Electrochemical Behaviour of TiCN and TiAlN Gradient Coatings Prepared by Lateral Rotating Cathode arc PVD Technology

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Abstract. TiCN and TiAlN gradient coatings were deposited on the AISI 316L stainless steel substrates by lateral rotating cathode arc (LARC) physical vapour deposition (PVD) technology. Corrosion and tribocorrosion behaviour was studied in 3.5 wt. \% NaCl solution. The thickness of coatings was about 3 µm. For both coatings the corrosion potential shifted to more positive values as compared to the uncoated substrate. The corrosion current density decreased for TiCN and TiAlN coatings indicating up to 40 folds higher polarization resistance. The coefficient of friction value of TiCN coating is three times lower and durability is six times higher than that of TiAlN coating under the same tribocorrosion conditions.

Introduction

It is well known that in the corrosive medium the breakdown of the films occurs due to crevice corrosion, pitting, galvanic corrosion, inter-granular corrosion, selective leaching, erosion-corrosion and chemical stress corrosion [1]. In addition to water, steel corroding chlorides (e.g. NaCl, KCl, CaCl\textsubscript{2}, etc.) are the most common chemicals in nature, thus stress corrosion caused by chlorides (expansion caused cracking) requires careful examination [1–3].

Transition metal nitrides hard coatings are widely used in industry due to high hardness, high electrically conductivity and good corrosion resistance [4]. However, coatings are often affected by corrosion due to chemicals used in aggressive environments. Therefore corrosion resistance of coatings is important topic nowadays [2,3]. Merl et al. [3] have proposed that the corrosion takes place on the macro- and micro-defects (pinholes, porous structure, etc.) in physical vapour deposited (PVD) coatings, where solution can reach substrate. However, macrodefects like inclusions on the coating surface is not always a place of the breakdown in corrosion resistance tests [3]. In a case of non-voluntary or limited voluntary wetting [5] it takes longer time for water intrusion and for corroding chloride ions to penetrate into pores and other types of defects.

Antonov et al. [6] have investigated gradient and non-gradient PVD coatings (TiCN, TiAlN, etc.) on cemented carbide substrate. The gradient deposition technology allows improving the adhesion between coating and substrate. PVD coatings could be applied to various substrates like metals, ceramics, cermets, polymers, and diamonds influencing the performance of final product.

Despite the fact, that TiCN and TiAlN coatings are tested against tribocorrosion, there are much less available publications about tribocorrosion of gradient type TiCN and TiAlN hardcoatings.

Depending on microstructure defects, the corrosion resistance of hard coatings like TiN and TiAlN can protect steel, leading to trans-passive state exhibition in NaCl solution [7]. Tribocorrosion is a combined surface degradation process in corrosive medium where tribological and electrochemical actions take place simultaneously [8,9]. The aim of the preliminary study is to find the PVD gradient coating (deposited onto stainless steel AISI 316L) with a highest protective efficiency against corrosion and tribocorrosion in 3.5 wt. % NaCl solution to assist the selection and
development of coatings for wear applications in corrosive medium, e.g. as a hard coating for drilling equipment for use in marine or similar conditions with a presence of water.

Experimental methods

Preparation of samples. The flat samples of stainless steel AISI 316L (25×15×5 mm) were polished with SiC sandpaper down to 0.5 µm. Substrates were cleaned with isopropanol for 50 min by using ultrasonic bath. The samples were sputter-cleaned in argon plasma with the bias voltage -850 V at 425 °C for 1h. TiCN and TiAlN (with the Al content of 60 at. %) coatings were deposited onto substrates in nitrogen atmosphere using a lateral rotating cathode arc (LARC) technology (Platit π-80 unit). The deposition temperature for both coatings was 450 °C.

Specimens are marked as following: uncoated (bare) stainless steel AISI 316L as reference (R), samples coated with TiCN (A) and TiAlN (B). All tests were repeated at least three times.

Structural characterization of coatings. A scanning electron microscope (SEM) Hitachi TM1000 equipped with energy-dispersive X-ray spectroscopy (EDS) was used for investigation of the surface morphology. The thickness of coating was measured by kalotest method with the kaloMAX tester in accordance with ball cratering technique developed by BAQ (Germany).

