High Power Impulse Magnetron Sputtering (HIPIMS) Pre-treatment for the Deposition of Hard Coatings

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Key Words: Sputter cleaning, Corrosion-resistant coatings, Adhesion, Sputter deposition

ABSTRACT

CrN and TiN functional coatings have been prepared by surface pre-treatment by the novel HIPIMS technology followed by reactive unbalanced magnetron sputtering deposition. During pre-treatment, HIPIMS was operated with a peak power density of 3 kWcm^{-2} in an inert gas atmosphere at pressure P_{Ar} = 1 mTorr (0.13 Pa). The ion current to the substrates reached peak values of 300 mAcm^{-2} and the substrate bias voltage was -1200 V. The ion flux comprised high metal ion-to-neutral ratios as well as metal species with charge states up to 2+ for both Cr and Ti. The pre-treatment by HIPIMS improved the adhesion of the films to steel due to ion intermixing at the interface. Critical loads achieved in scratch adhesion testing were 45 and 58 N for the Cr-etched CrN-deposited system (Cr-CrN) and Ti-TiN respectively compared to 20 N for Ar-etched CrN. The films had a thickness of ~3 µm, while the residual stress evaluated by glancing angle x-ray diffraction was -2.6 GPa for the Cr-CrN. SEM observations of the surface of the coatings showed no large scale growth defects. Pin on disk sliding wear testing showed that the wear tracks were smooth indicating small size of the wear debris. The wear resistance of the Cr-CrN coatings was as low as 5×10^{-16} m^{3}N^{-1}m^{-1}. The good performance of the coatings could be attributed to the defect free surface and excellent adhesion. Potentiodynamic corrosion tests of the Cr-CrN coatings showed low corrosion currents of 7×10^{-7} Acm^{-2} that may result from the defect free microstructure. The influence of etching duration and bias voltage on the quality of pre-treatment is discussed.

INTRODUCTION

CrN and TiN coatings have been introduced in the early 1980s and have a firm hold in a wide range of industrial applications. Demands on these coatings are forever increasing and it is rare that a new technology is available to improve the quality of these layers and in particular to reduce surface roughness whilst maintaining an excellent adhesion to steel substrates. Existing processes such as Ar gas ion pre-treatment of the substrate are not efficient in sputtering contaminating oxides from the substrate surface due to the low plasma density and lack of metal species to reduce the oxygen and often layers have a poor adhesion. Etching by arc discharges introduces a high number of droplets, which shadow the substrate surface and develop into micrometer size growth defects once the coating deposition process starts. To address these issues the novel high power impulse magnetron sputtering (HIPIMS) [1] technology has been utilized. HIPIMS employs highly ionized metal plasmas containing high fractions of metal ions, typically 30% for Cr [2]. The technology has been demonstrated for industrial scale equipment [3]. The current paper discusses the application of HIPIMS to etch steel substrates prior to deposition by conventional dc magnetron sputtering. The effect of HIPIMS pre-treatment on surface quality, adhesion, sliding wear and corrosion resistance is evaluated for the Cr etched CrN deposited system (referred to as Cr-CrN) and the Ti-TiN system.

EXPERIMENT DETAILS

The coatings were deposited in laboratory scale equipment utilizing a circular planar magnetron target size of 6 inch. The chamber was evacuated to a base pressure of 10^{-6} Torr. The coating deposition sequence is shown in Figure 1. The samples were heated and outgassed at 400°C for 1 hour. The substrate cleaning was performed by HIPIMS of Cr with an average power of 1.5 kW and peak power of 700 kW over a pulse duration of 50 microseconds for a range of high bias voltages on the substrates. Finally, the coating deposition was performed by conventional DC sputtering of Cr at a power of 1.5 kW and a gas mixture Ar:N_2 of 1:1. The coating thickness was 3 µm.

