Comparative study on protective properties of CrN coatings on the ABS substrate by DCMS and HiPIMS techniques

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ARTICLE INFO

Keywords: Electroplating Cr DCMS HiPIMS CrN coating ABS

ABSTRACT

The magnetron sputtering deposition of CrN coatings is environmentally friendly and has high surface gloss. Therefore it is a promising alternative to the electroplating deposition of Cr coatings as an effective method to metallize of ABS materials. Nevertheless, the coatings on the polymers suffered from cracks' initiation during temperature alternating processes, resulting in the degradation of decoration and protection function. In this work, we proposed a new application of the HiPIMS CrN coating for as the surface metallization method for ABS, and investigated its properties in comparison with the DCMS method. Based on the electric and spectroscopic characteristics of these two kinds of magnetron sputtering discharge and the resultant coating structures, the corrosion resistance, mechanical properties, as well as the weatherability of the coatings were studied and discussed. Results revealed that the HiPIMS coating had a dense nanocrystalline CrN (200) phase structure, rather than the loose amorphous/nanocrystalline composite structure of the DCMS CrN coating. Consequently, the HiPIMS CrN coating demonstrated superior corrosion resistance, mechanical properties, and meanwhile avoided the crack problem on ABS substrates. Finally, we developed a new CrN coating by HiPIMS as the protective coating for the purpose of replacing the electroplating Cr coating on polymers.

1. Introduction

Polymers have a considerable advantage over common metals due to the low density, flexibility, design versatility and low-cost production. Acrylonitrile Butadiene Styrene (ABS) is a widely used polymer in industrial applications. Surface metallized ABS are replacing traditional metallic materials in many fields, such as automotive components, bathroom hardware and electronic products [1–4]. Conventionally, the electroplating of protective functional coatings has been widely used for surface metallization of polymers [5–7]. However, carcinogenic vapors of the hexavalent chromium (Cr\textsuperscript{6+}) are released from the CrO\textsubscript{3} used in the electroplating bath, causing great harm to the environment and human health.

In the last decade, strong activities have started aiming at the systematic replacement of these polluting technologies, especially for Cr electroplating, with high performance 'clean' dry coating methods [8–10]. Magnetron sputtering (MS) is one of such techniques and has the advantage of coating most substrate materials due to low temperature deposition characteristics [11–15]. Paulo et al. [16] prepared CrN coatings with different nitrogen contents on the ABS surface by the direct current magnetron sputtering (DCMS). They optimized the ratio of Ar/N\textsubscript{2} to get the most appropriate electrochemical stability and interfacial adhesion. P. Sukwisute et al. [17] investigated the effect of sputtering power on the hardness and wear resistance of CrN thin coatings deposited on ABS substrates. It was found that sputtering power has a vital influence on the preferential orientation of crystal plane, grain size, hardness, Young's modulus and wear resistance of the coatings. The CrN coating deposited at a high sputtering power displayed the largest hardness which led to the highest wear resistance of the ABS surface. This reports indicated the promising applications of CrN coatings as protective layers for ABS plastic parts. However, Juergen et al. [18] showed that the CrN coatings suffered from cracking during the deposition processes due to the rise of the substrate temperature. Although preferential growth of crystallites in subsequent deposition closed these cracks, the coated surface presented bulged topographical features. They also emphasized the influences of higher coating toughness by Cr-CrN multilayer coatings on the density and height of the bulges.

https://doi.org/10.1016/j.surfcoat.2020.125890

Received 11 December 2019; Received in revised form 27 April 2020; Accepted 6 May 2020
Available online 11 May 2020

