MORPHOLOGY AND CORROSION PROPERTIES PVD Cr-N COATINGS DEPOSITED ON ALUMINIUM ALLOYS

MORFOLOGIJA IN KOROZIJSKE LASTNOSTI CrN PVD-PREVLEK, NANESENIH NA ALUMINIJEVE ZLITINE

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The attempt to find an alternative coating for corrosion protection of Al- alloys was made. PVD coatings are one of the possible alternatives for replacement of ecological unfriendly chromate coatings. Chromium-nitride (Cr-N) and Ni/Cr-N coatings were sputtered on aluminium substrates (AA7075 and cladded AA2024). Surface and sub-surface characterizations were performed by AFM and SEM. Special attention was given to defects incorporated into coatings, since they play important role in the corrosion protection of the coating/substrate systems. The cross-sections through the typical defects were performed by ion beam milling incorporated into the SEM. The Vickers hardness of the Cr-N with and without layer of Ni on both substrates was determined. After the coatings deposition, the values of Vickers hardness (10 mN load) increase for 10 to 100-fold compared to the substrates. The corrosion behaviour of Cr-N and Ni/Cr-N thin films was investigated in near neutral 0.1 M solution of NaCl using potentiodynamics electrochemical measurement. Cr-N and Ni/Cr-N coatings shift the corrosion potentials to more positive values. The best corrosion resistance among the tested coating/substrate systems were found for Ni/Cr-N on AA7075 substrate.

Keywords: Al-alloys, corrosion properties, CrN films, FIB, PVD coatings

Ena od možnih alternativ za zamenjavo ekološko neprijaznih kromatnih prevlek na aluminijevih zlitinah so PVD-prevleke. V prispevku opisujemo pripravo in karakterizacijo prevlek Cr-N in Ni/Cr-N na aluminijeve podlage (AA7075 in AA2024). Površinsko in podpovršinsko karakterizacijo CrN-prevlek smo izvedli z vrstično elektronsko mikroskopijo (SEM) in mikroskopom na atomsko silo (AFM). Posebna pozornost je bila namenjena karakterizaciji defektov v prevlekah, saj igrajo pomembno vlogo pri korozijski zaščiti sistema prevleka/podlaga. Defekte smo karakterizirali z vrstičnim mikroskopom (SEM), ki je dodatno opremljen s fokusiranim ionskim curkom (FIB) za odstranjevanje materiala. Določili smo trdoto prevlek po Vickersu na obeh vrstah aluminijevih podlag. Korozijske lastnosti prevlek smo merili v 0,1 M raztopini NaCl s potenciodinamskimi krivuljami. Cr-N- in Ni/Cr-N-prevleke premaknejo korozijski potencial proti pozitivnim vrednostim. Zaščita aluminijevih zlitin je boljša z dvojno prevleko Ni/CrN kot samo s prevleko CrN.

Ključne besede: Al-zlitina, korozijske lastnosti, CrN, FIB, PVD-prevleke

1 INTRODUCTION

Aluminium alloys are very important engineering materials employed in a variety of applications, which include automotive, constructive, chemical, petrochemical, cryogenics, transportation equipment, etc. Among other attractive properties, these materials exhibit relatively high strength to weight ratio, good corrosion resistance and high thermal conductivity. However, due to their low hardness, wear and abrasion resistance, the application of these materials to sliding part is quite limited. Conventionally, the improvement of the surface properties of aluminium alloys, particularly those involved in aircraft and aerospace application, like AA2024 and AA7075, has been the use of electrolytic hard chromium deposition and conversion chromate coating. However, the strong environmental regulations issued in the past few years to decrease significantly the emissions of the highly toxic hexavalent chromium, have led to the development of different technologies also able to improve the surface properties of such materials, but more friendly from the environmental point of view.[1–5] On the other hand, conversion chromate coating possesses

advantageous properties, like self-healing effect in case of mechanical coatings damage.

PVD technologies offer a promising alternative for the production of cost-effective, quality coatings with dry, clean and environment-friendly technology fully supported by legislation on environmental protection. The properties of various PVD coatings (metals, alloys, nitrides and oxides, carbides) have been well documented and systematically presented.[6,7] Ceramic materials have oriented covalent bonds; such materials are hard, brittle, chemical inert and with high melting-point temperature. Their wear resistance is excellent. Because of these properties, PVD coatings are in many cases a serious alternative to electrochemical coatings. For example, 1–5 μm thick layer of PVD coatings can replace 250 μm thick layer of hard chrome.