48th Annual Technical Conference Proceedings (2005) ISSN 0737-5921

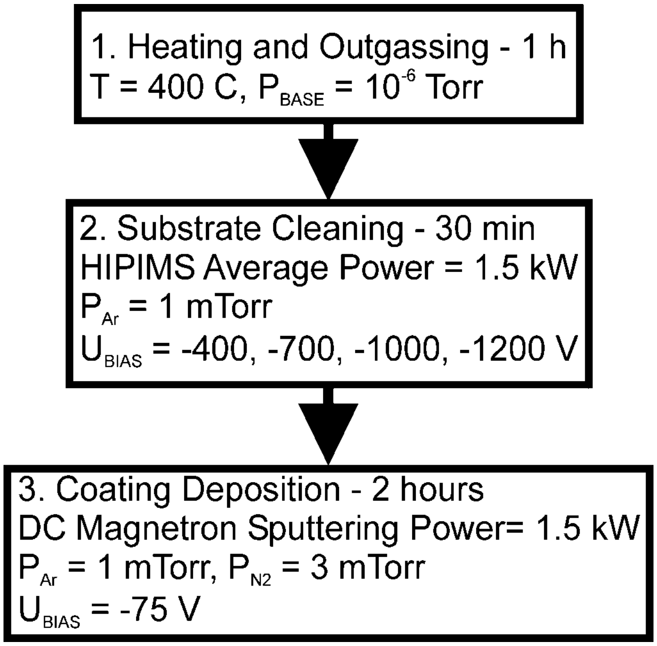

Figure 1. Coating deposition sequence – Cr-CrN.

For the Ti-TiN, the same conditions were used except that during deposition partial gas pressures for Ar and N_2 were P_{Ar} = 3 mTorr and P_{N2} = 0.5 mTorr, respectively. A coating thickness of 3 µm was deposited. For the Ti-TiN system two methods for etching were utilized: HIPIMS in conditions from Figure 1 was compared to conventional dc magnetron sputtering run at the same gas pressure and average power. Dc magnetron sputtering is known to produce low density (10^{10} ions cm^{-3}) argon plasma and high fluxes of Ti neutral ions, whilst the degree of ionization of the metal is particularly low (less than 1%). Two mirror-polished disk substrates (ø 30 mm) made of high speed steel (HSS) and 304 stainless steel were deposited on at the same time in all runs. HSS disks were used for wear and adhesion testing, while the stainless steel disks were used for corrosion evaluation. The coatings adhesion was evaluated by the critical load (L_C) value measured in scratch tests (diamond radius of 200 µm). A CSM sliding wear pin-on-disk tester was used to measure the friction and wear coefficient with Al_2O_3 ball counterpart, at a load of 5 N and a linear speed of 10cm/s. The corrosion performance was evaluated in an EG&G potentiostat in polarization corrosion tests in 3% NaCl. The testing area of the samples was ø10mm diameter and the rest of the sample were completely masked with beeswax.

RESULTS AND DISCUSSIONS

The coating surface was observed by scanning electron microscopy (SEM). Figure 2a and b show the surfaces for the Cr-CrN and Ti-TiN films. The surface is homogeneous and no large scale growth defects are observed. The overall roughness of the substrates increased by 20% due to the intensive sputtering of the substrate during the substrate cleaning step. In Figure 2a, the apparent structure is attributed to the carbide grains in the steel that sputter at a slower rate and are, therefore, left as prominent features on the surface after the cleaning step.

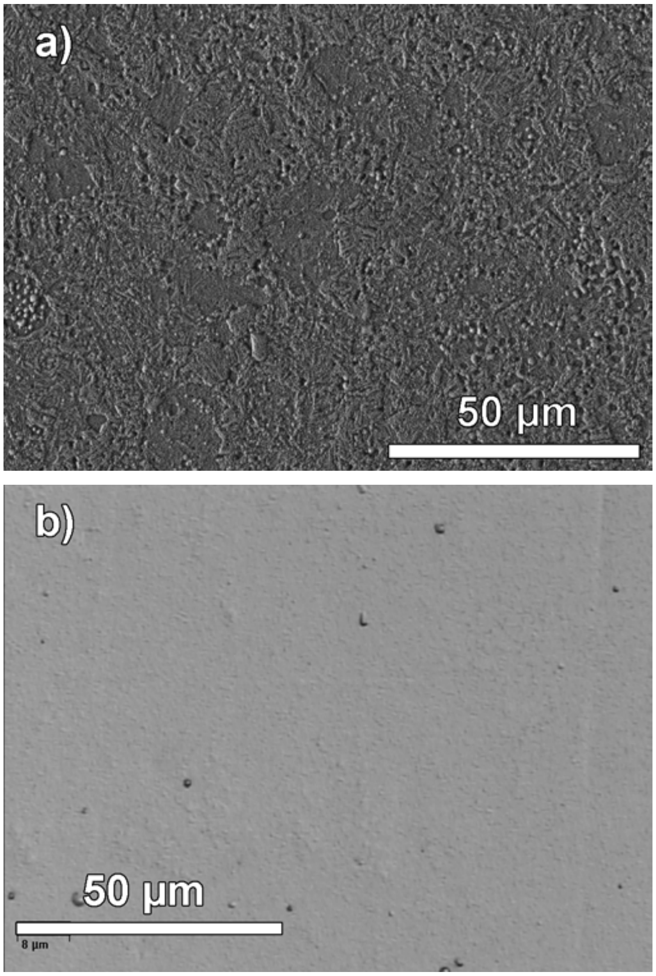

Figure 2. SEM micrographs of the surface of coatings where the substrate has been pretreated in a HIPIMS discharge: a) Cr-etched, CrN deposited (b) Ti-etched, TiN deposited.