Potentiodynamic polarization test. Potentiodynamic polarization measurements were performed in 3.5 wt. % NaCl solution in the three electrode cell using a saturated calomel reference electrode (SCE) and platinum (Pt) counter electrode (CE) with a working surface area of 2 cm². Specimens, isolated with a non conductive silicone, leaving an exposed surface area of about 1 cm² were used as working electrodes (WE). Autolab PGSTAT30 galvanostat - potentiostat system with General Purpose Electrochemical System (GPES) software (Metrohm Autolab B.V., Netherlands) was used for data recording and processing. After the open circuit potential (OCP) stabilization the limits of linear sweep voltammetry were set as -0.7 and 0 V (except for reference sample after 24 h immersion a range was from -0.8 to 0 V) by selecting a scan rate 5 mV·s⁻¹.

Penetration rate CR (the thickness loss per unit of time [mm·year⁻¹]), protective efficiency \( P_i \) [%], porosity \( F \) [%] of coating, the polarization resistances of the substrate and coating-substrate systems \( R_{pm} \) and \( R_p \) were calculated according with methods described in standard [10] and research work by Yoo et al [11].

Tribocorrosion test at open circuit potential. Tribocorrosion experiments were carried out with a Universal Micro Materials Tester (UMT-2) from CETR (Bruker) in a reciprocating mode (amplitude 1·10⁻³ m, frequency 1 Hz) with a stationary ball located above specimen (wear debris may remain in wear scar). All tests were done at ambient atmosphere environment (23±2 °C, relative humidity 30±5 %). Specimen was fixed to a reciprocating table equipped with an electrochemical cell as shown in Fig.1 a. Electrochemical cell was filled with 50 ml 3.5 wt. % NaCl solution, ensuring 1 cm level of liquid above the specimen connected to potentiostat as WE. Standard Ag/AgCl as RE and Pt as CE were used to provide a three electrode setup. EmStat® potentiostat with PSTrace software (PalmSens BV, Netherlands) was used for data recording and processing. Specimen was isolated with a non conductive silicone, leaving 1 cm² of exposed surface area. Prior to the wear test, sample was cleaned step by step with acetone, ethanol and then dried. Created system was stabilized for 1 h before starting the test. Recorded test was divided into three periods: (1) stabilization (1000 seconds), (2) tribocorrosion (7200 s) and passivation (1000 s). A zirconia (ZrO₂) ceramic ball with a diameter of 1 cm, made of high purity yttria-stabilized zirconia (YSZ, 95 % ZrO₂, 5 % Y₂O₃) manufactured by Tosoh/Nikkato corporation (Japan) with a surface roughness \( R_s = 0.03 \mu m \) (measured by Mahr perthometer, PGK 120, contact mode, according to DIN EN ISO 4287) was used as counter-body. Applied load was 9.8 N (1 kg).

Results and discussion

Microstructural characterization. SEM image of the as-deposited TiAlN coating surface morphology is shown in Fig.1 b. Defects including macroparticles (inclusions), voids and pinholes with sizes mostly less than 10 µm were observed on the surfaces of coated specimens. Therefore, a
relatively slow water and chloride ions intrusion in the coating can be expected due to limited pore wetting and chloride ions diffusion. The cross-section SEM images (not shown) of about 3 µm thick coatings (measured by kalotest method) show that TiAlN is more defected (containing more cracks, pores, etc., mainly due to the inclusions in the middle of a dense coating) as compared to TiCN one.

Fig.1. Schematic drawing of tribocorrosion test (a) and SEM micrograph of as-deposited coating TiAlN (b)

Potentiodynamic polarization test. Tafel plots, obtained for steel substrate and coated specimens, are shown in Fig.2 (after 10 min. and after 24 h immersion). Potentiodynamic polarization data from GPES is shown in Table 1. The corrosion potential ($E_{corr}$) of the steel substrate is about -0.357 V vs. SCE and corrosion current $i_{corr}$ is 1.793 $\mu$A·cm$^{-2}$. TiCN and TiAlN coatings after 10 min. immersion show that $E_{corr}$ shift towards the positive values (-0.185 and -0.177 V vs. SCE) with up to 20 folds lower $i_{corr}$ as compared to AISI 316L. After 24h immersion in 3.5 wt. % NaCl solution, $E_{corr}$ shift towards the negative side for all samples, indicating a loss of oxide layer protection for bare steel (sample $R$) and more intensive penetration of corrosive solution toward substrate for TiCN and TiAlN coatings, remaining one to three folds better pore resistance (see Table 1) as compared to AISI 316L. After 24 h immersion, the TiCN coating with $E_{corr} = -0.40$ V vs. SCE shows a higher pore resistance ($1.15 \times 10^5$ Ω·cm$^{-2}$) as compared to TiAlN coating ($2.24 \times 10^3$ Ω·cm$^{-2}$).