In the recent years, many efforts have been oriented to the development of anticorrosive coatings deposited by reactive sputtering in order to protect aluminium alloys like AA2024 and AA7075 used in aircraft application. Among conventional nitride and carbide PVD hard coatings, TiN and AlN sputtered on aluminium alloys were investigated. Diesselberg *et al.*[8] sputtered

TiN_x varying concentration of nitrogen and bias voltage to get different microstructructure of TiN_x. The lower concentration of nitrogen and the deposition at higher bias shows a positive effect on the corrosion protection. AlN_x sputtered coatings were investigated by Schafer and Stock[9]. AlN_x coatings on Al-substrate with higher concentration of nitrogen shift the pitting potential to more positive values. However, salt spray test showed opposite effect of nitrogen concentration; the coatings with less concentration of nitrogen are more stable. Liu *et al.* [10] studied effect of nitrogen ion implanted into aluminium substrate on the mechanical properties of TiN films. Implantation of nitrogen ion, increase the adhesion of TiN coating, therefore improve surface properties of aluminium by forming 80 nm thick AlN gradient layers. Corrosion properties were not reported.

On the other hand, sputtered chromium and reactively sputtered chromium nitride (CrN) act as very promising candidates due to their high internal resistance to corrosion, which arises from the instant formation of an oxide layer on the surface at room temperature.[11,12,13] In this paper, we present the investigation of PVD coating CrN and Ni/CrN for corrosion protection of aluminium alloys AA2024-cladded and AA7075. CrN thin films on aluminium substrates were prepared by sputtered deposition at low temperature. Surface and sub-surface characterization were performed on the coatings. Mechanical properties such as hardness and roughness were determined for each coating. The corrosion testing of PVD coatings, using electrochemical methods (potentiodynamic measurement), were performed in the 0.1M solution of NaCl.

2 EXPERIMENTAL

2.1 Substrate preparation

As substrates, the disks of aluminium alloys (AA2024 cladded and AA7075) were used. All the Al-substrates were chemically cleaned with a mildly alkaline cleaner Ridoline 1 % in an ultrasonic bath at 60 °C for 4 min, followed with distilled water bath and ethanol bath and drying with N_2. To study the effects of the surface preparation on corrosion performance of PVD coatings, the grinding (1000 and 4000 SiC papers) and polishing (0.25 μm diamond paste) of the substrate surface were performed in some cases. Ion etching to remove native oxide layer usng $Ar + H_2$ mixture (15 min) in vacuum chamber was performed in some cases.

2.2 Coating depositions

All coatings were prepared by sputtering at 150 °C in the depositing system with termionic arc (Sputron, Balzers). Cr-N and Ni/Cr-N were deposited on the substrates with and without ion etching. Additional interface layer of amorphous carbon (a-C) were performed to reduce the roughness of the substrates. The thickness of Cr-N coatings was ≈2,5 μm and Ni/Cr-N coating about 3 μm.

The vacuum chamber was evacuated to a base pressure of approximately 2 mPa. Nitrogen (purity 99.995 %) flow remained constant at 9.5 cm^3. During deposition the bias voltage and the substrate temperature were -30 V and 150 °C

2.3 Characterisation

Field emission scanning electron microscope (Zeiss Supra 35 VP) was used for study of the defect morphology in planar surface view and cross-sectional fracture view.

Focused ion beam (FIB) workstation[14] was used to prepare cross-section through the defects. We used FIB integrated in FEI QUANTA 200 3D microscope. Ion beam was used to remove precise sections of material (close to the selected defect) from the specimen surface by sputtering.

The surface morphology and roughness of the substrates and coating/substrate systems was also examined by atomic force microscope (Solver PRO).

Hardness was determined using the nanoindenter Fischerscope H100C. The load was varied between 10–1000 mN.

The electrochemical corrosion behaviour was studied using potentiodynamic polarisation tests in a solution of 0.1 M NaCl. Autolab three-electrode corrosion cell was used, with the working electrode embedded in a Teflon holder. An Ag/AgCl electrode served as a reference electrode and carbon rods as counter electrodes. The working electrode (WE) was a substrate with an area of 0.785 cm^2 that was coated with Cr-N and Ni/Cr-N. The polarisation curves were measured after 1 h of stabilization at the corrosion potential so that a quasi-stable potential was reached. The curves were obtained by sweeping the potential from the cathode to the anode. The sweep-rate setting was 1 mV/s using an EG&Par PC-controlled potentiostat /galvanostat Model 263 and Powersuite software.