The adhesion of the films was evaluated by scratch testing by measuring the critical load, L_C, necessary for spallation of the film from the substrate. The L_C for HIPIMS-etched Cr-CrN films was 45 N measured for samples etched at a bias voltage of -1200 V. For the case of HIPIMS-etched Ti-TiN films the critical load was 58 N achieved at a substrate bias voltage of -1200 V. Figure 3a shows a micrograph of the scratch exhibiting small chips on each side occurring intermittently after the critical load is exceeded.

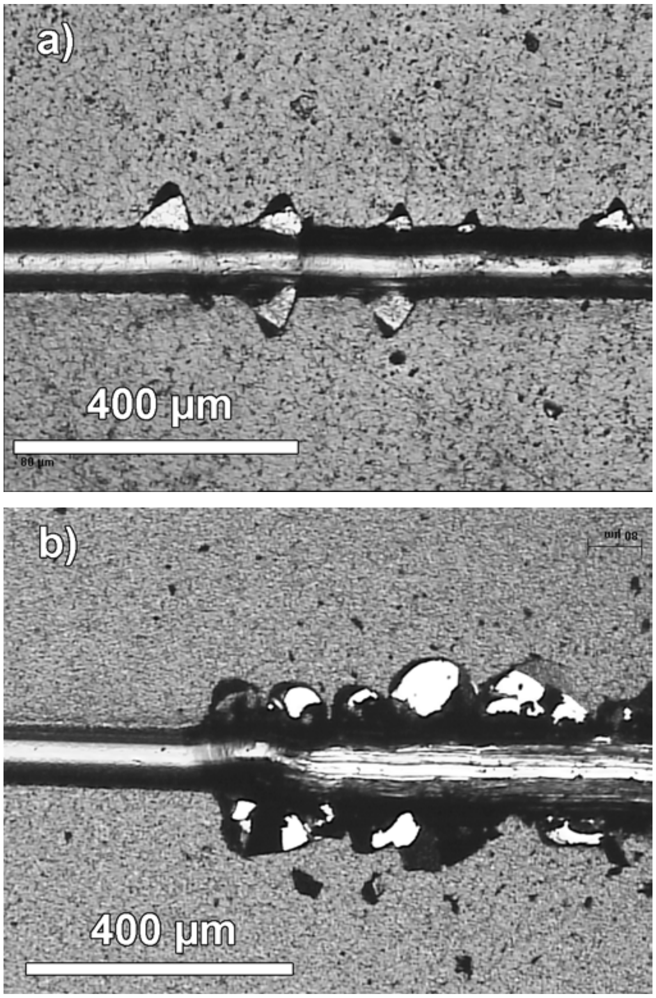

Figure 3. Ti-TiN coatings etched by different techniques a) etching by HIPIMS of Ti; b) etching by conventional dc-magnetron sputtering of Ti.

This behavior can be contrasted to films etched with conventional dc magnetron sputtering in the same gas pressure and bias voltage conditions as described in Figure 1. In this case of dc magnetron sputtering etching L_C = 45 N and is significantly lower than the HIPIMS case. Figure 3b shows a micrograph of the scratch for the case of etching in environment of a dc magnetron sputtering discharge. It can be seen that as soon as the critical load is exceeded, extensive spallation failure of the coating takes place and is present continuously on both sides of the crack. The sliding wear behavior of Cr-CrN coatings was evaluated in pin-on-disk tests. Figure 4 shows the evolution of the friction coefficient against an Al_2O_3 counterpart as a function of sliding distance. The average friction coefficient is 0.3, which is significantly lower than expected. In the first 250 m the friction coefficient is maintained at a level of 0.45 which is typical of CrN films against Al_2O_3, however at longer distances, μ drops to a value of 0.3 and is maintained over a distance of at least 3 km. Similar observation was recorded for a number of samples etched at different voltages in the range from -400 to -1200 V. SEM observations of the wear track at the end of the test showed that the substrate was not revealed, signifying that the friction coefficient was due to sliding between CrN, Al_2O_3 and a tribo-film probably composed of CrO [4].