Fig.2. Potentiodynamic polarization curves (Tafel plots) of tested specimens, (a) – after 10 min. immersion, (b) – after 24 h immersion

In contrast to the SEM results (Fig. 1b), a lowest porosity (about 0.012 %) and highest protection efficiency ($P_i$) (about 95 %) are obtained for TiAlN (sample $B$) as shown in Table 1. The TiCN coating shows similar performance to TiAlN one, conforming the high inertness of transition metal nitrides and carbonitrides [4,7,12].

Tribocorrosion test. Evolution of OCP before, during and after wear tests of reference sample $R$ (AISI 316L) sample $A$ (TiCN) and sample $B$ (TiAlN) is presented in Fig.3 a. The graph shows a significant drop in OCP of coated specimens from a moment when load was applied and reciprocating motion was started. OCP of bare steel (sample $R$) already reached close to maximum
negative OCP during stabilization period. For all samples, there was no visible passivation after removal of mechanical load. TiCN shows best performance in given tribocorrosion conditions.

Table 1. Potentiodynamic polarization data of specimens tested in 3.5 wt. % NaCl solution after 10 min and 24h immersion. Penetration rate \((CR)\), protective efficiency \((P_i)\) and porosity \((F)\) are also shown

<table>
<thead>
<tr>
<th>Potentiodynamic polarization measurements</th>
<th>Calculation results</th>
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<tr>
<td></td>
<td>(E_{corr})</td>
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<tr>
<td>(R_{10m})</td>
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<tr>
<td>(R_{24h})</td>
<td>-0.73</td>
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<tr>
<td>(A_{10m})</td>
<td>-0.19</td>
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<tr>
<td>(A_{24h})</td>
<td>-0.40</td>
</tr>
<tr>
<td>(B_{10m})</td>
<td>-0.18</td>
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<tr>
<td>(B_{24h})</td>
<td>-0.45</td>
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Note: \(X_{10m}, X_{24h}\) – after 10 min and 24 h immersion; \(R\) – reference; \(A\) – TiCN; \(B\) – TiAlN; \(\beta_a, \beta_c\) – anodic and cathodic slopes in Tafel plot. Deviations \(E_{corr}\) not more than ± 0.08 V, \(i_{corr}\) – not more than ± 0.10 A.

Three times lower and more stable coefficient of friction (COF) (0.25-0.30) for TiCN coating was found after 1300 s as compared to TiAlN coating and bare steel. A OCP shifting toward negative side with a simultaneous small increase in COF for TiCN (sample A) is observed after about 3500 s; removed macro droplets from coating during sliding led to loss of corrosion protective efficiency (Fig.3 b). TiAlN coating significantly lost protective efficiency at the same time when load and sliding was applied; after 1200 s substrate has become unprotected in wear zone, reaching OCP - 0.78 V vs. Ag/AgCl due to significantly removed TiAlN coating and created micron sized cracks as shown in Fig.3c. It could be concluded that TiCN coating exhibits three times lower COF value and six times longer protection of substrate as compared with TiAlN coating under the same tribocorrosion conditions mainly due to less defective structure.

Fig.3. Evolution of COF and open-circuit potential (vs. Ag/AgCl) (a), SEM images of wear tracks after tribo-corrosion tests on TiCN (b) and TiAlN (c) coatings
Conclusions

It was found that in case of gradient PVD coatings with thickness of 3 µm:

1) TiAlN coating ensures the best performance during short (10 min.) immersion in the 3.5 wt. % NaCl solution, providing up to almost 95% higher protective efficiency as compared to the bare steel grade 316L;

2) TiCN coating is providing higher pore resistance ($1.15 \times 10^5 \ \Omega \cdot \text{cm}^{-2}$) due to less shifting corrosion potential toward more negative potential (reaching -0.40 V vs. SCE) after long time (24 h) immersion as compared to TiAlN and bare steel;

3) COF of TiCN coating is three times lower (0.25-0.30) and durability (corrosion protective efficiency) is six times longer than for TiAlN coating and bare steel under the same tribocorrosion conditions;

4) TiCN coating is mainly losing only embedded particles, remaining from PVD process, while TiAlN coating is partially lost and damaged in tribocorrosion (wear scar).

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References


