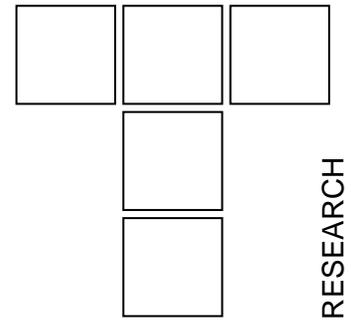


# The Effect of Ceramic Coatings on Corrosion and Wear Behaviour



*Surface engineering plays a great role in decreasing the cost of wear and corrosion losses in industrial applications. Generally, engineering materials must have some specific characteristics. These characteristics which are important in selecting material for specific applications related with material structure and life-time. Generally it is difficult to find all these features (mechanical and surface) in a single material. So the solution is found by increasing the strength of bulk material, and increasing wear and corrosion resistance of the surface. Therefore, engineering materials are selected from cheaper materials providing needed structural features, and the other surface characteristics are provided from coatings. Today, coatings are used in different fields of industry. Especially, in space industry components, gas turbines, turbine rotor blades, ceramic coatings are widely used for improving the oxidation and corrosion resistance and hardness, and for decreasing the wear. In this study, the corrosion protective properties of PVD-TiN coatings were investigated and the relations between corrosion protective properties and structural and wear properties were studied.*

**Keywords:** corrosion, ceramic coatings, TiN

## 1. INTRODUCTION

Corrosion is defined as “attack on a material by its reaction with the environment and the resulting deterioration of the materials properties”. Most often, it is related to an electrochemical reaction with a liquid or gaseous medium [1]. The most effective method preventing the harmful effect of the corrosion attack on the parts is adding a protective barrier between the part and corrosive environment. PVD-ceramic coatings have been widely used as thin protective layers. Especially the excellent properties of thin films of TiN such as high hardness, good wear and corrosion resistance, high electrical conductivity, chemical stability and good adhesion have led to many useful applications [2-4].

Ceramic coating materials are normally relatively noble, but there are many factors influencing the corrosion resistance of the coating-substrate system [1]. Corrosion resistance of a ceramic coating-substrate system depends on the surface properties of the coating, to its chemical composition, to its structure and to the physical defects of the coating

[5]. An improvement of the corrosion resistance of ceramic coating-substrate systems can be obtained by different measures [1].

The corrosion protective properties of nitride based PVD coatings mainly depend on the defects starting at the surface and extending through the coating [5,6]. The sources of these defects can be: a) inherent porosity of the coating itself, b) macro defects such as droplets, droplet peripheries, eroded sites due to arcing, uneven coating thickness due to substrate surface roughness and geometry, c) cracks due to internal stress or mechanical damages [5]. The corrosive medium can penetrate through these defects reacting with the substrate material causing galvanic corrosion [1,7]. Furthermore, ceramic coatings may crack in service owing to substrate plastic deformation when subjected to high intensity loading or impact loading, which will cause rapid crevice corrosion [7].

The surface roughness of the part to be coated also significantly influences the corrosion behaviour of the system. A higher substrate surface roughness results in a less complete coverage of the substrate with the coating material because of shadowing effects during PVD film growth [1]. Therefore, multilayer coatings, thicker coatings or smoother substrate surfaces improve the corrosion resistance

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of the system [4,5]. Amorphous coatings are inherently non-porous. Physical defects can be eliminated by choosing suitable coating techniques and operating conditions. Also cleaner chamber and substrate surfaces decreases defects [5]. The corrosion resistance of hard coatings like TiN, (TiAl)N, CrN depends very much on their microstructure [8,9]. Generally, fine grained coatings show best corrosion protection [8]. Furthermore, the deposition of denser coating structures improve the corrosion resistance of the system [1].

