Influence of the Composition of a Plasma-Forming Gas on Nitriding in a Non-Self-Maintained Glow Discharge with a Large Hollow Cathode

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Abstract—The article presents the results of an investigation into the influence of the composition of a plasma-forming gas (N_2, Ar, He) on nitriding of VT1-0 grade titanium (0.25%–Fe; 0.1%–Si; 0.2%–O) and commercial 40X steel (0.4%–C; 1.0%–Cr) in the plasma of a non-self-maintained glow discharge with a large hollow cathode. It is shown that the efficiency of nitriding of 40X steel weakly depends on the composition of the plasma-forming gas mixture, whereas nitriding of VT1-0 titanium in a helium–nitrogen mixture leads to a noticeable increase in the microhardness of the specimen's surface in comparison with nitriding in an argon–nitrogen gas mixture.

INTRODUCTION

One of the most effective approaches for improving the operational properties of machine parts and mechanisms is the use of materials with special surface layer properties modified by various methods. This is more economically feasible than manufacturing a whole part using stronger but expensive materials. Among the various methods for improving the operational lifetime and reliability of parts, in recent years there has been a trend for the development of ion–plasma surface processing. They include, in particular, ion nitriding [1–2].

In order to create nitrogen-containing plasma in large (0.1–1 m^3) vacuum volumes, mainly glow and arc discharges are used [1, 2]. Arc discharge makes it possible to obtain high values of discharge current (50–200 A) in a continuous mode of operation and at a low (0.01–1 Pa) plasma-forming gas pressure [2]. This facilitates efficient plasma generation with the concentration $n_e \approx 10^9$–10^{10} cm^{-3}. However, the presence of erosion products of the cathode material in arc discharges reduces the area of their industrial applications. The major disadvantage of glow discharge is the relatively high (10–100 Pa) plasma-forming gas pressure and high (600–700 V) discharge voltages [3]. Under such conditions, ions, supplied to the cathode (processed item), waste a major fraction of their energy due to multiple collisions in the cathode layer and inefficient cleaning of the processed materials' and items' surface of the oxide layer, which prevents nitrogen diffusion and, as a consequence, hinders nitriding.

From this point of view, discharges with electron oscillation [4–6] are of interest, for instance, non-self-maintained glow discharge with a hollow cathode. This kind of discharge functions stably at low (to 1 Pa) pressures as a consequence of an injection of charged particles from a supplemental plasma source, and the oscillation of electrons in the hollow cathode leads to an increase in the concentration of generated plasma.

Preliminary experiments with low volume discharge structures (600 cm^3) demonstrated promising prospects for this kind of discharge for low-temperature (to 500°C) nitriding of titanium [6]. In the course of the experiments a dependence was found between the intensity of nitriding and the type of gas added to the nitrogen.

This work is aimed at investigating the influence of the composition of a plasma-forming gas mixture on the nitriding of VT1-0 titanium and 40X steel in the plasma of a non-self-maintained glow discharge with a large hollow cathode (0.2 m^3). The selection of materials for the experiments is determined, on the one hand, by their promising wide commercial application, and, on the other hand, by the availability of preliminary experimental data, earlier obtained, and

published data on conventional nitriding in self-maintained glow discharge.

EXPERIMENTAL

Investigations into the influence of the composition of a plasma-forming gas mixture on the modified layer depth and the operational properties of materials were carried out on a test bench developed on the basis of an NNV-6.6-I1 commercial ion-plasma deposition apparatus (fig. 1). Glow discharge was ignited between a water-cooled tube anode *1* (surface area 150 cm^2) and a hollow cathode (vacuum chamber) *2* with the volume 0.2 m^3. In order to facilitate the ignition of glow discharge and its steady burning at low pressures, an electron source is used based on arc discharge with an integrally cold hollow cathode [7]. Emission of electrons occurred from plasma generated by cold hollow cathode arc discharge via meshes of fine (1 × 1 mm) grids *3*, which acted as an anode for the arc discharge and formed an equipotential gap for the separation of main and auxiliary discharge plasma. Thus, in such an electrode system type, non-self-maintained glow discharge, initiated and supported by self-maintained arc discharge with a cold hollow cathode, occurs.