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Till now, many researches have been concentrated on the topography, hardness, wear and corrosion resistance of CrN coatings prepared by DCMS [19–21]. However, much higher thermal expansion coefficient of the ABS than the CrN coatings triggers strong thermal intrinsic stresses in the coatings, which leads to brittle fracture after exceeding tensile strength in mechanically weaker regions. The density of the cracks on the surface depends both on the thermal stresses and the mechanical toughness of the coating. Generally, the properties of CrN coatings mainly depend on their composition, morphology and microstructure, which are greatly affected by the deposition process [22–24]. Generally, relatively low levels of ionized fluxes result in weak mechanical properties of the CrN coatings [25,26]. In the last years, several MS deposition methods have been developed with the aim of improving the ion fluxes of sputtered materials [27–29]. Benefiting from high instant discharge power, high power impulse magnetron sputtering (HiPIMS) has been manifested to take advantages in a high ionization degree of sputtered atoms, and low substrate temperature rise during deposition processes. It becomes a hot topic in material engineering researches and industrial applications [30,31]. HiPIMS has already achieved great successes in the modulation of the film microstructure, and the enhancement of CrN coatings properties [32–34].

Nowadays, the DCMS CrN coating instead of Cr electroplating has been widely studied, the HiPIMS technology has a new application potential in the surface metallization of polymer due to its high ionization degree and low-temperature deposition characteristics. In the present work, CrN coatings were prepared by DCMS and HiPIMS on ABS at the same average sputtering power. We focused on the comparative study of these two kinds of CrN coatings. Furthermore, the differences on the corrosion behavior and weatherability were investigated. The related mechanism was discussed in terms of the target power, plasma parameters and the structure of the coatings. Therefore, a new concept was brought forward to fabricate protective coatings for replacing electroplating Cr on polymers surface.

2. Experimental setup

2.1. The coating deposition processes

Experiments were performed in a custom built cylindrical magnetron sputtering system, 60 cm in diameter and 60 cm in height. The schematic description of the deposition system was introduced in Ref. [35]. P-type Si(100) wafers and ABS substrates were used as substrates. Before the deposition processes, the UV paint was sprayed on the ABS and cured to cover the surface defects of the substrates. The distance from the substrates to the target was ~13 cm, both ABS and Si substrates were coated in the same deposition process. The base pressure in the chamber was 3.0 × 10^{-3} Pa. All substrates were etched and pre-cleaned by an argon linear ion source (LIS) with 5 min. A high purity Cr target (400 × 100 mm², 99.99% purity) was used to deposit CrN coatings by DCMS (supplied by EnerStream 5) and HiPIMS (supplied by MELEC SPIK 3000A) techniques at the same average power of 4 kW. A large pulse frequency and a short pulse width could result in a high deposition rate and a low substrate temperature rise of the coating deposition [35]. Therefore, the pulse width and repetition frequency of the HiPIMS supply was chose as 100 μs and 500 Hz, respectively. Previous experiment results showed that the CrN coatings (atomic number ratio of N/Cr was about 1) deposited with intermediate N₂ were considered the most promising condition (described in the Supplementary Material). The Ar and N₂ flow rate was kept constant at 40 and 25 sccm, respectively. A negative bias voltage of 50 V with the frequency of 350 kHz and reverse time of 1.1 μs was applied on the substrate holder. The deposition pressure was 2.5 Pa and the deposition time was adjusted to achieve similar coating thickness about 500 ± 50 nm. During the etching and deposition processes, no external heat was conducted. After deposition, the substrates temperature was indicated to increase from room temperature to ~40°.

2.2. Discharge characterization

The target voltage and current waveforms of HiPIMS in working during one pulse cycle were monitored using a combined current transducer (LEM LT58-S7) and a voltage divider unit. The data were recorded with a digital storage oscilloscope (Tektronix TDS 1012C-SC). The optical emission spectroscopy (OES) (Acton SpectraPro SP-2500, Princeton Instruments) was applied to characterize the particle species and emission intensities. It scanned from 260 to 400 nm with the wavelength resolution of 1 nm to characterize the generation of Cr⁺ species. The details of the electric and spectroscopic measurements can be found in our previous publications [35,36].

