Ion-beam chemical-thermal treatment of aluminum

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Abstract. The paper reports on a study of A7 aluminum alloy exposed to thermochemical treatment with a nitrogen ion beam produced in a source based on a non-self-sustained hollow-cathode glow discharge. The material was placed in a plasma generated by a source with a thermionic and hollow cathodes and simultaneously treated by accelerated ions and neutrals of the working gas. No negative bias was used, allowing dielectric surface treatment with no cathode spots. The ion charge at the treated surface was compensated by electrons from the plasma. The specimen temperature was maintained independent of the ion beam energy and current using an active screen whose temperature was controlled by applying a negative bias. The method provides the formation of a nitride film on the Al surface.

1. Introduction

Nitride layers on aluminium products can improve their hardness and wear resistance, which is urgent for science and technology. One of the ways to form nitride layers is plasma immersion ion implantation. However, AlN is dielectric, and this greatly limits the capabilities of such technologies because a negative bias should be applied to a substrate [1], and the bias field required for nitrogen ion acceleration and surface cleaning is shielded by nitride layers. The problem can be partly solved by applying a pulsed bias at a frequency of no less than tens of kilohertz [2], but the potential at the surface of a nitride film will vary with its thickness, due to electric field attenuation in the dielectric layer, and so does the ion energy delivered to the surface. The second problem with negative bias is that an electric field is present at the interface between a dielectric film and a metal substrate, provoking microbreakdowns which can result in micropores [3]. The presence of micropores directly beneath the nitride film decreases its adhesion and precludes the further diffusion of nitrogen into the substrate. Another way of forming nitride layers is through ion beam surface treatment in which the ion energy is independent of dielectric films and the positive ion charge at the treatment surface is efficiently compensated [4], e.g., by electrons from near-substrate bulk plasma.

Here we present experimental data on combined surface treatment of aluminum with a nitrogen ion beam and gas discharge plasma and on such treatment in an acetylene-containing gas mixture. On the one hand, acetylene contains carbon which provides nitrogen hardening of substrates, and on the other hand, it contains hydrogen which binds residual oxygen on treated surfaces, precluding the formation of oxide films.
2. Experimental setup

In our experiments, we used a vacuum chamber of dimensions 600×600×600 mm (figure 1) pumped by a turbomolecular pump at a rate of 500 l/s. In the chamber, a non-self-sustained arc discharge (main discharge) was ignited by a PINK plasma generator with a thermionic and hollow cathodes [5]. The discharge was powered by a power supply with an output current of 5-120 A and operating voltage of up to 200 V. The power supply was equipped with an arc quenching system. The inner walls of the vacuum chamber served as the main discharge anode. The ion source comprised a water-cooled casing, which was electrically decoupled from the chamber walls, and a cylindrical stainless steel cathode cup of inner diameter 100 mm and height 50 mm on the inside. The emission electrode was fixed on the side flange of the vacuum chamber such that its hole was fully overlapped. In the emission electrode, there was a window of diameter 100 mm covered with a fine mesh grid (0.5×0.5 mm) which had a geometric transparency of ≈45 %. The cathode cup and the emission electrode were coaxially fixed at 25 mm from each other and were kept at ground (vacuum chamber) potential, forming a hollow cathode with a ring gap which opposed a coaxially located anode of dimensions Ø150×30 mm. The electrons produced in the main discharge penetrated through the emission grid into the hollow cathode and oscillated there, ionizing the gas supplied through the gas inlet of the ion source. Thus, an auxiliary non-self-sustained hollow-cathode glow discharge was ignited in the ion source. The ions from the auxiliary discharge plasma were accelerated in the cathode layer near the emission electrode toward the vacuum chamber, and part of the ions passing through the emission grid formed an ion beam. The auxiliary discharge was powered by a pulsed source with an output voltage of up to 300 V, average current of up to 20 A, frequency of up to 5 kHz, and pulse duty factor of 10-100 %, providing the generation of beams in steady mode. The working gases were argon, nitrogen, and acetylene. Acetylene was supplied only in the ion source to avoid chemical etching of the thermionic cathode in the PINK plasma generator.