3 RESULTS AND DISCUSSION

3.1 Microstructure

A typical surface morphology of PVD-hard coatings Ni/CrN on AA-7075 alloy is shown on **Figure 1a**. Top-view image is possible to distinguish typically growth defects for PVD-coatings: a) spherical droplets-cone structure, coming above the surface, typical wide size from 1 to few μm, b) pin- holes apparently going to the substrate, reaching the size up to the few μm c) big, not deep craters of wide size of 10–40 μm.

High surface roughness of Al-alloy substrate is shown on cross section image on **Figure 1b**. Surface roughness of AA-7075 substrate measured by AFM was $R_a ≈ 14$ nm, AA2024–cladd $R_a ≈ 11.3$ nm. After
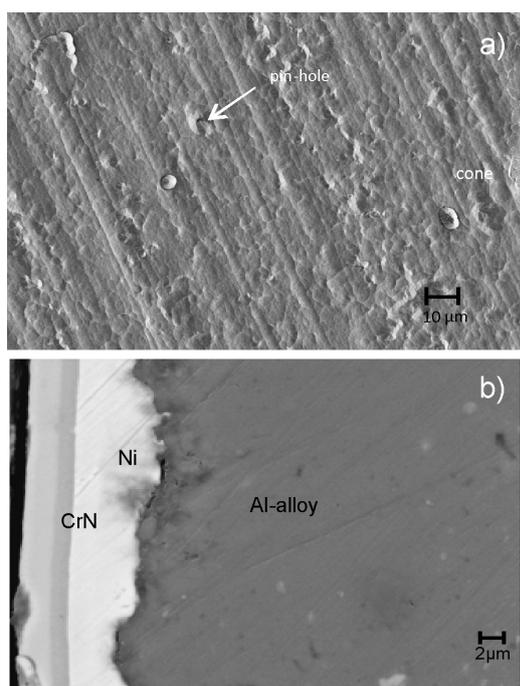
Figure 1: A top view of a) Cr-N coating on aluminium alloy AA2024 cladded substrate b) cross-section of Ni/Cr-N/Al-alloys
Slika 1: SEM posnetek a) mikrostrukture površine Cr-N-prevleke na aluminijevi zlitini AA2024, b) prereza Ni/CrN/Al-zlitina

deposition surface roughness increased for around $R_a \approx$ 34 nm on AA7075 substrate and $R_a \approx$ 26 nm on AA2024-cladd.

Microstructure characteristics of PVD-coatings, where surface defects have to be taken into account, play important role in the determination of corrosion properties of thin films. A few authors pay attention to the defect density and try to explain the origin of the growth defect on the PVD-coatings. To determine the origin of the defects the FIB cross section analysis were made on the two typical defects shown on **Figure 2**. The first defect (**Figure 2a–d**) has the form of a cone, while the second one (**Figure 2e–h**) resembles a pinhole. The question was weather these defects extend through the whole coating or not, and what is the origin for their nucleation. After consecutive serial sectioning, we found
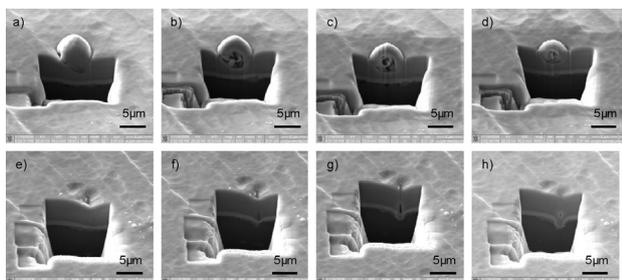

Figure 2: FIB cross section analysis were made on the two typical defects of coatings a-d) cone structure and e-h) pin-hole
Slika 2: SEM posnetek prerezov (narejenih s FIB) dveh tipičnih napak v prevleki; a)–d) konusna oblika napake in e)–h) luknjica (pin-hole)

that the first defect started to grow in the middle of the coating due to the incorporation of a foreign particle. **Figure 2c** shows that the region under the cone is not completely filled with material. The second defect extends through the whole coating and originates in a small hole in the substrate (**Figure 2e**). It is well known that PVD processes have a poor ability to cover a small hole due to shadowing effect. **Figure 2e–h** clearly shows that a small crater on the substrate surface cannot be covered completely and that a pinhole extending through the whole coating was formed. The corrosion takes place on such defects, while solution can reach the base material. The origin of the pinholes could be the corrosion products (wet cleaning) or dust particles that they are not removed from the substrate surface during the deposition. The high roughness of selected substrates could result the same effects. The cone microstructure, appearing quite an accident anywhere in the growing layer, (**Figure 2b**) are due to inclusions coming on the growing layer from the vacuum chamber, i.e. drops of metal target.