2.3. Coating characterization

In order to facilitate the sample preparation for characterization, the Si substrates are used for some microstructure characterization [16–18]. The crystallographic structures of the coatings on ABS were characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) with collecting angles ranging from 10° to 90° in conventional 0-0 configurations. The mechanical properties of CrN coatings and ABS substrates were seriously mismatched, which made it difficult to carry out ion thinning. Therefore, following with a focused ion beam (FIB, Auriga, Germany) process, the microstructure of the coatings deposited on Si (100) were studied by transmission electron microscope (TEM, Tecnai F20). Si (100) was also easy to achieve brittle fracture, which was conducive to the observation of fresh coating cross section. The surface micromorphology of the coatings on ABS substrates and the cross-sectional micromorphology of the coatings on Si (100) substrates were observed by the field emission scanning electron microscopy (SEM, Hitachi S4800).

Furthermore, the corrosion resistance, mechanical and weatherability properties of the coatings deposited on ABS substrates were characterized. Electrochemical measurements were carried out on an electrochemical workstation (Modulab, UK) by a conventional three-electrode electrochemical cell, which contains sample as a working electrode, saturated calomel working as the reference electrode and platinum plate as a counter electrode. Experiments were carried out at ambient temperature (25 ± 1 °C) in 3.5 wt% NaCl solution. The potentiodynamic current-potential curves were recorded at a sweep rate of 1 mV/s. The electrochemical impedance spectroscopy (EIS) measurements were registered at open circuit potential (OCP) in the frequency range of 10^4 to 10^{-2} Hz with 10 mV sinusoidal perturbation. The hardness (H) and elastic modulus (E) were evaluated using a load-controlled (MTS NANO G200) nanoindentation equipped with a Berkovich diamond indenter with a tip radius of approximately 150 nm. The characteristic H and E were chosen in a depth of around 1/10 of the coating thickness, where the measured value was not affected greatly by the substrate. Five indents were made on each coating samples to evaluate the average H and E from load–displacement curves using the Oliver-Pharr method. Resistance to environmental cycle test were performed in Programmable Temperature & Humidity Chamber (HS-050D) according to PV 1200: 2004–10. Surface morphology of the coatings after one cycle environmental recycling test were observed by a fluorescence optical microscope (LEICA DM 2500 M). One cycle lasts for 720 min (12 h) and the temperature and humidity profiles was shown in Fig. 1.

3. Results and discussion

3.1. The electric and spectroscopic characteristics of DCMS and HiPIMS discharges

The typical target voltage and current waveforms of the DCMS and HiPIMS discharge with a Cr target under Ar/N₂ mixture condition is shown in Fig. 2a. It can be seen that the voltage pulse is typical
rectangle wave with the target voltage keeping at \(~920\, \text{V} \pm 50\, \text{V}\), no voltage drop was observed. During the pulse, a peak current as high as about 98\, \text{A} was obtained on the target. Therefore a maximum power of HiPIMS 22.5 times higher than DCMS had been achieved. Through applying a high power pulse on the target with a short pulse length and low duty cycle, HiPIMS offers means to achieve high density plasma \([37,38]\). The results from the OES spectra as shown in Fig. 2b also confirmed that the emission intensity of \text{Cr}^+ line in HiPIMS was much stronger than that in DCMS.

3.2. Morphological and microstructural characterization

Fig. 3 shows the XRD patterns of the DCMS and HiPIMS coatings. The phase composition of both coatings are cubic \text{CrN} phase (PDF 65-2899). The HiPIMS coating shows (200) preferred orientation while the diffraction peaks of the DCMS coating are very weak, indicating that the DCMS coating has low crystallinity and incomplete crystal structure. Comparing the bright field TEM images of the two \text{CrN} structures (Fig. 4a,b), both coatings exhibit columnar structure along the growth direction. It can be found that the column boundaries of the DCMS \text{CrN} coating are clear while the boundaries of the HiPIMS \text{CrN} coating are fuzzy, which indicates that the structure of the HiPIMS \text{CrN} coating is more compact. (111), (200) and (220) planes are identified from the SAED pattern of the DCMS \text{CrN} coating while the HiPIMS \text{CrN} coating presents intense (200) texture. The high-resolution TEM (HRTEM) observations (Fig. 4c,e) clarify the nanocrystalline and amorphous composite structure of the DCMS \text{CrN} coating. Fig. 4d is the typical HRTEM image of the HiPIMS \text{CrN} coating showing high crystallinity and preferred orientation of (200). The lattice fringes spacing is 2.0136 \, \text{Å} which corresponds to the \text{CrN (200)} plane according to the inverse Fourier-filtered image (Fig. 4f). (200) crystallographic plane has the lowest surface energy in face-centered cubic (fcc) \text{CrN} structure compared with other orientations, so that it needs a long diffusion distance to be formed \([39,40]\). High density plasma of HiPIMS causes an enhanced diffusion capacity of absorbed atoms which gives rise to the formation of the intense (200) texture \([41]\).