Nitriding was performed under the plasma-forming gas pressure (gas mixture) 1 Pa, the burning voltage of the non-self-maintained glow discharge 300–400 V, and the ion current density 1–2 mA/cm^2. Specimens were fixed to an holder located under the potential of the hollow cathode (working chamber). Nitriding was performed over 1 h at the specimen temperature ~480–500°C. Heating and cleaning of the samples were carried out by means of bombardment by ions accelerated in the cathode layer of the non-self-maintained glow discharge.

In order to establish the optimal nitriding parameters, a series of experiments was performed with pure nitrogen, argon–nitrogen, and helium–nitrogen mixtures. The gas content percentage was selected from previously obtained modes [6] and was equal to 40% for argon and helium, and 60% for nitrogen.

Preliminary preparation of the samples before loading into the vacuum chamber included the following steps: grinding, polishing, washing with benzene and acetone in an ultrasonic bath for the removal of organic impurities, and wiping with alcohol-wetted cotton fabric. Final cleaning was performed in argon plasma over 10 min.

The structure and phase composition of the nitrided samples were studied by optical metallography (Olympus GX 71 optical microscope), scanning electron microscopy (Quanta 600 FEG scanning electron microscope), and X-ray structure analysis (ARL X'TRA diffractometer with CuK_α radiation). The microhardness was measured using a DM 8B AUTO automatic microhardness tester on the surface and over the depth of the samples, with a step of 10 μm from the surface of the samples, at a load on the indenter of 0.05 and 0.1 N.

Microhardness *HV* of the surface layer of specimens after nitriding in various gases, GPa. Initial microhardness of 40X steel was ≈2.7 GPa, and of VT1-0-grade titanium – ≈2 GPa

Material \ Plasma-forming gas	N_2	N_2 + Ar	N_2 + He
Steel 40X	11.4	10.8	11.8
Titanium BT1-0	2.0	2.7	3.4

RESULTS AND DISCUSSION

The measured results of the processed material's surface microhardness are summarized in the table.

From an analysis of the presented results it is possible to outline the following trends. Nitriding of 40X steel in pure nitrogen for one hour leads to a significant increase in the surface microhardness (table) and in its significant increase in the subsurface layer (Fig. 2). An addition of argon or helium to nitrogen does not modify the microhardness compared to processing in pure nitrogen. The thickness of the layer with increased hardness is about 100–150 μm, and maximal hardness is possessed by the subsurface layer, the thickness of which is 5–10 μm.

At the same time nitriding of titanium in a helium–nitrogen gas mixture leads to a higher increase in the microhardness both on the titanium surface (table) and deep in the bulk (Fig. 3) in comparison with nitriding in pure nitrogen or an argon–nitrogen gas mixture.

The use of helium in the mixture with nitrogen resulted in an increase in the surface microhardness by 1.3 times; the thickness of the modified layer with increased hardness is 20–35 μm.

From analysis of the microstructure of 40X steel sample cross-sections (Fig. 4a), made by scanning electron microscopy, after nitriding, it is possible to outline two distinctly different layers: surface (nitride) and intermediate (diffusive saturation), smoothly blending into the main bulk of the material. The thickness of the nitride layer is ≈20–35 μm depending on the composition of the plasma-forming gas mixture and is identified as Fe_4N.

As a result of the nitriding of VT1-0 titanium (Fig. 4b), nitride and diffusive layers are also formed. This is confirmed by metallographic studies of the sample cross-section. Since the titanium nitride layer is more brittle in comparison with the diffusive zone, it crumbles during preparation of the sample cross-section. The thickness of the nitride layer was 2–2.3 μm

