Wear and corrosion of TiBCN coatings by cathodic arc deposition

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Depositions of TiBN and TiBCN coatings were made by using cathodic arc deposition with a Ti 95B5 alloy target and a mixture of C2H2 and N2 gases. Selected characteristics and mechanical properties were evaluated as well. Results showed that the hardness of the coatings decreased in the order of TiBN, TiBCN, TiN. However, the surface roughness of the coatings increased in the order of TiBCN, TiBN, TiN, respectively. The friction coefficients of the TiBCN coating deposited on WC-Co substrates against a 6 mm soda lime glass ball was as low as 0.1 due to the increased C content. The passive behavior of TiBCN coating was obtained due to the limited number of pinholes from addition of B and C in the coatings, preventing transport of acid solution to the stainless steel.

Keywords: Cathodic arc deposition; Coating; Wear; Corrosion.

1. Introduction

TiN and TiCN coatings are commercially produced by thermal chemical vapor deposition (CVD) at high temperature and physical vapor deposition (PVD) at low temperature. Cathodic arc deposition (CAD) and magnetron sputtering are the most successful techniques to deposit these coatings at low temperature on WC–Co cutting tools, high speed steels [1–3] for various applications such as wear, corrosion, and erosion protection. Recently, much attention has been made to synthesize the B-doped TiN and TiCN coatings with high hardness, high wear resistance, high corrosion resistance, and good chemical stability [4–13]. For

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example, TiBN coatings are deposited by magnetron sputtering technique to increase their wear and corrosion resistance [7]. The TiBCN coating material has considerably attracted due to its combination of hardness, and wear resistance [9–13]. Shimada et al. [9] reported that the composite TiBCN coatings, by chemical vapor deposition (CVD) on WC–Co cutting tools exhibited superior flank and crater wear resistance compared with commercial TiN coatings. The structures of TiBCN are achieved by forming thermodynamically stable TiCN, TiB and other boride phases embedded in the amorphous TiBCN matrix [10]. Lin et al. [12] has succeed in the research of TiBCN nanocomposite coatings deposited by using pulsed magnetron sputtering of a TiBC compound target with various Ar/N₂ mixtures. They concluded that the TiBCN coatings with a nitrogen content of less than 8 at.% exhibited superhardness values in the range of 44 – 49 GPa. Double layered TiN/TiBC and composite TiCN, TiBC, and TiBCN coatings were deposited on WC–Co cutting tools at 800 °C by CVD [9]. The composite TiBC and TiBCN coatings increase the flank wear resistance of the WC–Co tools, better than a commercial TiN coating [9]. CAD is widely applied to the cutting tools due to the advantages of high deposition rate, good adhesion properties, and large uniform areas [11]. However, TiBCN coating is yet studied thoroughly by CAD technique. In this research, depositions of TiBN and TiBCN coatings were conducted by using Ti₉₅B₅ alloy target and mixture of C₂H₂ and N₂ gases. Selected characteristics and mechanical properties were evaluated as well.

2. Experimental Procedure

The depositions were carried out in a CAD system, which contains two circular cathodic arc sources (diameter of 102 mm) of Ti and Ti₉₅B₅ installed face-to-face at the cylindrical chamber wall. The TiN, TiBN and TiBCN coatings were deposited from the selected targets and mixing C₂H₂ and N₂ gases, respectively. Two kinds of the TiBCN coatings were obtained by varying the ratio of mixture C₂H₂ and N₂ gases at the flow ratio of 1:3 and 2:3 to obtain the varied compositions. All of the coatings were first deposited with thin TiN as the bonding layer to improve the adhesion. The substrates (SUS 304 stainless steel and WC-6%Co tungsten carbide coupons) were ultrasonically cleaned in acetone and alcohol for 20 min, respectively and installed on a substrate holder that was positioned 150 mm away from the targets. The substrate temperature was in the range of 200 – 250°C, which was generated only from the plasma heating during deposition period.
The coatings were characterized by low-angle X-ray diffraction at the range 20 to 80° with CuKα radiation of a wavelength of 0.15405 nm. Raman spectra of the deposited coatings were obtained using a Micro Raman spectrometer (UniRAM-3500) recorded wavenumber from 1000 to 1800 cm\(^{-1}\). The chemical compositions of the coatings were obtained by using scanning Auger Electron Spectroscopy (Microlab 350). The thickness of the coatings was measured by a Kalotest method. Scanning electron microscopy (SEM; model JOEL JSM-5600) was carried out to observe the surface morphology of the various samples. Hardness of the films was measured by using the Vicker’s indentation at the load of 10 g. The surface roughness (\(R_a\)) of the coatings was measured by surface profile meter with at least five measurements. Wear tests of coatings were performed on a ball-on-disc tribometer (CSEM). The tests were conducted with no lubricant along a circular track of 12 mm diameter against a 6.0 mm diameter soda lime glass ball at 0.3 m/s under a normal load of 5 N in ambient atmosphere. 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 \(-0.5\) to \(0.5\) V at the scanning rate of 1.0 mV/s. The corroded surface was then examined by using SEM.