Adhesion of the coating to the substrate is also an important factor with respect to corrosion protective properties. If the coating does not adhere well to the substrate the coating can easily delaminate hence exposed substrate surface can increase. The adhesion properties of the coating to the substrate is a function of the coating type and surface cleanliness. Also high-energy ion bombardment and heating of the coated surfaces may cause diffusion of the metallic layer between the metal and the coating to the substrate hence, corrosion resistance of the substrate could be improved [5]. Another possibility for the improvement of corrosion resistance is the deposition of interlayers and/or multilayered coatings. Such interlayers may be deposited by physical or electrochemical processes (PVD, ECD). The deposition of PVD interlayers of metals more noble than the substrate material can reduce the corrosion attack. Additionally, the number of pores and pinholes can be reduced, when new structures of the hard coatings are formed on the top of the interlayer. Marked improvements are, for example, found for 4  $\mu\text{m}$  thick Ti/TiN-PVD coatings when compared with 3  $\mu\text{m}$  PVD-TiN. The benefit of the Ti layer is additionally attributed to its passivation [1]. Other type interlayers are Ti for (TiAl)N coatings,  $\text{TiO}_2$  for TiN coatings and Cr for CrN coatings [8,10]. Also coating of the substrate with Ni-P, prior to ceramic coating, improves the corrosion resistance of the system [5]. In addition, PVD-Ti/TiN multilayers and PVD-nitride coating/plasma nitrided steel duplex coating systems offer an improved corrosion resistance [2,7].

Due to exposed area of the substrate to the corrosive environment, corrosion resistance of the coating-substrate system can be improved by replacing the substrate with more corrosion resistant material to the environment. In this case the ceramic coating applied mainly serve for corrosion protection of the system to mechanically induced types of corrosion such as erosion,

cavitation and fretting corrosion. If hard and non-porous ceramic coatings could be produced, less expensive materials normally not resistant to the environment could be used for the same purpose [5].

In this study, the corrosion protective properties of PVD-TiN coatings were investigated and the relations between corrosion protective properties and structural and wear properties were studied.

## 2. EXPERIMENTAL DETAILS

### 2.1. Sample preparation

TiN coatings were deposited onto mechanically polished (surface roughness  $R_a$  0.05  $\mu\text{m}$ ) high speed steel (AISI M2) substrates (66 HRC) by cathodic arc method. Substrate composition is as follows: C 0.88%, Cr 4.07%, Mo 4.70%, V 1.76%, W 6.63% and Fe balance. The cylindrical samples with dimensions of 20 mm diameter and 8 mm height were used for both wear and corrosion tests. The substrates were ultrasonically cleaned before coating deposition. The coating parameters are listed in Table 1.

Table 1. Coating parameters

Cathode current (A)	Coating time (min)	Bias voltage (V)	Coating temperature ( $^{\circ}\text{C}$ )	Vacuum pressure (mTorr)
55	60	-250	400	4

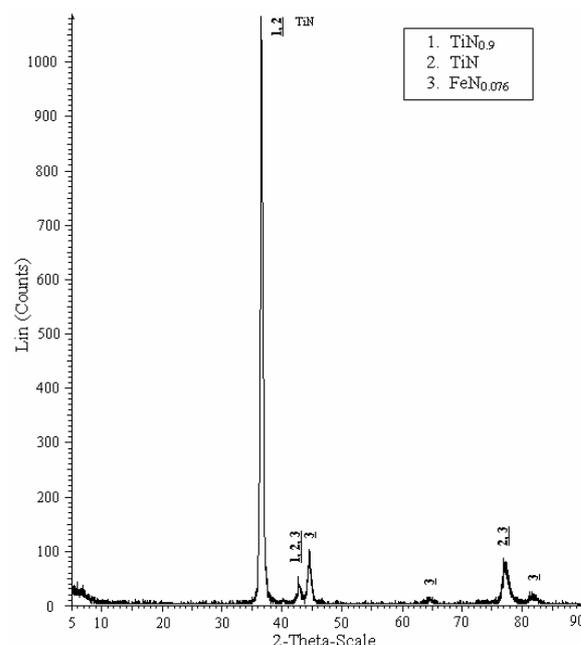


Fig. 1. XRD Spectra of the TiN coating.

