PREPARATION OF LARGE AREA SUBSTRATES USING HIGH APERTURE HALL CURRENT ACCELERATOR

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Abstract
A large aperture Hall current accelerator has been developed for ionic cleaning of substrates before deposition of protective and decorative layers. The accelerator has a large aperture of 1400 mm and a power up to 10 kW. High ionic currents permit one to use the source also for ion implantation. Various gases can be used for both purposes: argon, nitrogen, oxygen, etc. The current-voltage characteristics for nitrogen at various pressures are presented. The ionic implantation of nitrogen at discharge voltage 900 V and discharge current 3 A into austenitic stainless steel is performed. The depth profiles measured with the aid of secondary-ion mass spectroscopy for the austenitic stainless steel substrates nitrided during 30 and 90 min are presented. The load dependence of microhardness after ionic nitriding was measured. The possibility is discussed of the application of the novel Hall current accelerator for the pre-treatment of the large area substrates before thermal spraying of coatings in order to improve the adhesion.

Introduction

Plasma spray is a very effective, robust and unexpensive method for deposition of protective and wear resistant coatings on the large area substrates having complicated form. The quality of coated parts depends hardly on properties of interface between the coating and the substrate. Recently, it has been shown that an additional modification of the substrate can drastically enhance the the adhesion of the coating, and the overall performance of the coated part [1]. This technology called duplex coating uses the ionic implantation of the substrate in order to decrease the difference in composition and properties between the coating and the substrate. For example, the nitriding of the substrates before deposition of nitrides coatings allowes to increase the corrosion resistance and adhesion of the hard coatings [2]. Various methods for the ionic modification of substrates were developed. The ionic implantation methods traditionally used in the semiconductor technology permit one to form the alloyed layers buried rather deep in the material (several microns or even tens of microns) due to the high ballistic penetration depth of ions having energy of several hundreds of keV [3]. Unfortunately, this method does not fit the requirements of metallurgical applications due to the low ionic flux (below 1-3 $\mu A/cm^2$). The low intensity of ionic beams does not allow to produce the metallurgically significant concentrations of implanted element in a reasonable time. In the plasma immersion ionic implantation method (**PIII**) the lower energy of ions is used (20-100 kEV). Lower ballistic depth (about 100 nm) is compensated by the higher ionic flux (about 1 mA/cm^2) and

additional heating of the substrate (usually to 350-400 ºC) [4, 5]. PIII permits to produce the 2 to 10 μm thick alloyed zone. However, even the moderate heating can deteriorate the properties of several heat-treated alloys. Only recently the method of low-energy high current ionic implantation (**LEHCII**) was developed [6, 7]. In this method the energy of ions is below 1000 eV (ballistic penetration depth about 5 nm [9]) but the ionic flux is very high reaching 1 mA/cm^2. Particularly, the Kaufman broad beam ionic sources are used for this purpose [3, 7]. LEHCII permits to alloy with nitrogen the surface layers of steels having thickness of few μm even without additional heating [6]. Recently, the high power large aperture Hall current accelerator was developed [9, 10]. The Hall current accelerators have several important advantages in comparison with Kaufman sources [11–13]. Particularly, the Hall current accelerator has higher aperture (1400 mm scalable up to 3000 mm in our case), high power (up to 10 kW), is more robust and simple in exploitation. It is easy to combine the Hall current accelerator with existing technologies for deposition of coatings. It can be used not only for ionic cleaning [9, 10] but also for ionic implantation. Various gases can be used for both purposes: argon, nitrogen, oxygen, etc. The goal of this work is to chracterize the process of ionic nitriding of austenitic stainless steel with the aid of Hall current accelerator.