![Experimental scheme](image-url)
The test A7 aluminum specimens were polished, washed with benzene in an ultrasonic bath for 15 min, and fixed on a stainless steel holder of dimensions $\varnothing100\times10$ mm which was located 200 mm away from and coaxially to the emission electrode and was kept at floating potential. The temperature of the holder was measured with a chromel-alumel thermocouple. The vacuum chamber was pumped to a pressure of no worse than $5\times10^{-2}$ Pa. Before ion-plasma thermochemical treatment in nitrogen or in a nitrogen-acetylene atmosphere, the specimen surface was cleaned with an Ar ion beam for which a main discharge with a current of 85 A was ignited in argon at an operating pressure of $1.5\times10^{-1}$ Pa and an auxiliary discharge with a voltage of 300 V and current of 8 A was ignited in the ion source. Because the ion beam power was insufficient for heating the specimen holder to the required temperature (580°C), an active screen in the form of a stainless steel cup of dimensions $\varnothing140\times20$ mm was located coaxially to the holder without their electrical contact. Upon applying a negative bias from a source with an output voltage of up 1 kV and current of up to 5 A, the screen was heated and its thermal radiation heated the holder. Thus, the temperature of the holder was controlled by varying the bias at the screen. The time of ion cleaning and heating was 20 min. When the specimen temperature reaches its specified level, the argon atmosphere was replaced by nitrogen, and the pressure was set at 0.6 Pa and the auxiliary discharge voltage and current at 200 V and 10 A. One specimen was treated in pure nitrogen (specimen No. 1), and one specimen was treated in a nitrogen-acetylene environment (specimen No. 2). The nitrogen pressure was the same, and the amount of acetylene was such that its partial pressure was 10%. The time of isothermal aging was 4 h. After treatment, the specimens were cooled in vacuum at a pressure of no worse than $5\times10^{-2}$ Pa.

The surface of the specimens was examined on a scanning electron microscope Philips SEM 515, PMT-3M microhardness tester, and XRD-600 diffractometer in CuK$\alpha$ radiation at a beam incidence angle of 4°.

3. Results and discussion

After treatment, both specimens revealed a black surface layer. On specimen No. 2, the layer was continuous, and on specimen No. 1, it was covered with deep cracks (figure 2). The coating formed on specimen No. 1 was flaked off as large (hundred micrometers) plates partially overlapping each other. Such surface plates contain $\sim30\%$ of nitrogen, which evidences that the AlN content in this layer is high. In addition to nitrogen, this region contains $\sim7\%$ of oxygen. Thus, ion bombardment before thermochemical treatment fails to provide sufficient surface cleaning from oxides, and nitrides and oxides in our experiments were formed with about the same efficiency. This result agrees with other data on nitriding of aluminum and its alloys [6]. Such extensive film exfoliation could happen on cooling due to different (almost by an order of magnitude) linear thermal expansion coefficients of the film and substrate. At the same time, this explanation implies the presence of a sharp film–substrate interface. According to its analysis, the film spall region contains oxygen and nitrogen in about equal proportions, but this can be due to surface oxidation when the specimen is removed from the vacuum chamber. Our elemental analysis of specimen No. 2 suggests that mostly Al carbide is formed on its surface despite the 10% content of acetylene in the working mixture. The oxygen content in the layer remains almost unchanged through hydrogen is present in the ion flow. These data also point to a strong effect of the residual atmosphere on the formed layer.

According to XRD data, the surface of specimen No. 1 contains a large amount of cubic and hexagonal AlN (up to 43% and 10%, respectively). The content of Al2O3 reaches 32%. Along with AlN, it contains a large amount of Fe and its nitrides Fe(4-1)N (up to 14%) with cubic, rhombic, and hexagonal structure. On specimen No. 2, any substantial traces of Fe and its nitrides are not found and no hexagonal AlN is detected. The content of cubic AlN is up to 11%. The content of Al2O3 reaches 10%. The surface layer formed on specimen No. 2, compared to specimen No.1, is likely much thinner as its spectrum reveals a peak of aluminum whose content reaches 79%. The presence of Fe and its nitrides on the surface of specimen No. 1 is likely due to severe ion etching of the emission grid and cathode cup of the ion source, transfer of the erosion products to the specimen, and their efficient interaction with nitrogen. The presence of Fe and its nitrides in different modifications on the treated
surface can assist the formation of cubic and hexagonal AlN. When acetylene is supplied to the ion source, its cathode cup and the emission grid are covered with a layer of carbon whose ion etching factor is by an order of magnitude lower than that of iron, and this steeply reduces the delivery of iron to the treated surface and decreases the probability of the AlN formation. The above fact can explain the smaller thickness of the layer formed on specimen No. 2. The decrease in the Al2O3 content in specimen No. 2 can be due to hydrogen which is released via acetylene dissociation and bounded to oxygen.

Figure 2. SEM image and doped gas concentration: a) – specimen 1; b) – specimen 2.

According to microhardness measurements at an indenter load of 20 g, the surface hardness of specimen No. 1 is up to 1.2 GPa and that of specimen No. 2 is up to 0.6 GPa at an initial substrate hardness of $\approx 0.35$ GPa. The difference can be explained by different thicknesses and different phase composition of the layers.

### 4. Conclusions

Thus, the system described in the study allows ion beam plasma treatment of products kept at floating potential. After saturation of A7 aluminum with nitrogen and carbon through ion beam thermochemical treatment, its surface microhardness increases 2-4 times. The use of acetylene in the working gas mixture greatly decreases the concentration of sputtered cathode material and oxides on the treated surface. The obtained experimental data suggest that the presence of iron nitrides on the nitrided Al surface can favor the formation of different AlN modifications.

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