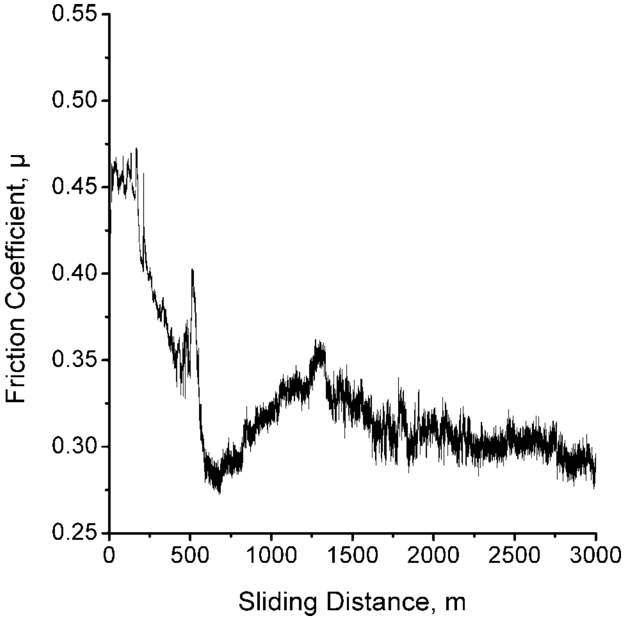

Figure 4. Friction coefficient of Cr-CrN coating against Al_2O_3 counterpart.

Figure 5 shows a micrograph of the wear track of the Cr-CrN film. Although grooving is observed, the scratches are small and the surface of the wear track is smooth. This type of wear is observed when the debris generated during sliding are small, suggesting a highly resistant coating system that wears layer by layer. In contrast systems where large particles can be detached from the coating exhibit highly rough wear tracks. The main contributors to large debris are portions of the coating detaching due to low adhesion strength as well as disturbed coating microstructure with loose attachment to the rest of the coating.

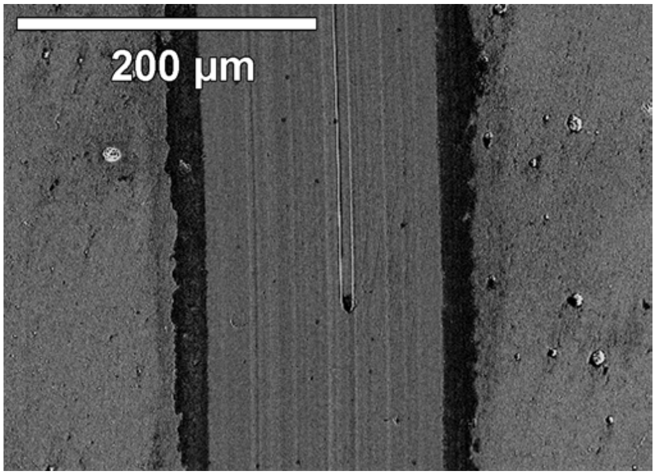

Figure 5. SEM micrograph of the surface of the sliding wear track in a Cr-CrN coating.

The high wear resistance of the coating is confirmed by measurements of the sliding wear coefficient presented in Figure 6. Generally, coatings prepared by different bias voltage during etching exhibited a low wear coefficient in the range 3-9 x 10^{-16} $m^3N^{-1}m^{-1}$. The wear rates for the Al_2O_3 counterpart were in the range of 10^{-18} $m^3N^{-1}m^{-1}$. The figure shows that the bias voltage during etching affects the wear coefficient coatings by a factor of up to 3.

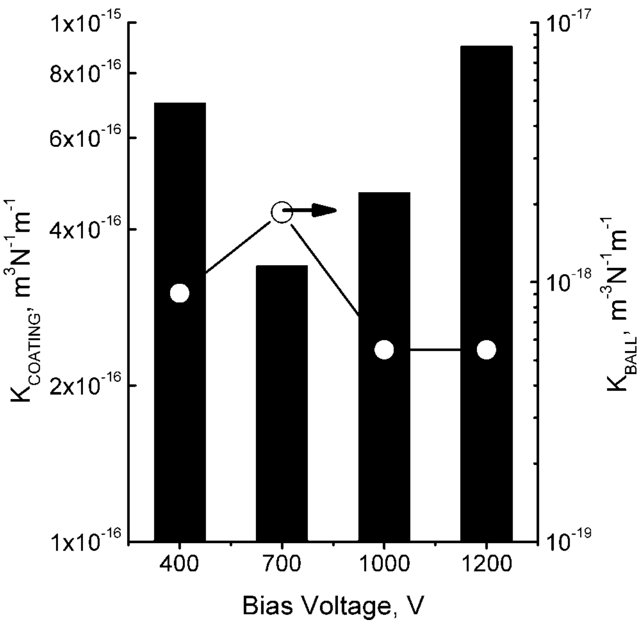

Figure 6. Sliding wear coefficient K for Cr-CrN coating and ball counterpart.