The origin of the big not deep craters (**Figure 1a**) can be explained by the falling away of the particles (corrosion products due to wet cleaning, dust particles) from the surface, soon after the starting the deposition.

3.2 Mechanical characterization

The Vickers hardness of the Cr-N, Ni and Ni/Cr-N coating, with deposited on AA2024 cladd and AA7075 substrates was determined. The bare substrate
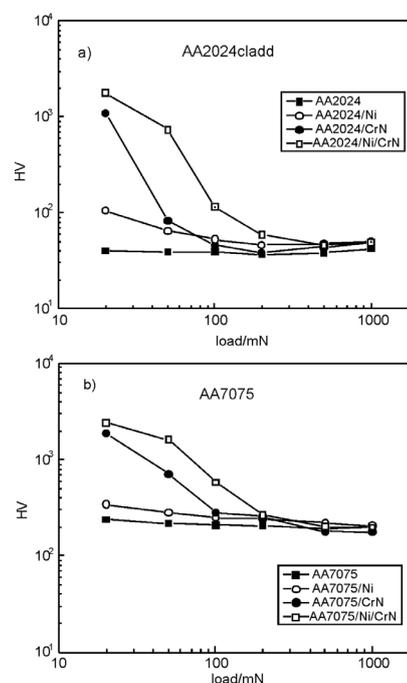

Figure 3: Hardness of the substrates and coatings for a) AA2024-cladded b) AA7075
Slika 3: Trdote po Vickersu pripravljenih prevlek: a) podlaga Al-AA2024, b) podlaga Al-AA7075
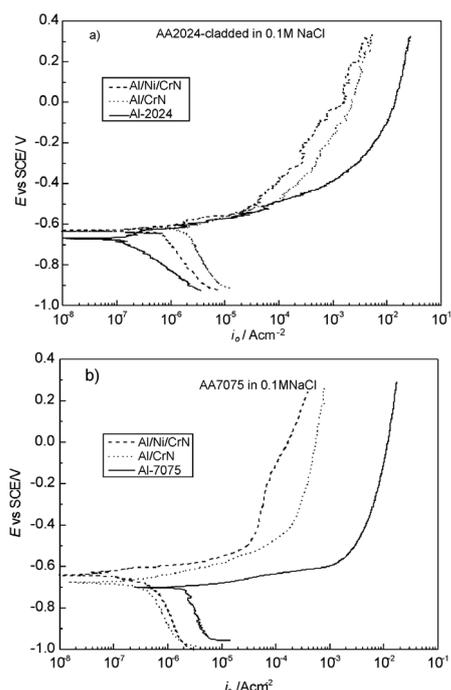
Figure 4: PD curves of various coatings, as indicated on figures, for a) AA2024-cladded substrate b) AA7075 substrate
Slika 4: PD-krivulje prevlek, označenih na sliki za a) podlage Al-AA2024, b) podlage Al-AA7075

Table 1: Corrosion potential (E_{corr}) and corrosion current density (i_o) after 1 h stabilisation for uncoated and coated substrates on **Figure 4**.

material	E_{corr}/V	i_o/(µA cm^{-2})
AA7075	–0.707	2.10
AA7075/CrN	–0.679	0.99
AA7075/Ni/NiCrN	–0.645	0.41
AA2024-cladd	–0.674	0.18
AA2024-cladd /CrN	–0.631	0.38
AA2024-cladd /Ni/NiCrN	–0.624	2.80

AA2024-cladd (**Figure 3a**) has a hardness of 40 HV and AA7075 substrates of 200 HV (**Figure 3b**). After the coating deposition, the values of Vickers hardness, measured at 10 mN, increase for 10 to almost 100-fold compare the substrates and then progressively diminishes at higher loads. In both cases, this is only a surface effect due to small thickness of the coatings (**Figure 3a and Figure 3b**).

