

Combined surface modification of commercial aluminum

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Abstract. The paper analyzes research data on the structure and properties of surface layers of commercially pure A7-grade aluminum subjected to treatment that combines deposition of a thin metal film, intense pulsed electron beam irradiation, and nitriding in low-pressure arc plasma. The analysis shows that the combined method of surface modification provides the formation of a multilayer structure with submicro- and nano-sized phases in the material through a depth of up to 40 μm , allowing a manifold increase in its surface microhardness and wear resistance (up to 4 and 9 times, respectively) compared to the material core. The main factors responsible for the high surface strength are the saturation of the aluminum lattice with nitrogen atoms and the formation of nano-sized particles of aluminum nitride and iron aluminides.

1. Introduction

The low hardness and the low wear resistance of aluminum limit the application of the material and its alloys in industry [1]. Generally, the service characteristics of materials are increased by hardening of their surface layers [2–4]. One of the widely used methods of surface hardening is thermochemical treatment [5]. Although the method has a series of advantages (possibilities to treat elements of any shape, large difference between surface and core properties, etc.), its use for treatment of aluminum suffers from serious shortcomings: the long process time; the presence of an oxide film on the surface of aluminum and its alloys, being a barrier to nitrogen supply to the surface; the formation of an

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aluminum nitride film on the surface, which prevents the penetration of nitrogen deep into the material and complicates the supply of potential to it during ion nitriding.

Here we analyze the structure and properties of commercially pure aluminum subjected to treatment that combines deposition of a thin metal film, intense pulsed electron beam irradiation, and nitriding in low-pressure arc plasma.

2. Material and research technique

The material under study was commercially pure aluminum of grade A7 (aluminium1070: 0.16Fe, 0.15Si, 0.04Zn, 0.03Mn, 0.02Mg, 0.01Ti, 0.01Cu, and the rest is Al). The Al specimens were 4.5-mm thick plates sized to 15×15 mm. Their modification was as follows. First, a steel film 0.5 μm thick was deposited on the Al surface using a Kvinta setup [6]; the steel was 12Cr18Ni10Ti (AISI 321: 0.12C, 11Ni, 19Cr, 1Ti, 2Mn, 0.8Si, 0.3Cu, 0.02S, 0.035P, and the rest is Fe). Then, the film–substrate system was irradiated with an intense pulsed electron beam on a SOLO setup at 17 keV, 30 J/cm², 200 μs, and 0.3 Hz; the number of pulses was 10 and 20 [7]. Finally, the specimens were nitrided on a NNV-6.6-II setup equipped with a PINK plasma generator [8]. For nitriding, a negative bias with a frequency of 50 kHz was applied to the specimens; the bias amplitude and the pulse duty factor were varied. The nitriding temperature was measured with a chromel-alumel thermocouple fixed on the specimen holder and was 540 °C. The nitriding times was 8 h. The hardness and the elastic (Young's) modulus of the specimens were measured in mechanical tests using a PMT-3 device with a Vickers indenter at a load of 0.2 N and 0.5 N and a Shimadzu DUH-211S ultra micro hardness tester at an indenter load of 10–300 mN. The wear rate was determined in tribological tests on a CSEM S/N 07-142 high-temperature tribometer by estimating the wear track cross-sectional area with a Micro Measure 3D station. The defect structure was examined using a Philips SEM-515 scanning electron microscope (SEM) and a JEOL JEM-2100F transmission electron microscope (TEM). The phase composition and the lattice state of surface layers were analyzed using a Shimadzu XRD-7000s diffractometer.

3. Results and discussion

3.1. Nitriding of aluminium in low-pressure arc plasma

Our study shows that when nitrided, the Al surface layer assumes an island structure (Fig. 1, a). The lateral size of islands is up to 5 μm and the size of their substructure is 100–500 nm (Fig. 1, b). The average height of islands estimated by interference microscopy (MNP-1 device) is 1.75 μm.

According to X-ray diffraction analysis, the main phase (≈84 mass%) in the nitrided layer is AlN (space group P6₃mc [9, 10]) with lattice parameters $a = 0.31165$ nm and $c = 0.49879$ nm; the size of coherent scattering regions is $D = 21.9$ nm; the microdistortion of the AlN lattice is $\Delta d/d = 3.5 \cdot 10^{-3}$. The second phase is Al with $a = 0.40487$ nm, $D = 73.6$ nm, and $\Delta d/d = 0.37 \cdot 10^{-3}$.