## 2.2. Characteristics of the TiN coating

The surface roughness  $R_a$  after the coating deposition was about  $0.23 \mu\text{m}$ . Fig. 1 shows XRD spectra of the TiN coating. The cross-section of the TiN coating was observed by scanning electron microscopy (SEM) (Fig. 2). The coating thickness was determined as  $1.12 \mu\text{m}$  by SEM, and also by calotest method. The nanohardness value of the TiN coating was 2927 Vickers (Fig. 3), and the critical load ( $L_c$ ) value for the scratch test was 58.3 N (Fig. 4). The good adhesion between the coating and the substrate was also observed by Daimler Benz adhesion test (Fig. 5).

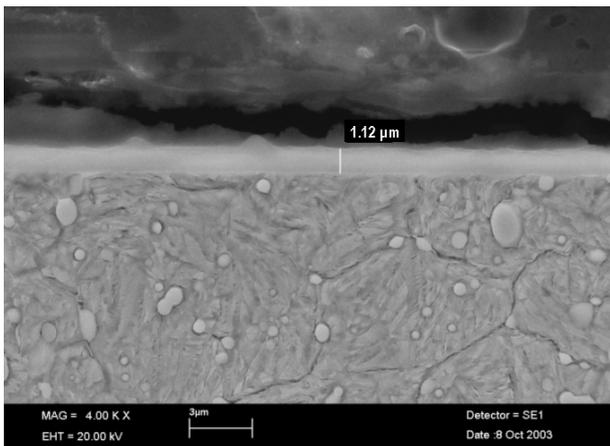


Fig. 2. SEM cross-sectional micrograph of the TiN coating

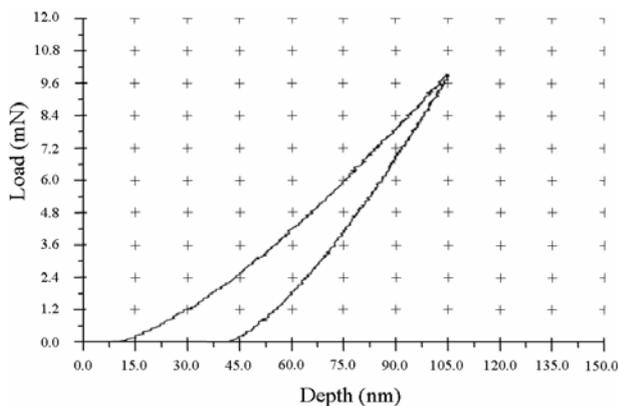


Fig. 3. Nanohardness load-depth graph. Maximum load 10 mN, loading rate 20 mN/min, indenter type vickers, indenter material diamond, hardness 2927 Vickers, elastic modulus 435 GPa.

## 2.3. Wear and corrosion testing

The wear behaviours of PVD-cathodic arc TiN coated and uncoated high speed steel (M2) samples were investigated in a wear tester adapted to pin-on-ring system (ASTM G-77) (Fig. 6 and Fig. 7).

DIN 100Cr6 rings (surface roughness  $R_a$   $0.12 \mu\text{m}$ , 61 HRC) with 26 mm diameter and 5 mm height were used as counter material. Counter material composition is as follows: C 0.99%, Mn 0.38%, Cr 1.42%, Mo 0.02% and Fe balance.