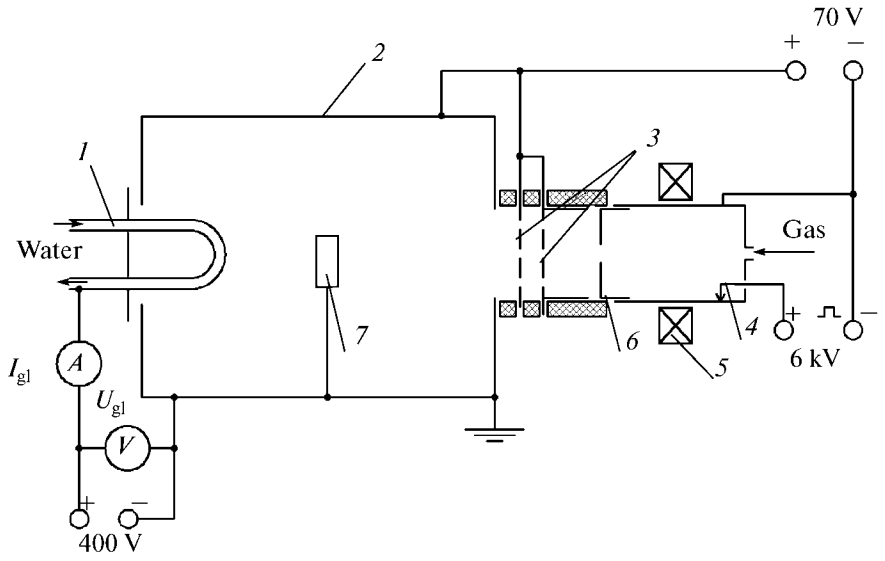

Fig. 1. Scheme of experimental setup: (*1*) water-cooled tubular anode for glow discharge; (*2*) vacuum chamber–cathode for glow discharge; (*3*) mesh anode for arc discharge; (*4*) ignition electrode for arc discharge; (*5*) magnetic coil; (*6*) diaphragm (*7*) processed samples.

for the helium–nitrogen mixture, 1.3–1.7 μm for the argon–nitrogen mixture and plasma-forming gases, and less than 0.5 μm for pure nitrogen.

Elemental chemical analysis over the depth of the specimens and the depth distribution of nitrogen as a function of the composition of a plasma-forming gas mixture (Fig. 5) were studied on the samples of 40X steel using a Quanta 600 FEG scanning electron microscope equipped with a Trident X-ray attachment, which facilitates the determination of the material's chemical composition.

At present several concepts are known which explain the process of nitriding in glow discharge [10]. However, up to now there is no common opinion concerning nitrogen saturation mechanism of materials processed in a gas discharge plasma. In one of the approaches explaining the saturation process, the leading role in nitriding in glow discharge is assigned to atomic nitrogen and the intensity of the process is determined, specifically, by its amount. One of the hypotheses, explaining the formation of atomic nitrogen in a gas discharge, in addition to dissociation by electron impacts, dissociative recombination and oth-

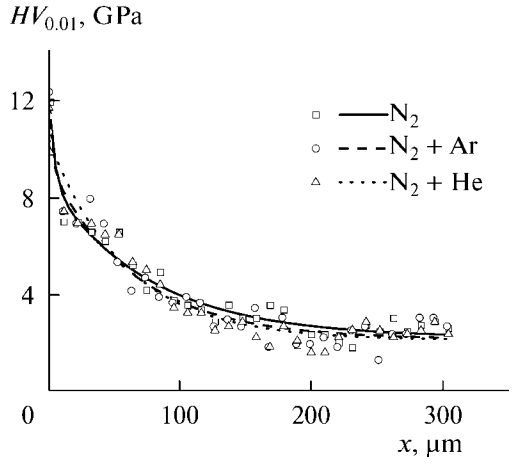

Fig. 2. Distribution of the microhardness over depth of the 40X steel specimens after nitriding for 1 h at ≈500°C.

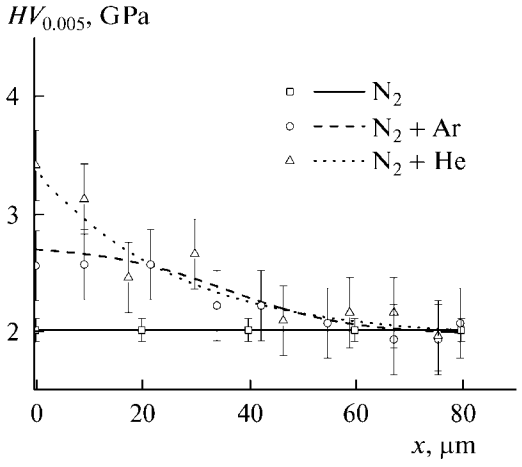

Fig. 3. Distribution of the microhardness over depth in VT1-0-grade titanium specimens 0 after nitriding in gas mixtures.