Electron diffraction analysis of thin foils shows that the AlN islands have a columnar structure with lateral sizes of columns of 0.4–0.5 μm (Fig. 2, a). The columns have a nanocrystalline substructure with a crystallite size of 15–25 nm (Fig. 2, b).

Indexing of the diffraction patterns (Fig. 2, c, d) reveals reflections that belong to the AlN lattice (space group P6₃mc, main phase) and Al lattice (space group Fm3m). In most cases, the reflections of the AlN and Al lattices are overlapped, and their confident identification by electron diffraction analysis is difficult. Comparing the data of X-ray and electron diffraction analyses, it can be noted that the sizes of coherent scattering regions of AlN agree well with the sizes of crystallites revealed by electron microscopy.

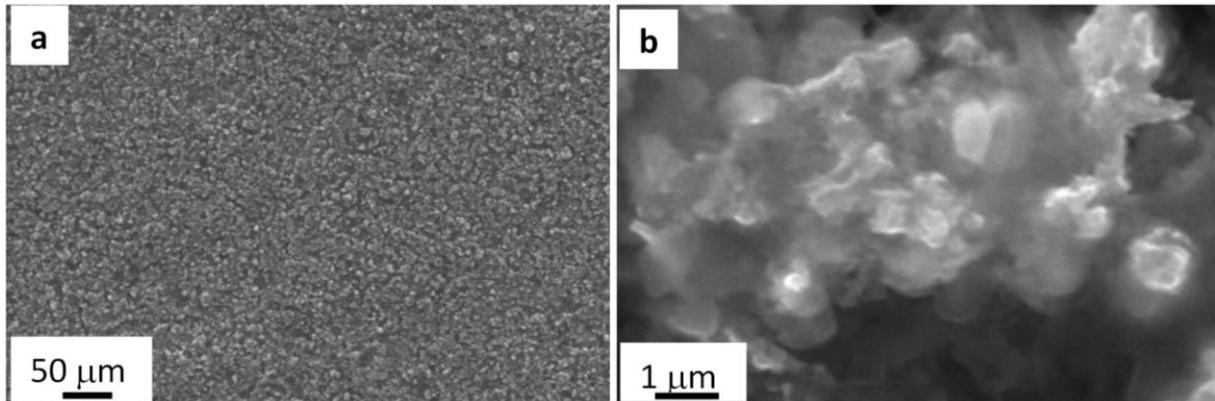


Figure 1. SEM images of the Al surface structure after nitriding in low-pressure arc plasma.