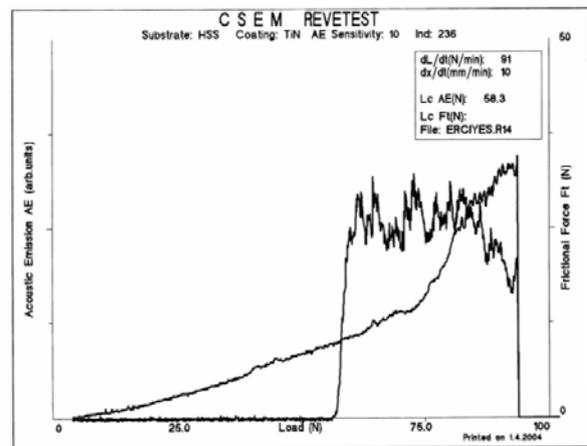


Fig. 4. Acoustic emission and frictional force graph for scratch test. Starting load 4.0 N, cut-off load 98.3 N,  $dL/dt$  91 N/min,  $dx/dt$  10 mm/min,  $L_c$  58.3 N

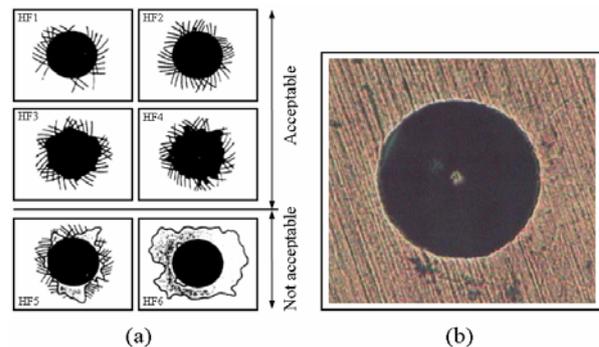


Fig. 5. (a) Daimler Benz adhesion test standards. (b) Rockwell C track formed on the TiN coated specimen.

Wear experiments were performed in dry sliding and room temperature conditions, and sliding speed (0.9 and 1.1 m/s) and normal load (25 and 50 N) were used as variable parameters. The test time was stable at 25 min. The wear track width on the specimens and the average coefficients of friction in steady-state sliding regime were determined. In corrosion tests, the corrosion medium was 1 N  $\text{H}_2\text{SO}_4$  solution (200 ml) and all the tests were carried out at room temperature, open to the air. The sample surfaces were cleaned by acetone and distilled water, and the samples were immersed in the corrosion medium for 1, 10, 40, 70 and 100 hours. The mass losses were determined. After the tests, the surface topography of the samples were observed by SEM.

Table 2. Wear test results

Experiment no	Sliding speed (m/s)	Load (N)	Time (min)	TiN coated / Uncoated	Wear track width (mm)	Coefficient of friction
1	0.9	25	25	Unc.	1.096	0.159
2	0.9	25	25	TiN	0.992	0.175
3	0.9	50	25	Unc.	1.758	0.218
4	0.9	50	25	TiN	1.300	0.187
5	1.1	25	25	Unc.	1.268	0.161
6	1.1	25	25	TiN	1.028	0.162
7	1.1	50	25	Unc.	1.892	0.198
8	1.1	50	25	TiN	1.362	0.197

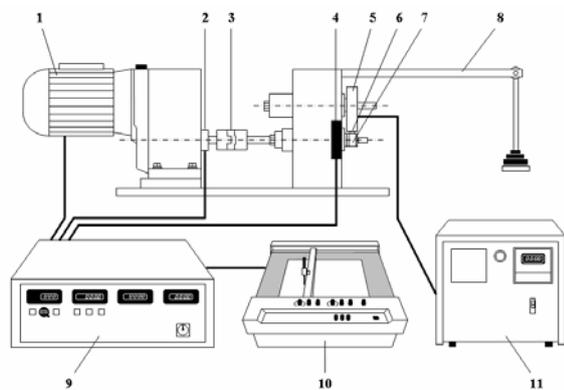


Fig. 6. Schematic of pin-on-ring system 1.motor, 2.tachometer, 3.coupling, 4.load measurement unit, 5.specimen holder, 6.specimen, 7.counter ring, 8.weight loading arm, 9.control unit, 10.x-y recorder, 11.high temperature unit.

