Cathodic Arc Deposited CrAlSiN Coatings by Pulsed Current Input

Wei-Che Huang¹, Cheng-Hsun Hsu¹ and Wei-Yu Ho²,*

¹Department of Materials Engineering, Tatung University, Taipei, 104, Taiwan
²Department of Materials and Energy Engineering, MingDao University, ChungHua, 523, Taiwan

*Corresponding author

Keywords: Cathodic arc deposition, Hard coating, Pulsed current, Corrosion.

Abstract. Cathodic arc deposition technique is one of the green processes of the physical vapor deposition (PVD) systems. In this study, Cr and CrAlSi dual metal targets were used in order to synthesize CrAlSiN coatings. By using the cathodic arc pulsed current techniques, three different settings of pulsed current duty cycles were used. The microstructure of the coatings observed by XRD analysis shows all the coatings are B1-Rock salt structure with diffraction peaks of (111) and (200). The pulsed current input as compared to the constant current had presented the higher hardness up HV3771. Corrosion test by polarization method shows the best corrosion resistance of the CrAlSiN was achieved by pulsed current input at high cycle time.

Introduction

The cathodic arc deposition technology is one of the most efficient PVD techniques and green manufacturing process [1-6]. Based on this technique a novel concept with the advantages of pulsed current input of the cathodic arc sources has been developed with the purpose of coating systems improvement in comparison with conventional arc deposited coatings. By means of the pulsed current supply for the cathodic arc sources, released flux of metal ions can be increased without further modification of the sources design. The increasing efficient demands of the cutting tool make this new technique necessarily to search new coating materials and the coating synthesis process. In the past decades CrAlSiN coatings with nano-composite structure and high hardness up to 42GPa have achieved an increasing acceptance in various fields of machining applications by increasing lifetime [7-11]. CrAlSiN has been proven to have high oxidation resistance due to the presence of coexisting Al₂O₃, Cr₂O₃ and SiO₂ passive layer near the surface retarding the diffusion of oxygen into the coating. However, in order to study the effect of pulsed arc current on the properties of the CrAlSiN coatings, the main goal presented here is to the usage of the above-mentioned technology by changing the duty cycle of pulsed current input to further improve its properties.

Experimental

Nano-composite CrAlSiN coatings deposited on specimens made of tungsten carbide (dimensions: dia. 20 mm x 6 mm) and SUS304 stainless steel by cathodic arc evaporation technology were designed and fabricated. The coating machine consists of two sets of standard cathodic arc ion evaporators, auxiliary a circular substrate holder connected with bias power supply. Two cathodic arc evaporators were equipped with chromium targets (99.9% purity) and Cr₃₀Al₆₀Si₁₀ (at.%) target, respectively. Three types of CrAlSiN coatings were obtained by varying the duty cycle of the arc source current, such as sample a (dc 90A), sample b (pulsed 90/150A with duty cycle of 1 millisecond) and sample c (pulsed 90/150A with duty cycle 3 millisecond), respectively. Specimens were cleaned with acetone in an ultrasonic bath, and then rinsed in ethanol. Before deposition, the samples were heated to 200 °C. Crystallographic structure of coatings was investigated by X-ray diffraction method using a grazing incidence angle of 2° and Cu Kα radiation (λ = 1.54060A). The surface morphologies were investigated by scanning electron microscopy and the thickness of the films were measured by ball crater observation carried out by Calotest. The hardness of coatings
was measured in a Vicker’s indentation equipment with the applied load 25g. The surface roughness ($R_a$) of the coatings was measured by surface profile meter with at least five measurements. Polarization test was conducted to distinguish the corrosive behavior of the coated SUS 304 stainless steel. The corrosive medium of 1M H$_2$SO$_4$ solution was used to simulate the aggressive aqueous environment. The electrode potential was scanned from – 0.8 to 0.8 V at the scanning rate of 1.0 mV/s. The corrosion potential (Ecorr) and the corrosion current density (Icorr) were deduced from the polarization plots. The corroded surface was then examined by using SEM.

Results and Discussion

X-ray diffraction analysis was carried out to study the microstructure of the coatings, as shown in Figure 1. The diffraction peaks of the coatings show a similar feature which reveals well-defined polycrystalline fcc-NaCl microstructure. The main diffraction peaks indexed as (111) and (200) preferred orientation centered at 37.1° and 43.7° being observed. XRD peaks related to Si$_3$N$_4$ of the as-deposited coating are not shown due to the amorphous structure existing in the coating. According to the JCPDs and literature [7-11], the main phase of CrAlSiN coatings was CrAlN embedded in the amorphous Si$_3$N$_4$ matrix.