Fig. 5 shows the surface and cross-sectional morphology of the \text{CrN} coatings deposited by DCMS and HiPIMS. The cross sectional morphologies of both \text{CrN} coatings on Si substrates reveal the columnar structure. On the DCMS \text{CrN} coating’s surface, it is possible to observe the cauliflower-type morphology resulting from the stacking of several columns which consist of grains, 15–25 \, \text{nm} wide, that agglomerate to form larger surface structures, 70–150 \, \text{nm} wide. It can be assigned to the transition “Zone T” structure in the Thornton structure model \([42]\), amorphous and micro grains exist at the same time, and the crystallinity is poor. This type of structure is associated with the unstable growth under limited surface diffusion conditions. At the higher ion flux bombardment during the deposition process of the HiPIMS \text{CrN} coating, recrystallization and the refinement of grains occurs, the cauliflower-like surface morphology is no longer observed. Instead, the film surface displays strongly packed individual granular features with dimensions of about 40–60 \, \text{nm}, the structure can be assigned to the “Zone 3”. By comparison it can be seen that the \text{CrN} coatings has undergone structural transition from a loose columnar microstructure to a dense nanocrystalline one when the coating deposition method was changed from DCMS to HiPIMS. In this study the average sputter power

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**Fig. 1.** An environmental test cycle.

**Fig. 2.** (a) Typical target voltage and current waveforms of HiPIMS and DCMS under the Ar/N\(_2\) mixture condition (b) their corresponding OES spectra.

**Fig. 3.** The XRD patterns of DCMS and HiPIMS \text{CrN} coatings.
Fig. 4. Overview images and the corresponding SAED patterns of the DCMS and HiPIMS CrN coatings (a) (b), HRTEM images of the DCMS and HiPIMS CrN coatings (c) (d), with (e, f) corresponding inverse Fourier-filtered images from inside the yellow box in (c, d). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
was kept constant for all depositions and therefore the microstructural transformation should be due to the increasing ionization fraction of Cr on the growing film as demonstrated in Fig. 2.

3.3. The characterization of the corrosion resistance, mechanical property and weatherability

The corrosion resistance characteristics of the both coatings are presented in the form of electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves. As shown in the Nyquist diagrams (Fig. 6a), an obvious increase in the capacitive arc radius is found for the HiPIMS CrN coating, which illustrates more superior corrosion resistance than the DCMS CrN coating. The Bode plots in Fig. 6b further confirm the similar conclusion. The larger |Z| at low frequency as well as the phase angle near −90° in a wider frequency range for the HiPIMS CrN coating indicates a better corrosion resistance compared to the DCMS CrN coating.

Table 1
The results of the electrochemical experiments.

<table>
<thead>
<tr>
<th>Samples</th>
<th>E_{corr} (V)</th>
<th>i_{corr} (A·cm^{-2})</th>
<th>R_p (KΩ·cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCMS CrN</td>
<td>0.24</td>
<td>1.86 × 10^{-9}</td>
<td>3.95 × 10^{4}</td>
</tr>
<tr>
<td>HiPIMS CrN</td>
<td>−0.03</td>
<td>4.49 × 10^{-10}</td>
<td>1.23 × 10^{5}</td>
</tr>
</tbody>
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Fig. 5. Surface (a) (c) and cross-sectional (b) (d) morphology of the DCMS and HiPIMS CrN coatings.