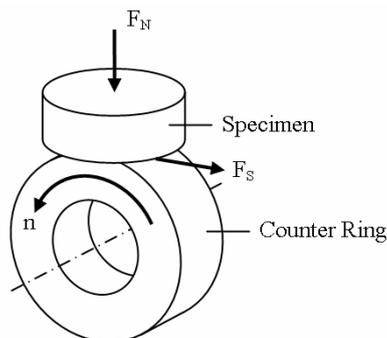


Fig. 7. Contact geometry and forces for pin-on-ring system.

### 3. RESULTS

#### 3.1. Wear test results

The wear track width and coefficient of friction values are listed in Table 2. It was found that wear track width values increased with load and also with sliding speed. At the same load and speed value, wear track width of uncoated specimens was

larger than that of TiN coated specimens. This indicates that TiN coated specimens have a higher wear resistance. It was found that coefficient of friction values of uncoated and TiN coated specimens were quite similar, and it was not observed a clear variation with increased load and sliding speed. Especially, coefficient of friction values of uncoated and TiN coated specimens at the same load were almost the same at 1.1 m/s sliding speed. In some experiments, it was observed a decrease in coefficient of friction with increased sliding speed. It is suggested that the frictional heat produced at high sliding speeds is able to cause surface oxidation and results in a decrease in the coefficient of friction. These results are similar to the results reported in references [11-13].

SEM micrograph (Fig. 8) and EDX analysis (Fig. 9) taken from the worn surface of TiN coated sample have showed the presence of iron and titanium based oxides (e.g.  $Fe_2O_3$  and  $TiO_2$ ). Also, SEM micrograph and EDX analysis taken from the worn surface of uncoated sample (Fig. 10) have showed the presence of iron based oxides.

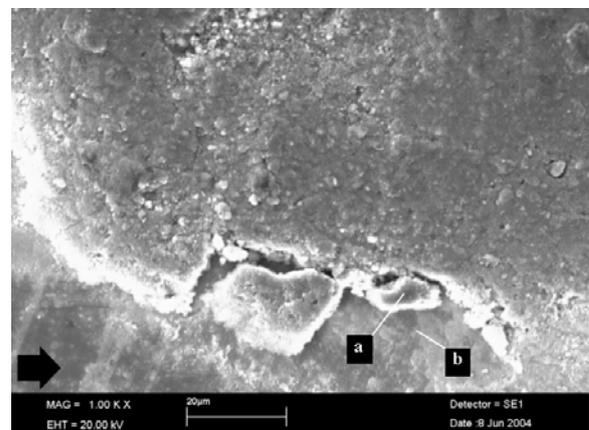


Fig. 8. SEM micrograph of worn surface of TiN coated sample. The arrow indicates sliding direction. ( $V=0.9$  m/s,  $F=50$  N,  $t=25$  min).

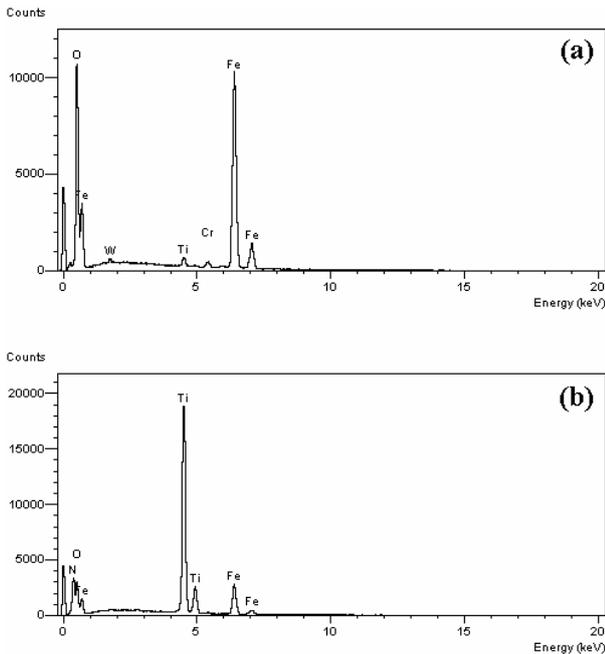


Fig. 9. EDX analysis taken from point a and b in Fig. 8. (a) elemental composition of point a: O 41.20%, Ti 1.19%, Cr 0.91%, Fe 56.07%, W 0.63%. (b) elemental composition of point b: N 3.12%, O 32.42%, Ti 50.04%, Fe 14.42%.