![Figure 1. XRD analysis of the CrAlSiN coatings deposited with different arc duty cycle. (a) constant 90A, (b) pulsed 90/150A, 1ms, (c) pulsed 90/150A, 3ms.](image)

Surface morphology of the CrAlSiN coatings deposited with the different parameters was shown in Figure 2. The results revealed that droplets formed during deposition from the cathode are randomly distributed on the coating surface in small sizes, varying from a fraction of a micrometer to 3 µm. The presence of these droplets is due to the disadvantage of the cathodic arc deposition method. The power input is important to the cathode affecting the temperature in the cathode spot and volume of melted materials. Increasing the arc current may lead to a greater number of droplets or a larger droplet size. However, from Figure 2 and Table 1, the surface morphology can be shown that the density of droplets does not significantly change with the duty cycle.

Table 1 shows the basic properties of the CrAlSiN coatings including thickness and roughness. The thickness of the coatings ranged from 2.8 to 3.9µm are related to the arc source current which increase the half cycle time of the high current resulting in increase of thickness. Using the modified pulsed arc technique, an increase of average arc current caused a distinct rise of the deposition rate at approximately the same substrate temperature [7]. The average surface roughness (Ra) of the three types of CrAlSiN coatings were 0.211µm, 0.216µm and 0.248µm, respectively. It can be seen that the roughness values of the coatings with pulsed current input are of the same level compared to the roughness of the coating with constant current. Thus cathodic arc produced CrAlSiN coatings with similar roughness by applying either constant 90A or pulsed 90/150A current in this work.
Figure 2. Surface morphologies of CrAlSiN coatings deposited at different arc source current output. (a) constant 90A, (b) pulsed 90/150A, 1 ms, (c) pulsed 90/150A, 3 ms.

Table 1. Basic properties of three types of CrAlSiN coatings.

<table>
<thead>
<tr>
<th>coating</th>
<th>Duty cycle (ms)</th>
<th>Thickness (µm)</th>
<th>Roughness (µm)</th>
<th>Hardness (Hv0.025)</th>
<th>Ecorr (V)</th>
<th>Icorr (µA/cm²)</th>
<th>(Rp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0</td>
<td>2.8</td>
<td>0.211</td>
<td>2644</td>
<td>-0.35</td>
<td>0.44</td>
<td>6506642</td>
</tr>
<tr>
<td>(b)</td>
<td>1</td>
<td>3.6</td>
<td>0.216</td>
<td>3379</td>
<td>-0.21</td>
<td>0.19</td>
<td>16266053</td>
</tr>
<tr>
<td>(c)</td>
<td>3</td>
<td>3.9</td>
<td>0.248</td>
<td>3771</td>
<td>-0.19</td>
<td>0.15</td>
<td>23118408</td>
</tr>
</tbody>
</table>

Hardness of the CrAlSiN coatings on tungsten carbide substrate is shown in Table 1. The hardness of the CrAlSiN coatings with different arc source current input shows an increase trend by increasing the duty cycle. The use of the modified pulsed arc process may result in a higher degree of ionization of the metal-plasma, and higher energy in the plasma-particles, as well. As the duty cycle of pulsed current increases, the hardness of the coating also increases, a dependence on the pulsed cycle could be proved. The maximum hardness of the CrAlSiN coatings is happened to the arc source current input of 90/150A of duty cycle 3 millisecond with the value of HV3771.

In 1M H₂SO₄ solution, potentiodynamic measurements generated polarization curves of potential (E\text{corr.}) relative to SCE vs. current density (I\text{corr.}), as presented in Figure 3. It shows that sample C which is with CrAlSiN coating deposited at the pulsed current duty of 3 ms exhibits more passive behavior by observing higher E\text{corr} value obtained. Corrosion current density is commonly utilized as an important parameter to evaluate the kinetics of corrosion reactions. From the Table 1, it can be seen that I\text{corr} is slightly low for the coatings deposited by using pulsed current input. However, the I\text{corr} of the samples are nearly of the same level, the corrosion resistance of the samples is further compared by calculating the Rp value [11] which is derived by the combination of E\text{corr}, I\text{corr} and the other parameters, as shown in Table 1. Clearly, CrAlSiN deposited at higher duty cycle of pulsed current possessed higher value of Rp. This increase value represents better corrosion resistance being achieved, that indicated by high E\text{corr} and low I\text{corr} during the test. The corrosion resistance is normally proportional to the Rp value measured through polarization test. From Figure 4, the coated stainless steels are shown with pit hole on the surface after the test. As expected, a pitting corrosion on the CrAlSiN coated substrate was occurred due to minor defects and the inert phenomena of the coatings. This may suggest that the passive behavior of the coatings. However, limited number of pinholes was presented. The coatings deposited at pulsed current may decrease the number of pinholes, preventing transport of acid solution to the stainless steel. This can be attributed to the more dense structure by applying pulsed current.
Conclusions

CrAlSiN coatings were obtained by changing the duty cycles using pulsed current cathodic arc deposition technique with Cr and CrAlSi dual targets. The observed microstructure by XRD analysis shows all the coatings are fcc-Rock salt structure with diffraction peaks of (111) and (200). CrAlSiN coating with the high duty cycle of pulsed current input as compared to the coating with constant current present the higher hardness up HV3771. Polarization test shows the result of the best corrosion resistance of the CrAlSiN with pulsed current at high duty cycle.

References