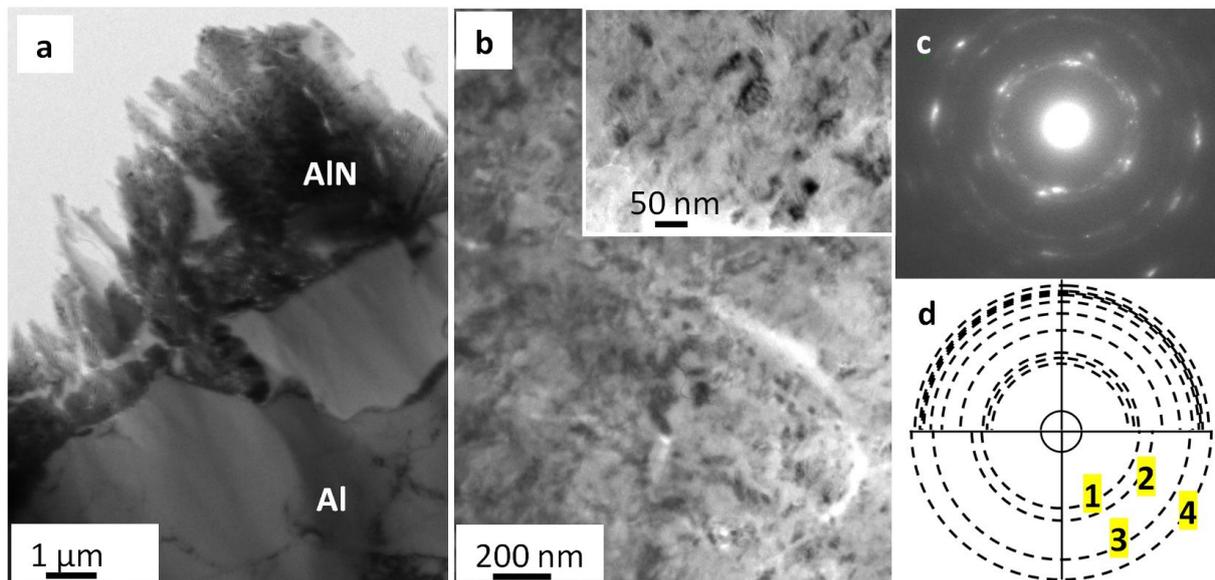


Figure 2. Structure of commercially pure aluminum nitrided in low-pressure arc plasma: a, b – bright fields; c – electron diffraction pattern; d – indexing (diffraction rings in the upper part correspond to AlN, and in the lower part, to Al with reflections: 1 – [111], 2 – [200], 3 – [220], 4 – [113]).

The nitride layer is separated from the adjacent Al volume by a sharp boundary along which chains of pores with a size of 10–50 nm are observed (Fig. 3, white arrows). The Al volume adjacent to the nitride layer has a fragmented (subgrain) structure, suggesting the formation of thermal stresses in the nitrided material and their subsequent relaxation (Fig. 3, b). The fragment size varies from 1 μm to 2 μm. In the fragment volume, there is a substructure of chaotically distributed dislocations.

Thus, the study demonstrates that nitriding in low-pressure arc plasma provides the formation of a thin (2–4 μm) nanocrystalline surface layer with an island structure in commercially pure aluminum. The nitride layer is separated from the main material volume by an interlayer containing micropores.

3.2. Nitriding of aluminium in low-pressure arc plasma

To improve the nitriding efficiency, a 12Cr18Ni10Ti film was deposited on the surface of A7 aluminum, and then, the film–substrate system was nitrided in low-pressure arc plasma. Data of nanoindentation showed that when nitrided, the film–substrate system was hardened through a depth of no more than 1 μm. Therefore, before nitriding, the film–substrate system was irradiated with an intense electron beam, and the thus formed surface alloy was nitrided in low-pressure arc plasma.

Measurements of the hardness show that a hardened layer of thickness up to 30 μm is formed in the system during nitriding; the microhardness of the nitrided surface layer is more than 4 times higher than that of the specimen volume. The modified specimens were subjected to tribological testing. It is shown that the combined method of surface modification increases the wear resistance of the material ≈ 9 times and decreases the friction coefficient ≈ 1.3 times.

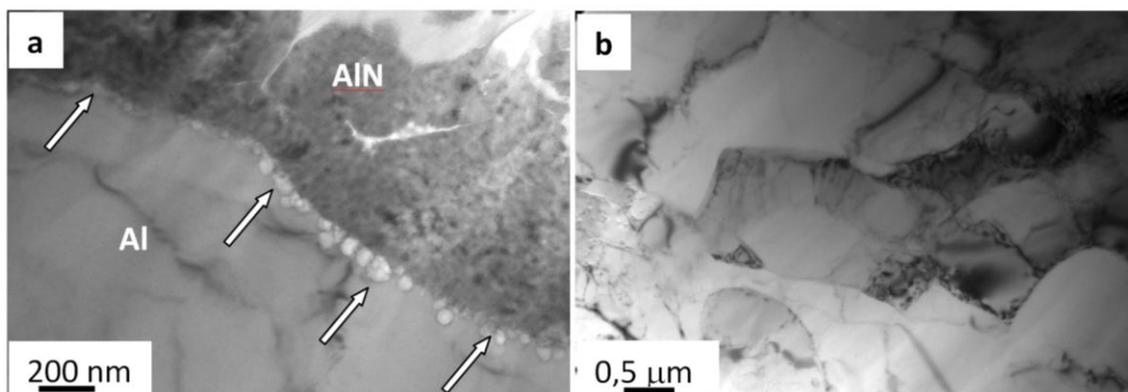


Figure 3. Structure of commercially pure aluminum nitrided in low-pressure arc plasma; the pores along the interface between the nitride layer and the main Al volume are shown by arrows.