Experimental

Hall current accelerator described elsewhere [9, 10] has a form of elongated loop with vertical aperture fo 1400 mm (Figure 1). Horizontal aperture (distance between the parts of the loop) is 55 mm. The nitrogen implantation into austenitic stainless steel 12X18H9T (Russian standard GOST 5632) was studied at discharge voltage U = 900 V, discharge current I = 3 A during 30 and 90 min. No additional heating of the samples was used. The composition of the steel was controlled by the spark spectral analysis according GOST 22536.13 "Carbon steel and cast iron. Methods of spectral analysis". The carbon content was measured coulonometrically according GOST 22536.1. The steel contains (in wt. %) 0.11 C, 17.0 Cr, 8.8 Ni, 0.35 Ti, 0.28 Mo, 0.55 Si, 0.35 Mn, Fe (matrix). Samples having dimension 20×15 mm were cut from the rolled stainless steel strip of thickness 2 mm, ground and polished. After degreasing in ethanol and distilled water, the sample matrix (four samples with overall length 20×4 = 80 mm) was mounted into a holder positioned before the Hall current accelerator at the distance of 10 cm (Fig. 1). The surface of the samples was parallel to the surface of the accelerator. The longitudinal axis of the sample matrix was perpendicular to the axis of the accelerator (Fig. 1). This geometry permitted to characterize the distribution of properties of ionically implanted material in the gradient of the ionic flux.

The distribution of C, N, Fe, Cr and Ni in the samples after nitrogen ionic implantation was determined using the secondary ion mass spectroscopy (SIMS). An *ims 3f* secondary ion mass spectrometer (Cameca, France) has been used for in-depth analyses of the films and substrates. O_2^+ ions accelerated with energy 12.5 kV were used as primary ions. The primary ion current I_p ranged from 250 to 1800 nA. The primary ion beam was rastered over a square area 250×250 μm. The secondary ions, accelerated by 4.5 kV, were collected from a square area 100×100 μm in the middle of the rastered area. The energy band pass filter for the secondary ions was 50 eV, centered at the maximum energy of the secondary ions. The distributions of C, N, Ti, Fe, Cr and Ni were studied by profiling isotopes $^{12}C^-$, $^{14}N^-$, $^{24}C^-$, $^{28}CO^-$, $^{26}CN^-$,

$^{56}Fe^{+}$, $^{52}Cr^{+}$ and $^{60}Ni^{+}$ respectively. The $^{26}CN^{-}/^{24}C^{-}$ ratio was used for the estimation of nitrogen concentration by depth profiling due to the very low intensity of $^{14}N^{-}$ line. The depth of the sputtered craters were measured with a *Talysurf 10* instrument (Rank Taylor Hobson, UK). Each crater was measured several times in the central region of the crater. The deviation in the average depth ranged from 2 to 11%. The microhardness of the nitrided samples was measured at various loads (from 0.1 to 0.85 N) with the aid of *PMT* instrument (LOMO, Russia).

Results and discussion

In Figure 2 the voltage-current characteristics for nitrogen discharge are shown for various nitrogen pressures *p*. It can be seen that the at *p* below 30 mPa the slow increase of discharge current *I* proceeds with increasing dicharge voltage *U*. At *p* = 49 mPa the voltage-current characteristic differs drastically from those at low *p*. The high discharge current of about 6 A can be reached already at 2 keV. In Figure 3 the dependence of microhardness on the transversal coordinate is shown for sample matrix implanted by nitrogen at *U* = 900 V, *I* = 3 A during 90 min for two loads of 98 and 830 mN. The microhardness measured at high load reflects the bulk value hardness of stainless steel and remains almost unchanged. Microhardness measurements at low load are sensitive to the properties of the surface layer. Microhardness increases after nitrogen implantation. The microhardness is maximal in the zone close to the source loop (Fig. 1). The followed measurements of the microhardness load dependence and SIMS measurements of the nitrogen depth profiles were performed in this zone of the sample matrix. The full current density (sum of the electron and ionic current) measured in this zone was about 1 mA/cm^2. The microhardness measured along the sample matrix decreases outwards of source axis. At the distance about 80 mm from the source axis the microhardness of surface layer is lower than that of the bulk one. It can be explained by the combined influence of (already low) nitriding and (still rather high) heating by ionic beam. In Figure 4 the dependence of microhardness on the load is shown for the untreated stainless steel substrate and after nitriding during 30 and 90 min. The indentation depth changes from 14 μm at 0.1 N (90 min) to 50 μm at 0.8 N. Therefore, at high loads the thickness of nitrided layer is negligible in comparison with indentation depth, and the hardness of the bulk material is measured (about 3.2 GPa in all three curves). The hardness of untreated material is nearly independent on the load. The implantation of nitrogen increases the surface hardness of the material. After 30 min the hardness at loads below 0.3 N is higher than that of untreated sample. With increasing duration of ionic nitriding the surface hardness increases as well. After 90 min the hardness at 0.1 N is almost two times higher than that of the untreated material. The thickness of the nitrided layer increased as well, namely the hardness drops down to the bulk value only at load of 0.6 N. The depth of the nitrided layer could be rougly estimated from the curves shown in the Fig. 4. It can be supposed that the measured hardness reaches the bulk value if the thickness of the hardened layer is less than 0.1 of indentation depth. This estimation gives about 3 μm for the thickness of the hardened layer.