3.3 Corrosion characterisation

The results from the potentiodynamic measurements of the CrN and Ni/Cr-N coatings on the substrates of aluminium alloys (AA2024-cladd and AA7075) in the 0.1M aqueous sodium chloride solution are shown in **Figure 4**. After 1 h of stabilization at the open-circuit potential, the corrosion potential (E_{corr}) for the AA2024-cladd substrate in was approximately –0.67 V (**Figure 4a**). Following the Tafel region, the alloy
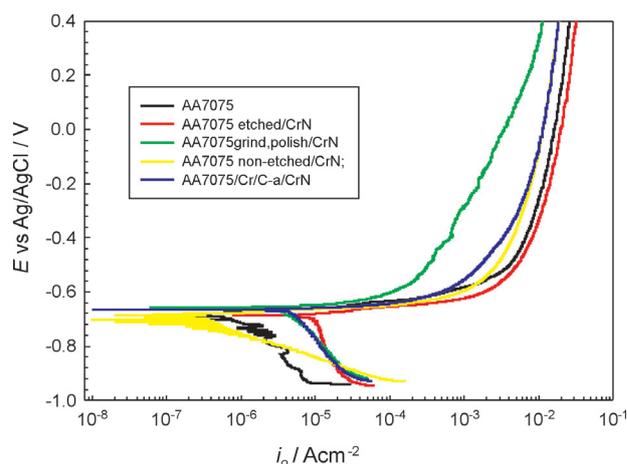

Figure 5: PD curves of Cr-N coating with the different surface substrate preparation as indicate in the figure
Slika 5: PD-krivulje Cr-N z različno predpripravo podlag, kot so označene na sliki

exhibited a narrow range of passivation, with breakdown potential E_b of about –0.63V, due to native oxide layer formed on pure (cladded) aluminium. In the case of the AA7075, the E_{corr} in 0.1 M NaCl was approximately –0.70V.

E_{corr} shifted to a more positive potential with the application of the Cr-N and Ni/Cr-N coatings, reaching -0.62 V and -0.63 V versus on the AA2024-cladd (**Figure 4a**). The E_{corr} of the CrN and Ni/Cr-N coatings on the AA7075 reached a value of -0.67 V and -0.64 V (**Figure 4b**).

The corrosion current density is often used as an important parameter to evaluate the kinetics of corrosion reactions. Corrosion protection is normally proportional to the corrosion current density (i_o) measured via polarization. In our case, where PVD coatings of Cr-N are chemically not reactive, the corrosion current density indicates pores in the coatings, where the electrochemical reaction of the substrate takes place. The i_o values from **Figure 4** show that the Cr-N coating on on both Al-alloys corroded faster than the Ni/CrN coating under open-circuit conditions; this means that the active area of the substrate due to coating porosity is higher in the case of Cr-N than in the case of Ni/Cr-N coatings. However, the overall corrosion process was still dominated by locally active dissolution, which occurred as the substrate was exposed via coating porosity.

Cr-N coating did not improve the corrosion properties for aluminium substrates in the extent as is well known for corrosion protection of steel substrate[6]. The effects of the surface preparation (grinding, polishing, etching) and interface layers were investigated further on AA7075 as is shown on **Figure 5**. Performance of Cr-N coatings can be slightly improved with the proper surface preparation (grinding, polishing) as is shown with the green curves (green and yellow curves). No effect of etched and non-etched substrate, with (Ar+H$_2$) plasma in the vacuum chamber before the deposition, was observed

on the PD performance of Cr-N protective layer (**Figure 5**). The deposition of an interface layer could influence the performance of the coatings as well. Thin interface layer of a-C (amorphous carbon) was sputtered in order to reduce the high roughness of the substrate. A slight improvement was observed. PD curves show that although there is some effect of surface preparation on the corrosion performance of Cr-N, Cr-N alone is not suitable coating for corrosion protection of soft aluminium substrates.

4 SUMMARY

The deposition of Cr-N and Ni/Cr-N was carried out. Physical, surface analytical and electrochemical measurements were performed on coated and uncoated AA2024-cladded and AA7075 substrates. Cr-N and Ni/Cr-N coatings increase the surface hardness of both Al-alloys substrates to 10-fold. At the measure loads of 10 mN.

FIB cross section analyses were made on the two typical defects of coatings (cone structure and pin-hole). Cone microstructure, appearing quite an accident in the growing layer, are due to inclusions coming on the growing layer from vacuum chamber (drops of metal target, dust, etc). A small crater (probably due to surface roughness) on the substrate surface cannot be covered completely due to shadowing effect and that a pinhole extending through the whole coating was formed. The corrosion takes place on such defects, while solution can reach the base material.

Corrosion behaviour of Cr-N and Ni/Cr-N thin films was investigated in near neutral 0.1 M solution of NaCl using potentiodynamics electrochemical measurement. Cr-N and Ni/Cr-N coatings shift the corrosion potentials to the more positive values. The best corrosion resistance among the tested coating/substrate systems were found for Ni/Cr-N on AA7075 substrate.

Acknowledgements

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