Magnetron deposited TiN coatings for protection of Al-Cu-Ag-Mg-Mn alloy

Tatiana V Stepanova¹*, Andrey V Kaziev¹, Mikhail V Atamanov², Alexander V Tumarkin¹, Svetlana A Dolzhikova³, Nelly Ph Izmailova³, Maxim M Kharkov¹, Maria M Berdnikova³, Dmitry V Mozgrin¹ and Alexander A Pisarev¹

¹National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe highway, Moscow 115409, Russia
²Inacotec JSC, 4b5 Bardina st., Moscow 119334, Russia
³Ufa Engine Industrial Association, 2 Ferina st., Ufa 450039, Russia

Corresponding author e-mail: shtanya@list.ru

Abstract. TiN coatings were deposited on a new Al super-alloy by magnetron sputtering in argon/nitrogen environment. The deposited layer structure, microhardness, adhesion, corrosion resistance, and fatigue life were investigated and tests demonstrated improved performance of the alloy.

1. Introduction

Aluminum alloys are widely used in the aircraft industry, and one of the specific applications is for compressor blades. This engine part is subjected to sand wear, atmospheric and water corrosion, and fatigue. To improve the performance of aluminum alloys in this application, three approaches are used: development of new materials, thermal treatment, and surface modification.

Surface modification is widely used in processing of steels, and plasma treatment has become a competitive technology from the point of view of product quality, technological flexibility, cost efficiency, and environmental aspects. Plasma treatment of aluminum alloys has no wide industrial application yet, though remarkable amount of papers are focused on their plasma treatment. The traditional way of improving characteristics of aluminum alloys is physical vapor deposition (PVD), particularly by magnetron sputtering, and Ti nitride demonstrates increase of hardness, corrosion resistance and wear resistance [1-3]. Presently, TiN films are successfully used for coating of the compressor blades of the jet turbine engines to inhibit erosion and enhance strength characteristics [4]. However, using solely TiN films generally does not guarantee the required quality of protection against erosion by micro particles, therefore coatings with improved anti-erosion properties are necessary [3, 5]. Erosion by micro particles can also accelerate corrosion of blades in saliferous water vapor, and in turn, corrosion of the aluminum substrate accelerates erosion of the protecting films by particles.

The temperature of aluminum alloys during deposition must be low (below 150–200°C). Therefore, TiN coatings deposited on aluminum usually have a columnar microstructure that is typical for low-temperature film deposition. This kind of the structure incorporates voids, pores, small holes and...

* To whom any correspondence should be addressed.
through channels [6] that may reduce the corrosion resistance [7], coating hardness and erosion resistance. Another challenge associated with film deposition is degradation of the fatigue properties. So far, the latter issue has remained unaddressed.

NRNU MEPhI jointly with USATU and Inacotec JSC have recently devised a technique of coating for improving the wear- and corrosion-resistance of a custom aluminum super-alloy AA2139 (Al-Cu-Ag-Mg-Mn) that does not degenerate its fatigue properties. In this paper we present the results of examining the microhardness, corrosion resistance, adhesive, and fatigue properties of the Al alloy samples coated with TiN films.

2. Experimental setup
TiN coatings were deposited in a magnetron sputtering system at Inacotec JSC. A scheme and a photo of the apparatus are shown in figure 1.

![Figure 1. Experimental apparatus: 1—ion source, 2—sample carousel, 3—sample holder, 4—DC magnetron (optionally unbalanced), 5—vacuum chamber, 6—pressure gauges, 7—mass-flow controllers, 8—shutter, 9—vacuum pumping.](image)

The samples were attached to a sample carousel 2 in a vacuum chamber 5 at a distance of 80 mm in front of the magnetron cathode. The vacuum chamber was evacuated with a cryopump to a base pressure of 1×10⁻⁴ Pa. A gas-fed cold-cathode ion source 1 at a distance of 100 mm (in the processing region) had the beam cross-section area of 60×500 mm. The power supply power was 5 kW, with the maximal voltage output of 3 kV.

Prior to deposition, the samples were sputter-cleaned by 2.2–2.4 keV Ar ions (anode current 0.35–0.4 A) for 5 min at Ar pressure $p_{Ar} = 0.09$ Pa. TiN coatings were produced by reactive sputtering of Ti target in a magnetron discharge with the discharge voltage ~ 400 V (cathode current ~ 10 A) at a total Ar+N₂ pressure $p = 0.12$ Pa with the composition Ar:N₂ = 5:1. Sputter magnetron 4 operated in a pulsed DC mode at the repetition rate of 30 kHz and duty factor of 50%. During the deposition, the samples were biased with $U_b = -60$ V. Half of the samples were treated with magnetron operated in balanced regime, and the other — in unbalanced magnetron configuration. The unbalancing was induced by an auxiliary electromagnetic coil next to the magnetron’s permanent magnet pack. The deposition process lasted for 10 min. Thickness of deposited films was 1 µm. The temperature of samples was measured using type E thermocouple and did not exceed 40°C. Following the deposition, the samples were cooled down to 25°C in the Ar-filled chamber at $p_{Ar} = 5×10^4$ Pa.

The microstructure of samples was examined using a scanning electron microscope (SEM) Tescan Vega 3 SBH equipped with an energy-dispersive X-ray spectrometer (EDS) Oxford Instruments X-Act.

Surface hardness was measured by Future-Tech Corp. FM-800 microhardness tester. The adhesive properties of coatings were studied using Anton Paar Revetest scratch tester. Fatigue tests were carried out in an electrodynamic shaker.
The corrosion resistance of samples was investigated in express tests in 10 wt% KOH solution (pH = 15). Aluminum intensively reacts with alkali solution, so hydrogen gas bubbles appear immediately after the beginning of the tests. The sample was put on the table of an optical stereo microscope, several drops of the alkali solution were put on the sample surface, and reaction was video recorded.

