is observed also in the case of consecutive Ar^+ and O^+ ion implantation into copper nickel alloy $Cu_{50}Ni_{50}$ [7]. Segregation of copper atoms onto a surface under irradiation by Ar^+ ions decreases accumulation of oxygen atoms upon subsequent O^+ ion implantation more than by an order of magnitude.

Upon consecutive irradiation by O^+ and N^+ ions the maximum nitrogen concentration in nanosized surface layers of stainless steel decreases more than twofold to 6 at % (Fig. 5a). It appears that in this case the nanosized surface layer is enriched with chromium and oxygen atoms to 26 and 28 at %, respectively (Fig. 6).

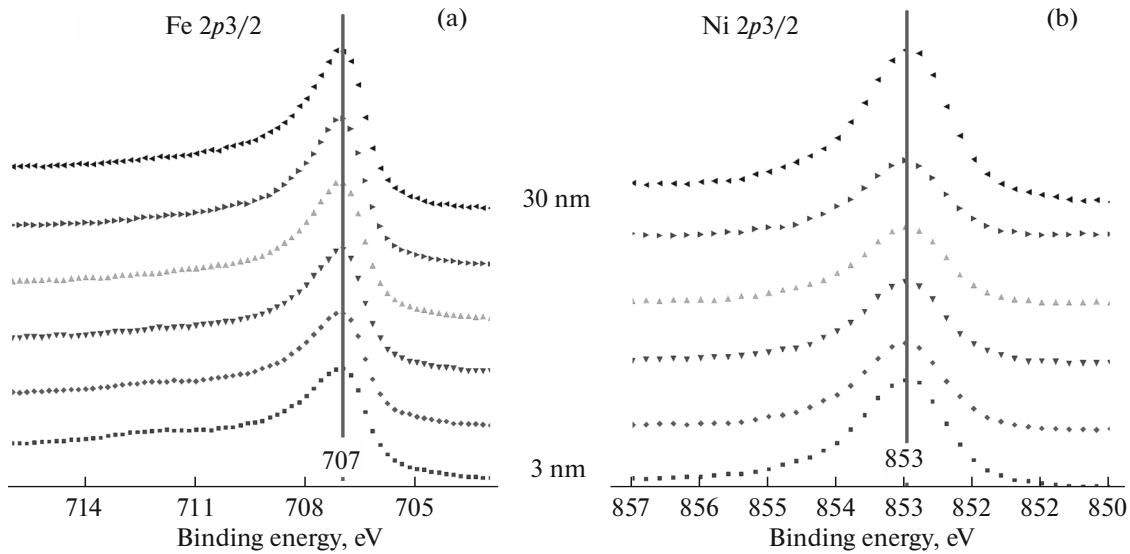


Fig. 4. Fe 2p_{3/2} (a) and Ni 2p_{3/2} (b) XPS spectra from surface layers of a sample irradiated by N⁺ ions.

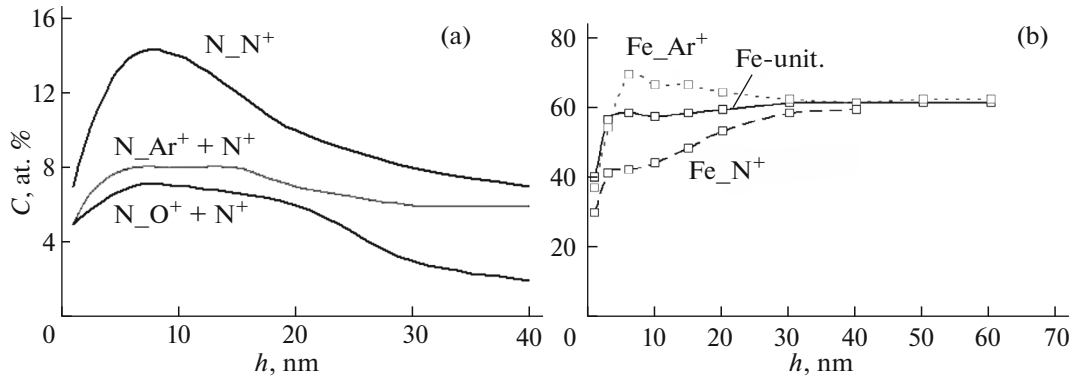


Fig. 5. Nitrogen distribution in surface layers of samples after N⁺, Ar⁺ + N⁺, and O⁺ + N⁺ ion implantation (a) and iron distribution in initial samples after Ar⁺ ion implantation and N⁺ ion implantation (b).

Enrichment with chromium and oxygen atoms is accompanied by formation of chromium oxide Cr₂O₃ and chromium hydroxide CrOOH (Fig. 7a) [4, 5]. Chromium nitride CrN is also formed in addition to these compounds (Fig. 7). It is assumed that the decrease in nitrogen accumulation upon preliminary irradiation by O⁺ ions can be attributed to the fact that chromium atoms, which determined nitrogen accumulation to 14 at %, in this case, are occupied by oxygen in oxide Cr₂O₃ and hydroxide CrOOH phases.

Therefore, based on the presented experimental results it is possible to conclude that accumulation of nitrogen atoms in nanosized surface layers of 03Kh17N12M2T stainless steel upon N⁺ ion implantation is mainly determined by the existence of chromium atoms in alloy.