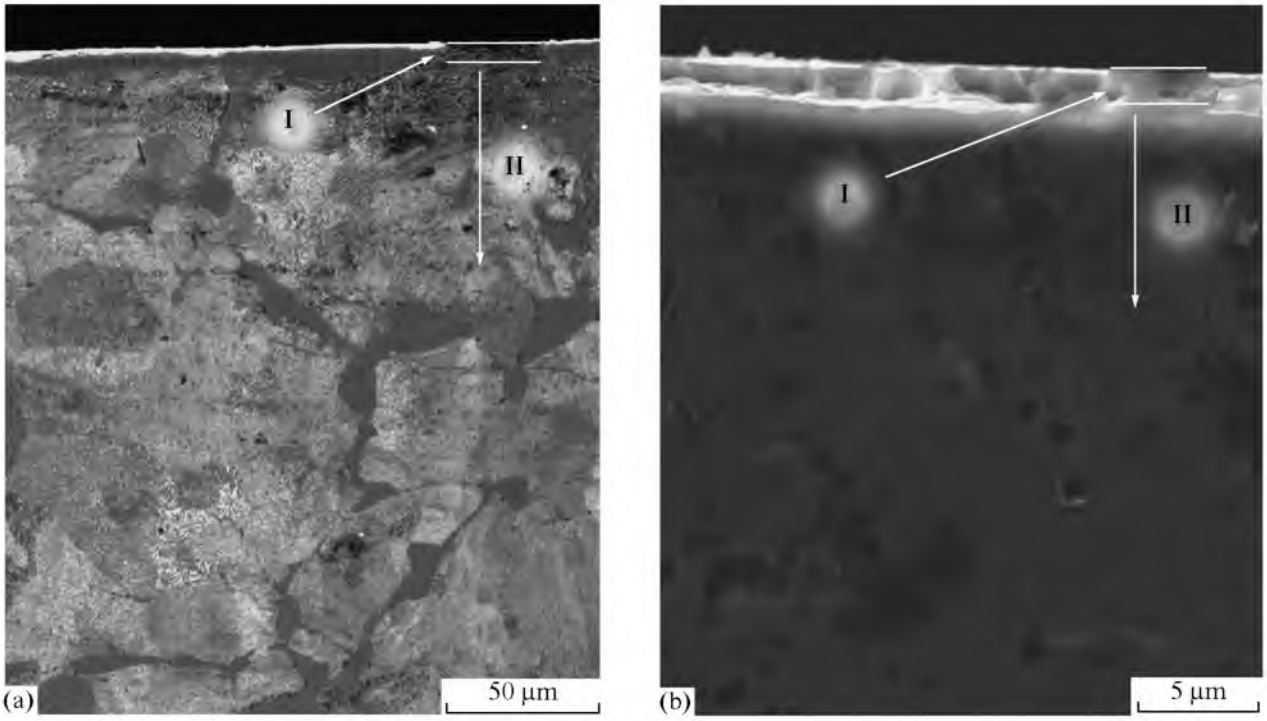

Fig. 4. Structure of the samples cross-sections of 40X steel (a) and VT1-0-grade titanium (b) processed by nitriding at 480–500°C for 1 h in the N_2 + Ar: I—nitride layer II—layer of diffusive saturation with nitrogen smoothly blending into the main bulk of the material.

ers, may be the course of ion–molecular reactions, which lead to the dissociation of the nitrogen molecule resulting in the formation of a neutral atom and an ion of nitrogen. The ions can acquire sufficiently high energy and can recharge at a cathode potential drop, which contains almost the entire discharge voltage. As a consequence of the directed motion of particles in the cathode layer and subsequent recombination, a layer of adsorbed nitrogen particles is formed on the surface, and under the continuing action of the incident flux, particles of the adsorbed layer can be sputtered or become embedded in the surface forming a solid solution. Under such conditions the nitrogen concentration value is a determining factor for the beginning of nitride formation, which, in turn, hinders nitrogen diffusion from the surface into the processed material.