3. Experimental results

3.1. Microstructure

Microstructure of the cross-sections of films prepared in balanced and unbalanced magnetron configurations, observed in SEM, is shown in figure 2. One can see that the thickness of the film is approximately the same in the two cases. There were no visible cracks and pinholes in the film.

EDS analysis showed that the coating was composed of Ti and N without impurities in the coatings.

![Figure 2](image)

**Figure 2.** Cross-sections SEM images of Al alloy samples with 1-µm TiN films deposited in balanced (left) and unbalanced (right) magnetron regimes: (a) mounting, (b) TiN film, (c) Al alloy substrate.

3.2. Microhardness measurements and scratch tests

Microhardness was measured using Vickers indenter with loads normal to the surface in the range of 10–500 gf. The results of microhardness measurements as well as the SEM images of the indentation spots are given in figure 3.

One can notice that there are no cracks outside the dent, even at the maximal applied load. This indicates good adhesion of the film to the substrate.

Scratch tests were performed under progressive load, linearly increasing from 0.5 to 50 N at a rate of 49.5 N/min at the length of 5 mm with the indenter velocity of 5 mm/min. Rockwell C diamond spherical indenter tip of 200-µm radius was used. The critical loads were detected by means of an acoustic sensor and visual analyses of SEM images of scratches. Figure 4 shows an example of acoustic emission and indenter penetration during scratch test, and figure 5 shows typical images of the scratch in characteristic regions. One can see increase of the acoustic signal at the load of about 6 N, which is connected with cracking of the deposited film that can be observed in SEM images. With increase of the load, cracking increases, and the acoustic signal intensifies. One can see small cracks at the first SEM image. At the load above 15 N the signal starts to fluctuate, and SEM images demonstrate disintegration of the film: the number of cracks and the gaps between them are getting
larger. Finally at the end of the scratch, the deposited film is destructed completely, and in some parts of the scratch is completely removed from the scratch bottom.

**Figure 3.** Surface microhardness of untreated and TiN coated samples (left); SEM images of indentations (right).

**Figure 4.** Acoustic signal (left) and penetration of the indenter (right) in scratch tests. The vertical lines give characteristic lengths of beginning of cracking, disintegration, and destruction of the deposited film estimated from SEM image of the scratch.
It is important to mention that the start of cracking leading to appearance of the acoustic signal at about 5 N happens when the indenter penetrates about 5 µm in the sample, while the thickness of the film is five times less (about 1 µm). That means that the film is rather tough under loads. It is also important that there are only small cracks outside the scratch and there is no exfoliation of the film outside the scratch even at the largest load of 50 N when the indenter penetrates 60 µm in the sample (60 times the thickness of the film).

No significant influence of the magnetron unbalancing on adhesive properties has been observed, however the performance of coatings deposited in the balanced regime was slightly better. The samples coated in the balanced magnetron regime had average characteristic critical loads of about 6 N (beginning of cracking) and about 17–18 N (intensive fracturing). The corresponding values for coatings deposited in the unbalanced regime were 5 N and 15–16 N.

### 3.3. Corrosion resistance

The untreated Al alloy samples exposed to 10 wt% KOH solution exhibited intensive formation of gas bubbles in less than 1 s after the beginning of the test. After 10 min, severe erosion of the surface was observed. TiN coatings significantly inhibited the corrosion of the Al alloy. Formation of gas bubbles on the surfaces coated with 1-µm TiN films both in balanced and unbalanced magnetron regimes was observed after 5 min of exposure to alkaline solution. Noticeable erosion of the surfaces took place after about 2 h of the test. That is, the corrosion resistance of samples was significantly enhanced due to protective TiN films.

### 3.4. Fatigue tests

Samples after fatigue tests are shown in figure 6. The sample was clamped at its thicker end, while the thinner end was subjected to the oscillating load. The load value varied in the range of 12–20 kgf/mm², the vibration frequency was 1680–1880 Hz. Each test procedure lasted until either the sample was fractured or after $20 \times 10^{6}$ cycles.

**Figure 5.** SEM images of the scratch in the regions of beginning of cracking (left), disintegration of the film (middle) and its destruction (right).

**Figure 6.** Samples after fatigue tests.
After the tests, the micro- and macrostructure of samples were studied in optical microscope Olympus GX51 with magnifications 100, 200, and 500. Prior to examination, the samples were grinded, mechanically polished, and etched with Keller’s reagent ($\text{H}_2\text{O} — 95 \text{ cm}^3$, $\text{HNO}_3 — 2.5 \text{ cm}^3$, $\text{HCl} — 1.5 \text{ cm}^3$, $\text{HF} — 1 \text{ cm}^3$).

Samples without TiN film demonstrated the following results: one sample loaded to 20 kgf/mm$^2$ and two samples loaded to 16 kgf/mm$^2$ were broken, while all 6 samples loaded to 14 kgf/mm$^2$ did not fail after $20 \times 10^6$ cycles. The samples with TiN film demonstrated better performance: all 4 samples loaded to 16 kgf/mm$^2$ did not fail after $20 \times 10^6$ cycles, though the sample loaded to 18 kgf/mm$^2$ was broken.

Analyses of unbroken samples did not reveal any cracks. Broken samples had three specific regions: the region of crack initiation and stable crack growth, the region of accelerated crack growth, and the fracture area.

4. Conclusion

Magnetron-sputtered protective TiN films enhanced the surface microhardness 1.3–2 times compared to the initial value. The corrosion resistance of the surface in tests with alkali solution was significantly improved due to TiN films. The coatings demonstrated very good adhesion and showed no exfoliation after microhardness and scratch tests.

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