In the Figure 5 SIMS depth profiles are given for 30 and 90 min treatments. The depth of nitrided layer is about 0.3 μm after 90 min and about 0.1 μm after 30 min. Therefore, the estimation given above delivers overestimated values for the thickness of hardened layer. On the other hand, the microhardness values are understimated

even by load of 0.1 N. Therefore, the measurement of nanohardness with lower loads are needed for the correct estimation of the surface hardness. The thickness of the nitrided layer obtained in our experiments without additional heating of the samples is only slightly lower than that of layer obtained in comparable conditions (700 keV, 2 mA/cm^2, 60 min) by heating up to 280 °C [6]. The thickness of penetration layer is two orders of magnitude higher than the ballistic penetration depth for 900 V and about 2 to 4 orders of magnitude higher than the length of conventional bulk diffusion of nitrogen. Therefore, the paradoxally deep penetration of nitrogen cannot be explained either by ballistic penetration or by conventional diffusion. The mechanism of this process remains not understood and has to be clarified. In particular, the role of very high ionic current and possible non-equlibrium phase transformations have to be studied.

Therefore, The large aperture high power Hall current accelerator permits one to perform the ionic nitriding of the large area substrates improving the surface hardness of the stainless steel. This treatment can be used for the preparation of substrates for subsequent coating with the aid of plasma spraying, vacuum arc deposition, magnetron sputtering etc. On the other hand, the recently developed Hall current accelerator will allow to investigate carefully the paradoxally deep penetration of nitrogen by changing the ion energy, current, substrate temperature and duration of treatment.

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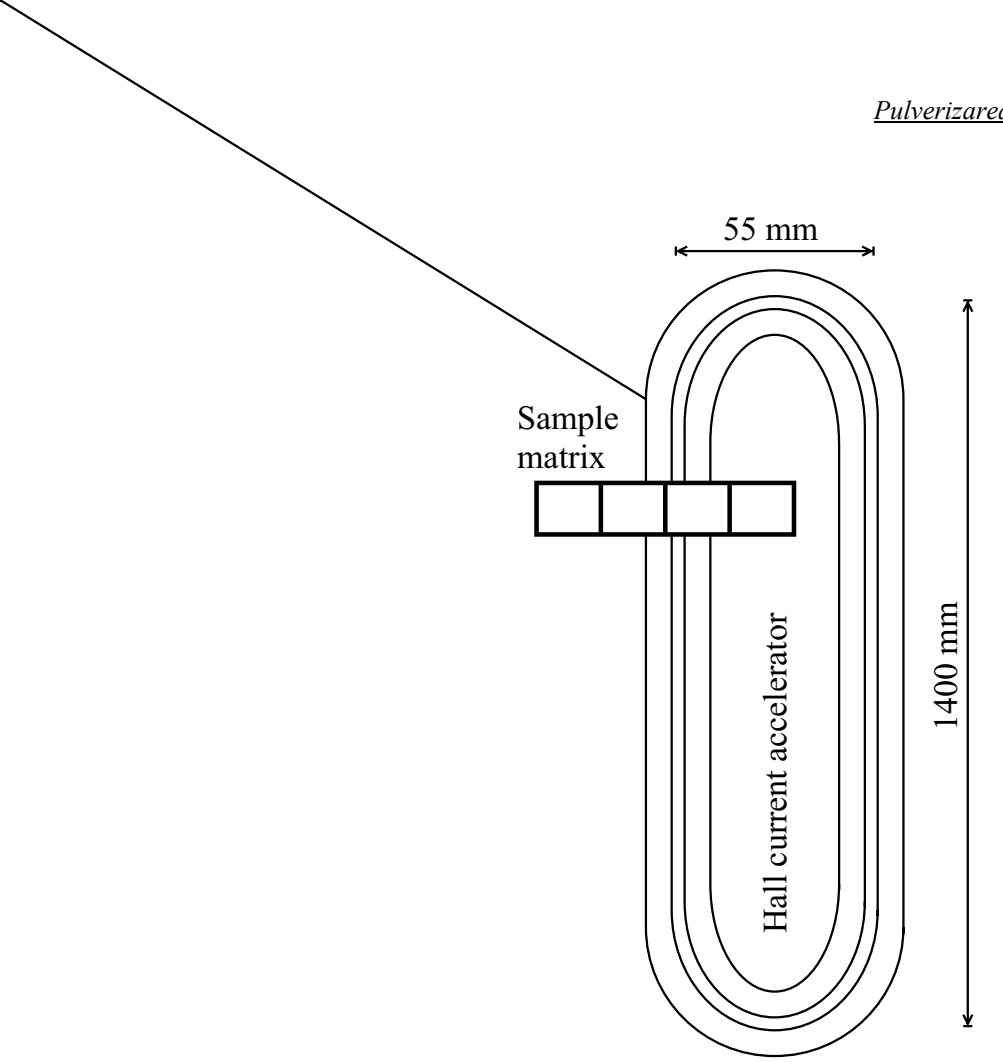