It can be suggested that the high adhesion and defect-free surface the coatings lead to a smooth layer-by-layer wear of the coating which promotes a low wear coefficient. The differences observed as function of bias voltage during pretreatment may be attributed to the change in roughness and adhesion of the coatings. The corrosion resistance of the Cr-CrN coatings was evaluated in potentiodynamic corrosion tests. Figure 7 presents the polarization curves.

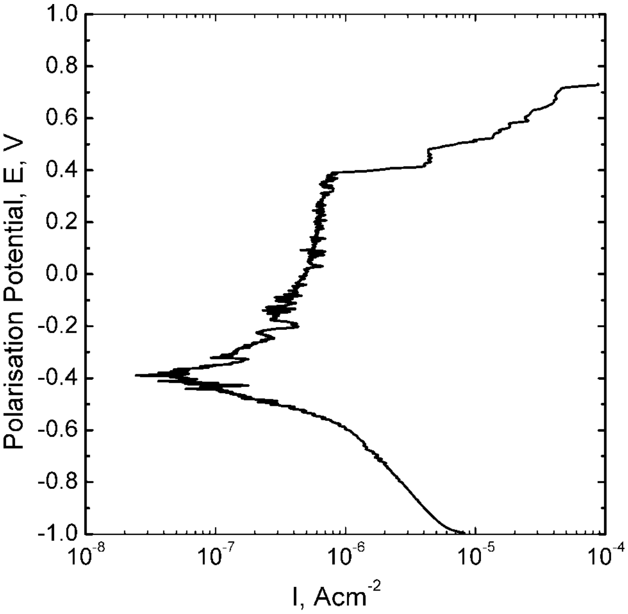

Figure 7. Polarization curve for a Cr-CrN coating etched at – 1200 V.

The corrosion potential marked at the zero current is -0.4 V. As the voltage increases the current increases non-linearly and reaches saturation in the range from 0 V to 0.4 V—this is the so-called passivation region where the coating is covered with a dense oxide layer that prevents (passivates) the corrosion activity. At +0.4 V the dissolution of chromium starts and the coating fails rapidly with currents increasing by three orders of magnitude. The corrosion current during saturation reached 7 x 10^{-7} Acm^{-2}, which represents an extremely low value and can be linked to the high density of the coating-substrate system. Due to the lack of large scale defects in the coating, the structure is highly dense and prevents corrosion from attacking the substrate directly. Thus, the corrosion activity is concentrated within the essentially inert CrN layer.

INDUSTRIAL UPSCALING

Preliminary results have shown that the HIPIMS technology can be reliably operated on industrial scale commercial equipment with cathode size of >500 cm^2 [3] utilizing a power supply manufactured by AC Sp.z.o.o. Defect-free CrN/NbN coatings with nanoscale multilayer (superlattice) structure prepared by HIPIMS etching and dc magnetron deposition have been successfully deposited in a commercially available Hauzer HTC 1000-4/ABS system with chamber volume of 1 m^3. These coatings have demonstrated corrosion protection of 304 stainless steel in a salt spray environment over more than 1000 hours. They have also shown an excellent adhesion with critical load of $L_C = 56$ N whilst exhibiting a smooth wear track and low sliding wear coefficients.

CONCLUSIONS

HIPIMS-etched dc magnetron deposited Cr-CrN and Ti-TiN coatings have been deposited in laboratory scale conditions. Due to the HIPIMS etching the coatings exhibited a defect-free smooth surface with an excellent adhesion with critical loads L_C of 45 N and 58 N for Cr-CrN and Ti-TiN respectively. The coatings performed well in sliding wear tests showing low friction coefficient and low wear rates. The high integrity of the layers achieved by HIPIMS etching contributed to the superior corrosion resistance of the Cr-CrN films showing corrosion currents in the range of 7×10^{-7} Acm^{-2} in potentiodynamic corrosion tests. Industrial upscaling of the HIPIMS technology provided defect-free CrN/NbN nanoscale multilayer films with excellent adhesion with $L_C = 56$ N, superior corrosion performance in 1000 hour salt spray tests and good resistance in sliding wear.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the European Union under CRAFT project No. G5ST-CT-2002-50355

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