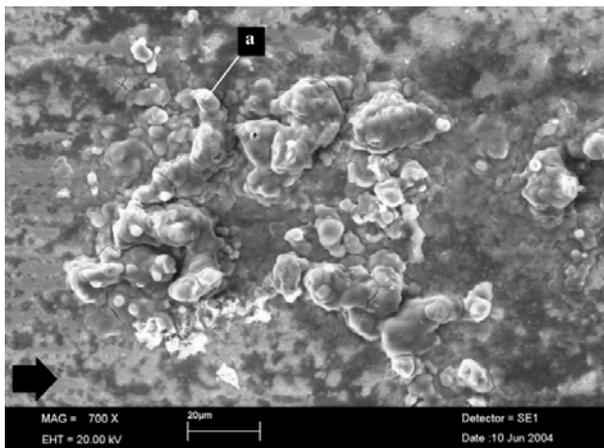


Fig. 10. SEM micrograph of worn surface of uncoated sample. The arrow indicates sliding direction. Elemental composition of point a: O 34.11%, Fe 65.89%. ( $V=1.1$  m/s,  $F=25$  N,  $t=25$  min).

Fig. 11 shows SEM micrograph of right side of wear track on TiN coated sample. EDX analysis taken from the point a in Fig. 11 showed the presence of iron based oxide, and the analysis taken from the point b, c and d showed the titanium contents of 26.93%, 73.77% and 80.55%, respectively. This indicates that the coating removes from the surface by polishing wear mechanism, not by delamination, because of the good adhesion between the coating and the substrate. This improves the wear and also the corrosion resistance of the system.

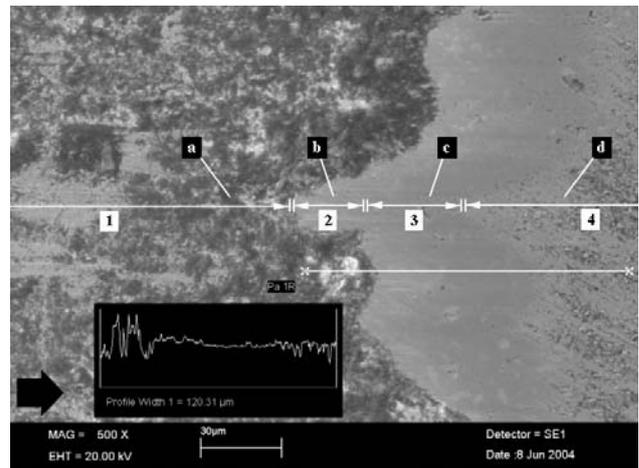


Fig. 11. SEM micrograph of right side of wear track on TiN coated sample. The arrow indicates sliding direction. ( $V=1.1$  m/s,  $F=25$  N,  $t=25$  min).

### 3.2. Corrosion test results

The mass losses of the samples as a function of immersion time (1, 10, 40, 70 and 100 h) were presented in Fig. 12. It was found from the graph that the mass losses increased with immersion time. At the same immersion time, mass losses of uncoated samples was larger than that of TiN coated samples. This indicates that TiN coating improves the corrosion resistance of the system.