Fig. 6. Nyquist plots, Bode plots and potentiodynamic polarization curves for the various samples.

Fig. 7. The hardness (H), elastic modulus (E) and H/E of DCMS and HiPIMS CrN coatings.

was kept constant for all depositions and therefore the microstructural transformation should be due to the increasing ionization fraction of Cr on the growing film as demonstrated in Fig. 2.
The EIS data is fitted by using the equivalent circuit model ($R(QR)$). The region demonstrates the superior corrosion resistance of the coatings. The polarization resistance ($R_p$) was calculated according to the fitting circuit model, the corrosion potential ($E_{corr}$) and the corrosion current density ($i_{corr}$) derived from polarization curves (Fig. 6c) are summarized in Table 1. It can be seen apparently that the $i_{corr}$ of the HiPIMS CrN coatings decrease about one order of magnitude, and $R_p$ of the HIPIMS CrN coating increase one order of magnitude compared with the DCMS coating. It can be concluded that the HiPIMS CrN coating has excellent corrosion resistance, which is related to its dense nanocrystalline structure.

One of the most important end-user specifications is that the deposited CrN coatings provide functional protection for the polymer substrate in a variety of high and low temperature environments. Fig. 7 shows the hardness (H), elastic modulus (E) and H/E of DCMS and HiPIMS CrN coatings. We can see that the H and E of HiPIMS CrN coating are higher than that of the DCMS CrN coating. At present, the technical bottleneck of the PVD CrN coatings on ABS surface is that the coatings are easy to crack with the variation of environment temperature in application. The corresponding crack patterns of both coatings on the ABS substrates after environmental cycle tests are shown in Fig. 8. Usually, thermal intrinsic stresses occur in the coatings deposited on the ABS substrate after the temperature alternating from 80 °C to −40 °C. The quite difference in thermal expansion coefficients and elastic modulus between the coatings and the ABS substrates triggers through-thickness fracture after exceeding tensile strength in mechanically weaker regions. We can see that the cracks of the DCMS CrN coating are intensive and distribute in a strip. The surface of the HiPIMS CrN coating is in good condition without cracking after thermal alternation. By the comprehensive comparison, the HiPIMS CrN coating has better cracking resistance under the climate alternation conditions. Differences in the thermal expansion coefficient ($2.3 – 2.9 \times 10^{-6} \text{ mm}^{-1} \text{ K}^{-1}$) of the CrN coatings with various microstructures are small, not even if mentioning the much higher thermal expansion coefficient of the ABS substrates ($50 – 60 \times 10^{-6} \text{ mm}^{-1} \text{ K}^{-1}$) [43,44]. As a result, the explanation of the crack resistance of HiPIMS CrN coatings under thermal stress can be attributed to the high toughness of the coatings. The H/E which represents fracture toughness of the both coatings in Fig. 7 confirms this conclusion.

4. Conclusion

The electric and spectroscopic measurements show that the HiPIMS has higher target ionization rate than the DCMS because of the high instant discharge power. The CrN coatings prepared by DCMS and HiPIMS at the same average power on ABS substrates are comparatively investigated. The results show that the loose amorphous/nanocrystalline composite structure was obtained in the DCMS CrN coating, while the dense nanocrystalline CrN phase with intense (200) texture was formed in the HiPIMS coating at the same $N_2$ flux. The HiPIMS CrN coating has superior corrosion resistance, mechanical properties. The crack problem on ABS substrates is avoid due to high toughness. In consideration of protective performance for ABS, HiPIMS CrN layer should be the optimized design to replace of the Cr electroplating.

Credit authorship contribution statement


Declarations of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The research was supported by the project of National Natural Science Foundation of China (11705258), National Science and Technology Major Project (2017-VII-0012-0108).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.surfcoat.2020.125890.

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