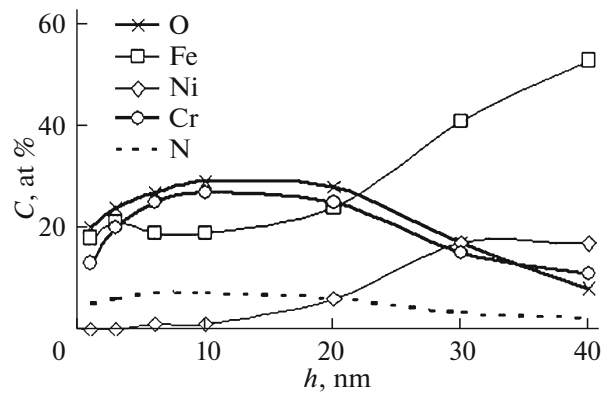


Fig. 6. Concentration profiles of element distribution in surface layers of stainless steel after consecutive irradiation by O⁺ and N⁺ ions.

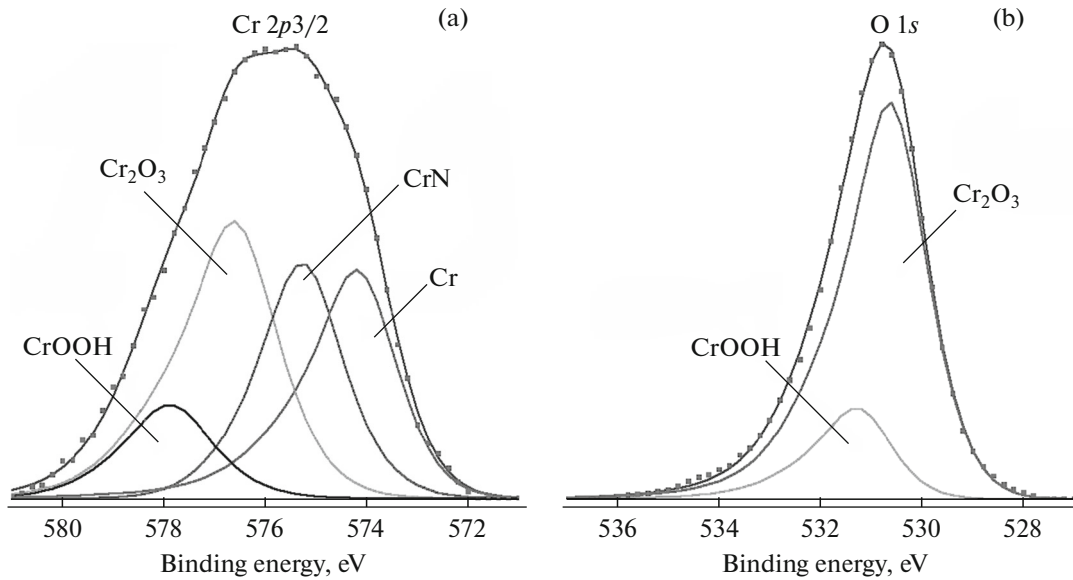


Fig. 7. Cr 2p_{3/2} and O 1s XPS spectra acquired at a depth of 10 nm in a sample consecutively irradiated by O⁺ and N⁺ ions.

CONCLUSIONS

N⁺ ion implantation into 03Kh17N12M2T stainless steel is accompanied by accumulation of nitrogen atoms in nanosized surface layers up to 14 at %, formation of metal nitrides, mainly chromium nitride CrN, and nitrogen interstitial solid solution into a crystal-line lattice of a multicomponent system.

It has been demonstrated that accumulation of nitrogen atoms in nanosized surface layers of 03Kh17N12M2T stainless steel upon N⁺ ion implan-tation is mainly determined by chromium atoms.

FUNDING

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

REFERENCES

1. D. A. Kozlov, B. A. Krit, V. V. Stolyarov, and V. V. Ovchinnikov, *Inorg. Mater.: Appl. Res.* **3**, 216 (2010).
2. S. N. Bratushka and L. V. Malikov, *Vopr. At. Nauki Tekh., Ser.: Vak., Chist. Mater., Sverkhprovodn.*, No. 6, 126 (2011).
3. V. L. Vorob'ev, P. V. Bykov, V. Ya. Bayankin, S. G. Bystrov, V. E. Porsev, and O. A. Bureev, *Fiz. Khim. Obrab. Mater.* **3**, 18 (2013).
4. V. I. Nefedov, *X-ray Electron Spectroscopy of Chemical Compounds* (Khimiya, Moscow, 1984).
5. C. D. Wagner, *Handbook of X-ray Photoelectron Spec-troscopy*, Ed. by C. D. Wagner, W. M. Rigus, and L. E. Davis (Perkin-Elmer, Eden Prairie, 1979).
6. *Practical Surface Analysis by Auger and X-Ray Photo-electron Spectroscopy*, Ed. by D. Briggs and M. Seah (Wiley, New York, 1983).
7. V. L. Vorob'ev, F. Z. Gil'mutdinov, P. V. Bykov, and V. Ya. Bayankin, *Khim. Fiz. Mezosk.* **19**, 76 (2017).

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