Fig. 1 Scheme of the Hall current accelerator and position of sample matrix

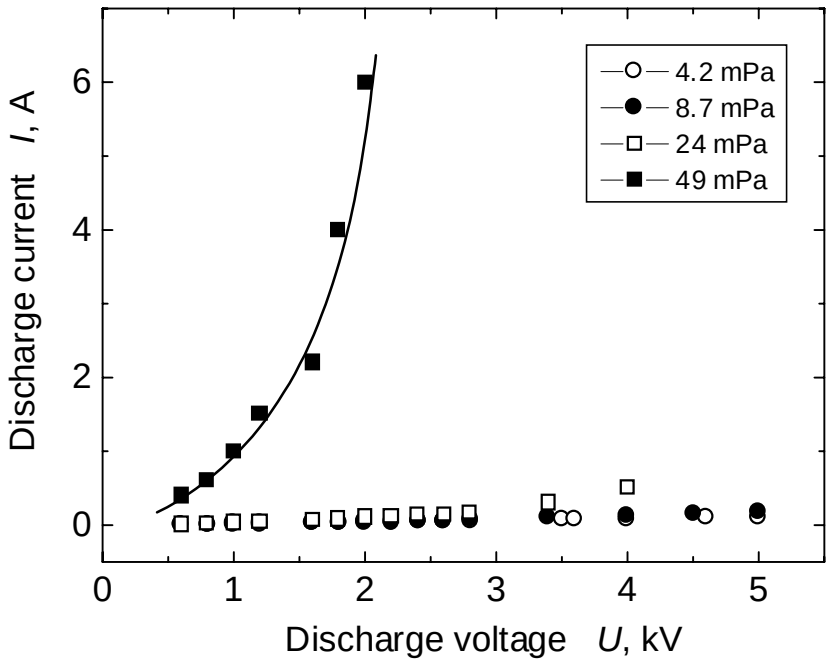

Fig. 2. Current-voltage characteristic for nitrogen for various pressures.