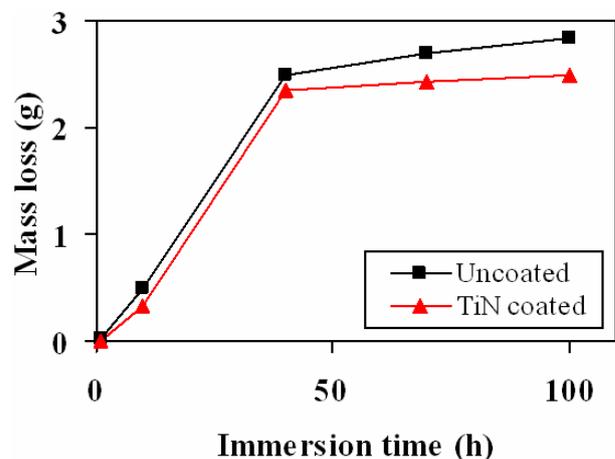


Fig. 12. The mass losses of the samples as a function of immersion time (1, 10, 40, 70 and 100 h).

SEM micrographs of TiN coated and uncoated sample surfaces after 10 and 100 h immersion in 1 N H<sub>2</sub>SO<sub>4</sub> solution (200 ml) were presented in Fig. 13-Fig. 16.

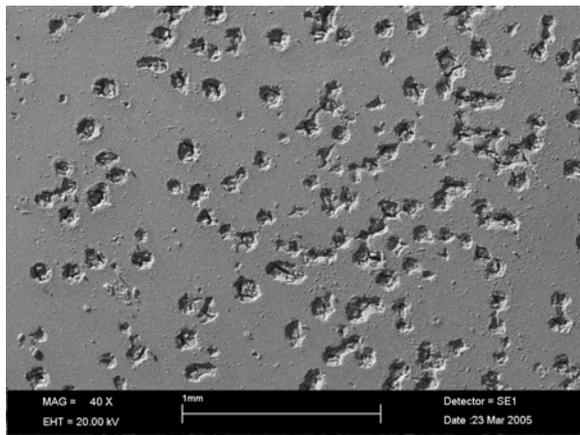


Fig. 13. SEM micrograph of TiN coated sample surface after 10 h immersion in 1 N H<sub>2</sub>SO<sub>4</sub> solution.

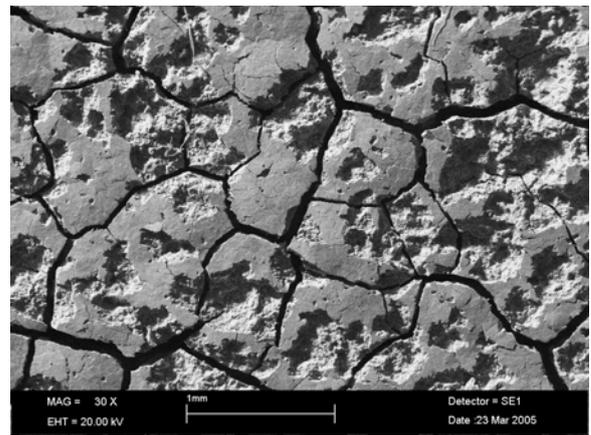


Fig. 16. SEM micrograph of uncoated sample surface after 100 h immersion in 1 N H<sub>2</sub>SO<sub>4</sub> solution.

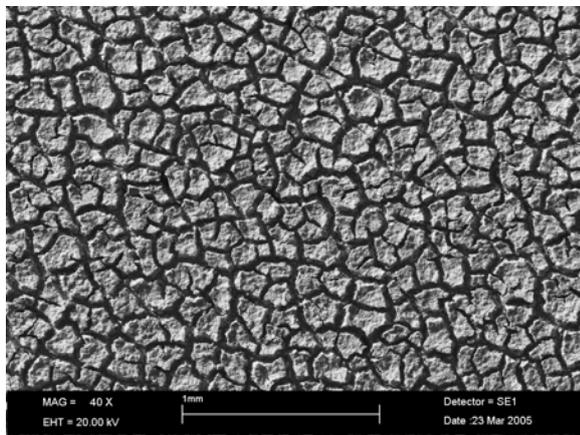


Fig. 14. SEM micrograph of uncoated sample surface after 10 h immersion in 1 N H<sub>2</sub>SO<sub>4</sub> solution.