After combined modification, the material reveals a multilayer structure consisting of a surface layer (Fig. 4, layer 1), a transition layer (Fig. 4, layer 2), and a heat-affected layer.

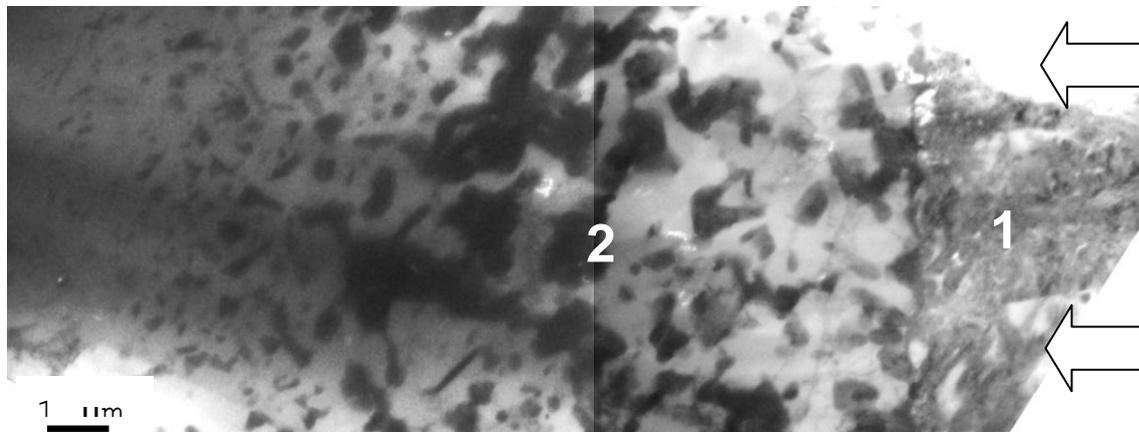


Figure 4. Structure of 12Cr18Ni10Ti film-coated A7 aluminum after electron beam treatment and subsequent nitriding in low-pressure arc plasma (the nitrided surface is marked by arrows): 1 – surface layer; 2 – transition layer.

The surface layer has an island structure similar to that presented in Fig. 1 and Fig. 2; the average height of islands is 3.45 μm . The islands represent aluminum nitride, as evidenced by transmission electron microscopy, scanning transmission electron microscopy, and X-ray diffraction analysis. There is also a small amount of particles of α -Fe-based solid solution.

The transition layer is up to 40 μm and represents aluminum hardened by second phase particles (Fig. 4, layer 2). As shown by TEM and STEM, the inclusions are aluminum nitrides, aluminides, and α -Fe(Cr, Ni, Al). In the layer adjacent to the columnar structure, the size of second phase particles is 100–250 nm. With depth from the modified surface, the number of particles per unit area decreases and so does their size (Fig. 4).

The main volume of the material and its modified surface layer are separated by a heat-affected zone in which a band structure typical for deformed aluminum arises. Apparently, the strains in the material are induced by thermoelastic stresses that arise in its surface layer at the stage of intense electron beam irradiation [11, 12].

Reasoning from the mechanical properties, tribological characteristics, and structural phase state of the modified material, it can be concluded that the increase in its surface microhardness and wear resistance is due to several physical mechanisms of hardening: (1) saturation of the Al lattice with nitrogen atoms, (2) precipitation of submicro- and nano-sized second phase particles, including aluminum nitride particles, and (3) band substructure formation in its heat affected zone.

4. Conclusion

Thus, we analyzed the structure and properties of commercially pure A7 aluminum after combined surface modification that included electron beam irradiation of the material coated with a 12Cr18Ni10Ti steel film and its subsequent nitriding in low-pressure arc plasma. It is shown that the combined method of surface modification increases the wear resistance of the material more than 9 times and the microhardness more than 4 times while decreasing the friction coefficient μ 1.3 times. The increase in the strength and tribological properties of the material is due to several physical mechanisms of hardening: (1) saturation of the Al lattice with nitrogen atoms, (2) precipitation of submicro- and nano-sized second phase particles, including aluminum nitride particles, and (3) band substructure formation in the heat affected zone.

Acknowledgments

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5. References

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