The studies of the phase composition of nitrided samples, performed by X-ray analysis using a grazing beam, showed that nitrogenation of 40X steel at 480–500°C leads to the formation of a near-surface layer with complex phase composition, including the following phases: Fe_2N; Fe_3N; Fe_4N; and Fe_3O_4. The analysis of data obtained for nitrided samples of VT1-0 titanium in all gas mixtures shows that the following phases are formed: α-$TiN_{0.3}$; ζ-Ti_4N_{3-x} (Fig. 6). It should be noted that the phases TiN and Ti_2N were not detected, that can be attributed to low nitride layer thickness.

In the studied discharge type, as a consequence of the fact that nitriding occurs at a low (≈1 Pa) pressure, the free path length of the ions, bombarding the processed sample surface, is comparable with the width of the cathode layer. Under such conditions the ions, with energy equal to the cathode potential drop (300–400 V), efficiently sputter the oxide film, which prevented nitrogen diffusion into the sample, thus pro-

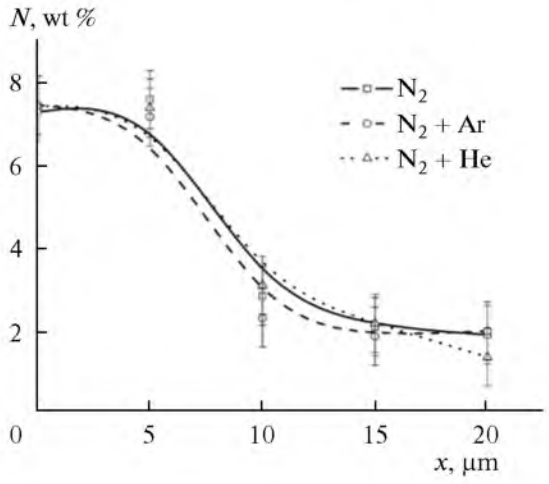

Fig. 5. Depth distribution of nitrogen in samples of 40X steel after nitriding in a gas mixture.

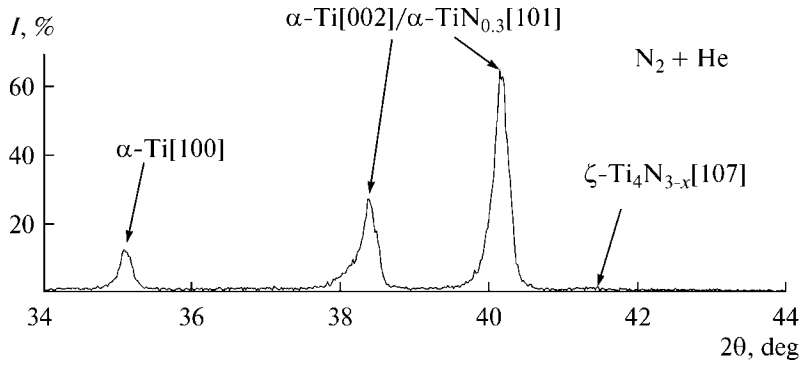

Fig. 6. Section of the X-ray pattern of the VT1-0-grade titanium surface layer, processed by nitrogenation in the plasma of hollow cathode glow discharge.

moting the creation of favorable conditions for titanium nitriding.

CONCLUSIONS

The possibility for the nitriding of 40X steel and VT1-0 titanium samples in the plasma of a non-self-maintained glow discharge with a large hollow cathode, at low (to 1 Pa) pressures, when the processed samples are located under the cathode potential has been demonstrated. Nitriding of commercial VT1-0 titanium in the plasma of a hollow cathode non-self-maintained glow discharge at low pressures and relatively low (below 500°C) temperatures leads to the formation of a multilayer structure consisting of a near-surface layer, up to 2.5 μm in thickness, which possesses relatively high (up to 3.4 GPa) hardness, due to the formation of titanium-based nitride phases. Under the near-surface layer a layer of diffusive saturation is formed, up to 35 μm in thickness and 2.5 GPa in hardness.

The structure and microhardness of the nitrided layer of commercially pure titanium significantly depend on the composition of the plasma-forming gas. The highest titanium surface microhardness is achieved when using a helium–nitrogen gas mixture (N_2–He).

Nitriding of 40X steel in the plasma of a hollow cathode non-self-maintained glow discharge results in the formation of a multilayer structure with a surface hardness of 11–12 GPa and a thickness up to 150 μm. In this case the nitriding intensity weakly depends on the composition of the plasma-forming gases.

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