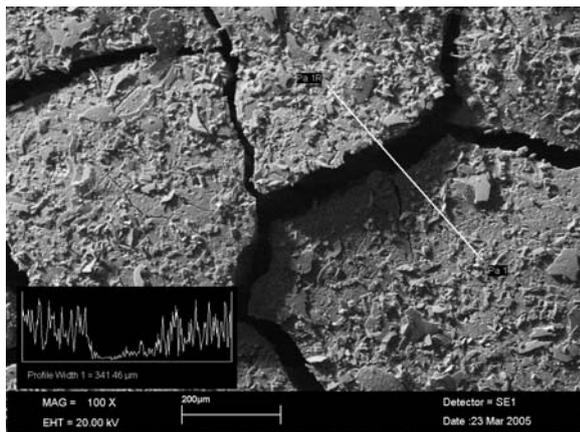


Fig. 15. SEM micrograph of TiN coated sample surface after 100 h immersion in 1 N H<sub>2</sub>SO<sub>4</sub> solution.

Ceramic coatings are chemically inert in neutral or acidic media, but generally have inherent porosity and macro defects. Therefore, when subjected to a corrosive atmosphere, coated materials will form galvanic cells at the defects near the interface since ceramic coatings are electrochemically more stable than most substrate materials (e.g. steels). Once aggressive ions such as chloride penetrate the coating through these small channels, driven by capillary forces, the exposed area will begin to experience anodical dissolution, which will usually extend laterally along the interface between the coating and the substrate. Corrosion may be then accelerated to high rates since the coating presents a large cathodic area compared to the very small exposed substrate, which serves as an anode. Thus the protection of the substrate is no longer effective, leading to a strong local corrosion attack [7]. After the tests, no corrosion pit was found on the surface of the TiN coating after 1 h immersion test and the surface was as bright as the former surface. But the uncoated sample surface was so lustreless after 1 h immersion test. This indicates that TiN coating not only presents an attractive golden colour but also maintains this appearance for a long time even in strong corrosive mediums. However, a large number of corrosion pits were observed on the surface of the TiN coating after 10 h immersion test (Fig. 13). After the same immersion time the whole surface of the uncoated sample was completely covered with cracks. An increase was observed in mass loss between 10 and 40 h immersion time. It was because of the joining and spilling of the corrosion pits and cracks. After 40, 70 and 100 h immersion the similar surface cracks were observed on the surface of the uncoated sample and also TiN coated sample. Also small TiN coating parts were found on the surface of the TiN coated sample (Fig. 15). Although these parts do not totally cover the

substrate surface, nevertheless they substantially decrease the exposed active substrate surface area. On the contrary of TiN coated sample, large holes were observed on the surface of the uncoated sample (Fig. 16).

#### 4. CONCLUSIONS

TiN coatings were deposited onto mechanically polished high speed steel (AISI M2) substrates by cathodic arc method and the corrosion protective properties of the coatings were investigated and the relations between corrosion protective properties and structural and wear properties were studied. The results obtained can be summarized as follows:

1. Ceramic coatings like TiN improve the wear resistance of the system because of high hardness, low friction characteristics, dense coating morphology and improved adhesion properties.
2. Ceramic coatings like TiN improve the corrosion resistance of the system because coating materials are normally relatively noble and coating layer acts as a protective barrier between the part and corrosive environment.
3. Wear damage and corrosion damage of the TiN coatings are similar. Good adhesion between coating and substrate does not allow the coating to be delaminated easily and remaining coating continues the protective function to the last.
4. However, the high wear resistance of ceramic coatings actually improve the corrosion resistance of the system in some applications by maintaining the protective barrier function of the coating.
5. To develop the protective properties of the ceramic coatings, it is necessary to produce coatings without inherent porosity and macro defects. Furthermore, increased hard coating thickness, lower substrate roughness, denser coating morphology by suitable processes and process parameters, PVD interlayers/multilayers, ECD interlayers and duplex coatings improve the corrosion resistance of the ceramic coating-substrate system.

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