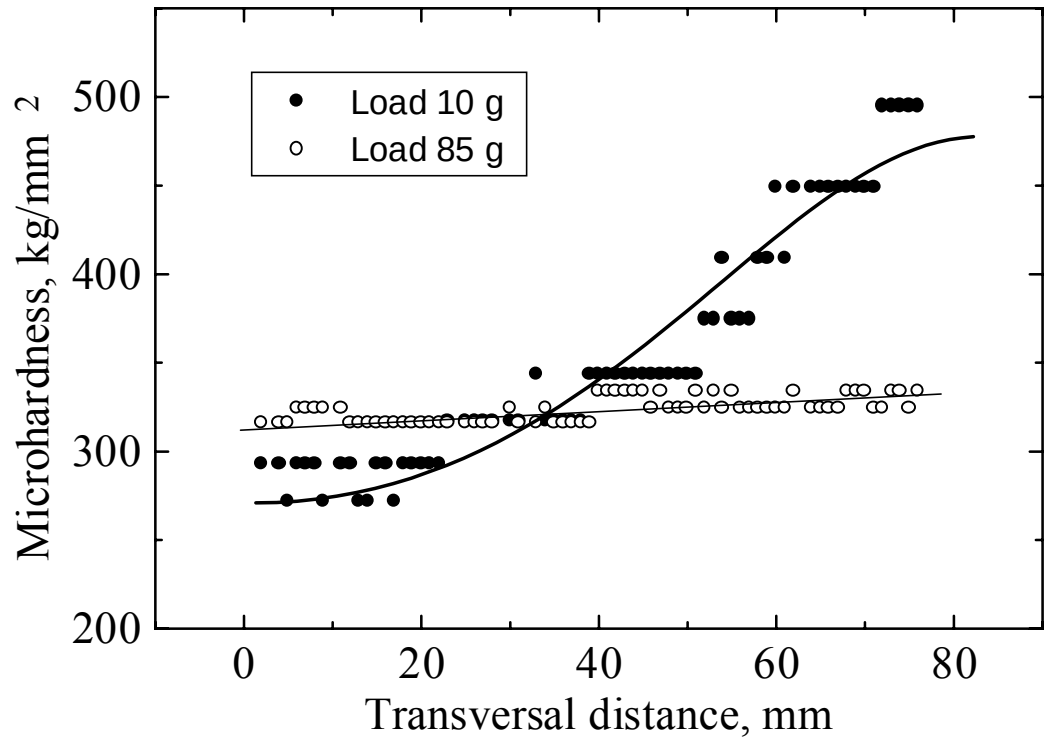

Fig. 3. Distribution of microhardness along the axis of sample matrix (cf. Fig. 1)

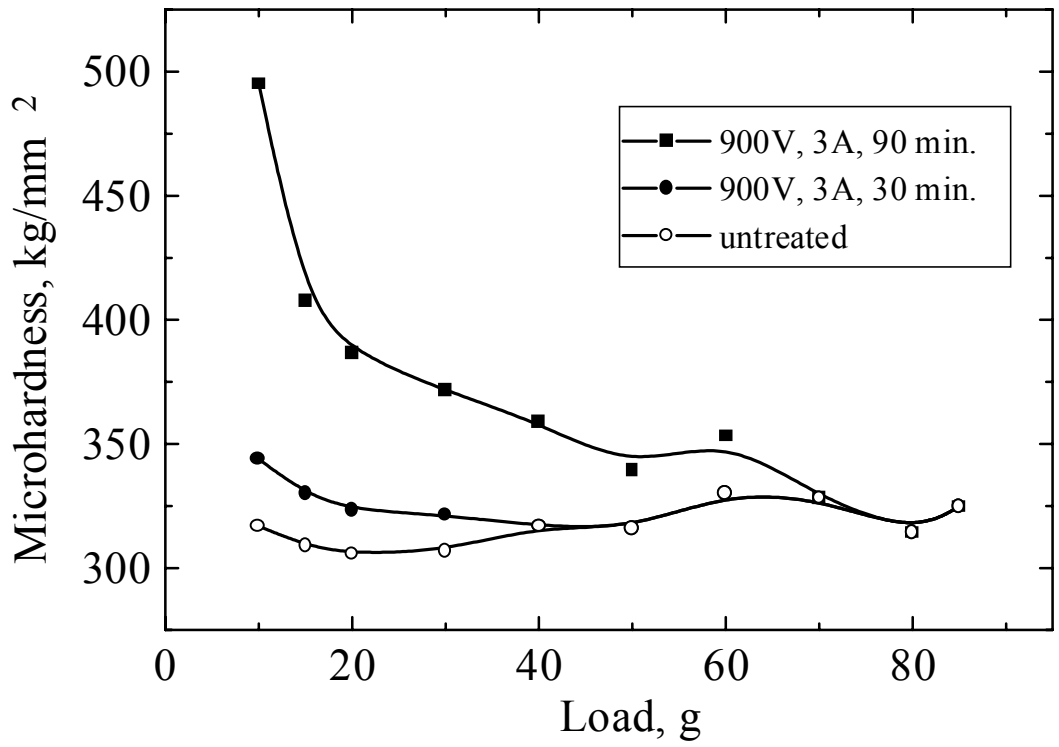

Fig. 4. Dependence of microhardness on load for untreated and nitrided stainless steel samples

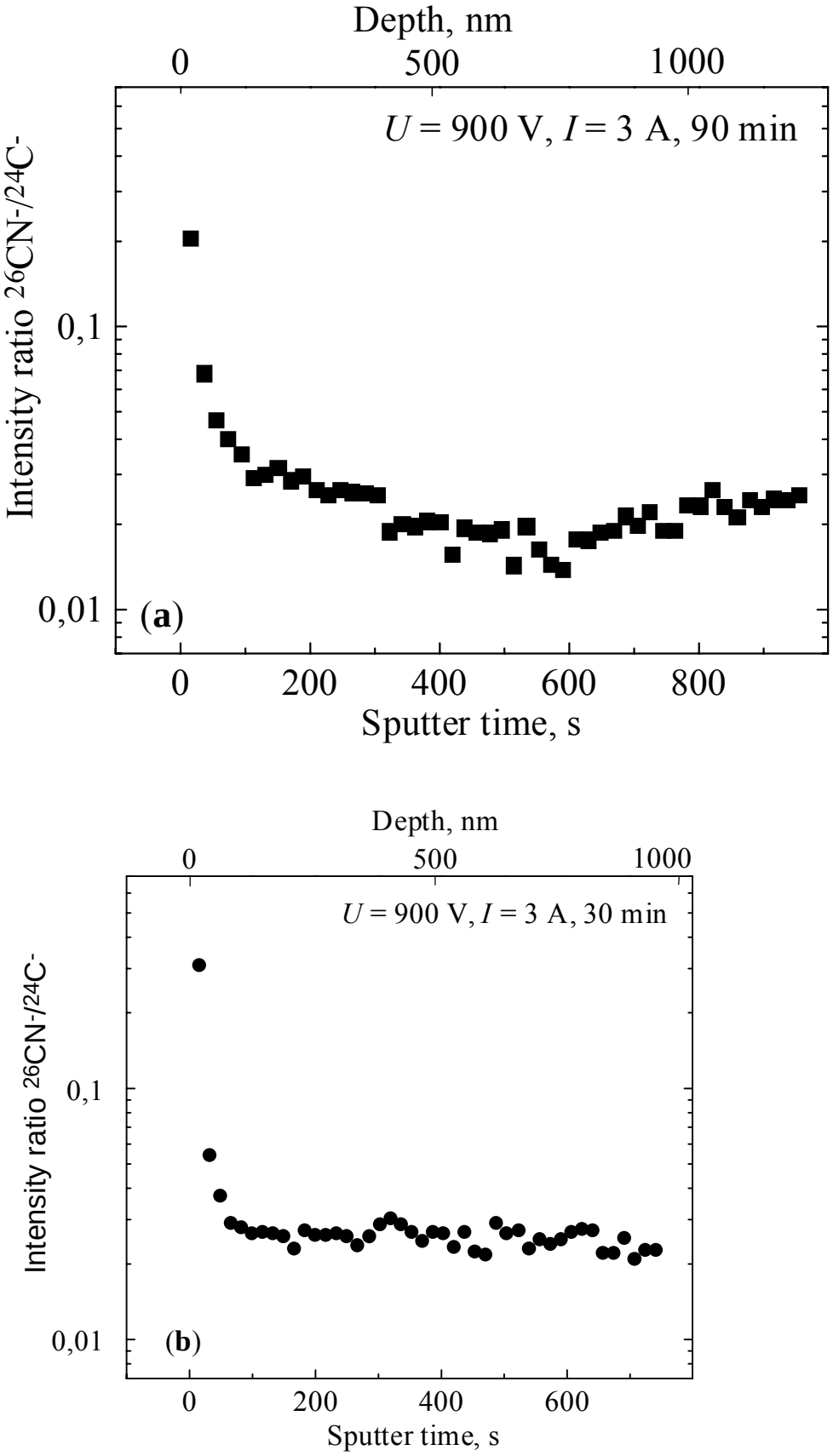

Fig. 5. SIMS depth profiles for the nitrogen implanted into stainless steel at the discharge voltage U = 900 V and discharge current I = 3A. Implantation time t = 90 (a) and 30 min (b).