3. Results and Discussion

Fig. 1(a) shows the typical X-ray diffraction spectra of the TiN, TiBN and TiBCN coatings deposited under similar process parameters. The position peaks of the coatings suggest a cubic B1 NaCl-type structure. The TiBN coating display very similar peaks with the TiN coating indicating an essentially solid solution of B in the coating. For TiBCN coatings, the diffraction position peaks of (111) is shifted to the lower angle as the carbon content increases and broaden peaks are observed (Fig. 1(b)), suggesting nano-crystallines and amorphous phases co-existed in TiN matrix [16]. The Raman spectra of the TiBN and TiBCN coatings are shown in Fig. 2. Obvious difference between the spectra of the TiBN and TiBCN coatings can be observed. Compared to the TiBN coating, the spectra of TiBCN coatings consist of a main G band at 1560 cm\(^{-1}\) due to the lattice vibration of sp\(^2\)-bonded carbon atoms (graphite). Since B-N, B-C and C-C phases were not observed by X-ray diffraction, this result can be taken as an indication that B-N, B-C and C-C was presented in amorphous phases. This agrees well with previous results [9,14,15].
Fig. 1. XRD patterns of (a) the TiN, TiBN and TiBCN coatings. (b) abstract of 2θ from 30 to 40°.

Fig. 2. Raman spectra of TiBN and TiBCN coatings.

The chemical compositions of the coatings are presented in Table 1. The synthesized coatings TiBN and TiBCN were subjected to Ti$_{95}$B$_5$ target in a mixture of C$_2$H$_2$ and N$_2$ gases. The content of the carbon increased obviously as
the C$_2$H$_2$/N$_2$ gases increased and the B content slightly decreased from 5.18 % to 4.75 %. Ti content was also decreased as the C$_2$H$_2$/N$_2$ gases increased. At the same time, a drop of N content was obvious as the C$_2$H$_2$ gas flow ratio increased. The result of the composition changes was due to the Ti$_{95}$B$_5$ target poison as the C$_2$H$_2$ gas increased and replacement of N to C during the process. The thickness of the coatings increased and the surface roughness decreased as the C$_2$H$_2$/N$_2$ gases increased. From the XRD analysis, the broaden peaks of the TiBCN coatings mean the grain size is reduced with increasing carbon content of the coatings. At the same time, the amorphous structure is co-existed. The result of decreasing roughness was mainly dominated by the decomposition of C$_2$H$_2$ gas to form amorphous B-N, B-C, C-C phases during the process. The hardness of the coatings was decreased in a series of TiBN, TiBCN, TiN. The difference in hardness of the coatings is believed to be due to the result of solid solution of B in TiBN or co-existence of nano-crystallines and B-N, B-C and C-C amorphous phases in TiBCN, respectively.

Table 1. The chemical compositions and properties of the coatings (t: thickness, R$_a$: average surface roughness, HV: hardness at the load of 10 g, value ± 50).

<table>
<thead>
<tr>
<th>Coating</th>
<th>C$_2$H$_2$/N$_2$ (sccm)</th>
<th>Ti (at.%)</th>
<th>N (at.%)</th>
<th>B (at.%)</th>
<th>C (at.%)</th>
<th>t (μm)</th>
<th>R$_a$ (μm)</th>
<th>HV (10 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>0/30</td>
<td>53.05</td>
<td>46.95</td>
<td>-</td>
<td>-</td>
<td>2.7</td>
<td>0.37</td>
<td>1938</td>
</tr>
<tr>
<td>TiBN</td>
<td>0/30</td>
<td>50.30</td>
<td>44.52</td>
<td>5.18</td>
<td>-</td>
<td>2.4</td>
<td>0.23</td>
<td>3673</td>
</tr>
<tr>
<td>TiBCN-1</td>
<td>10/30</td>
<td>47.53</td>
<td>15.84</td>
<td>4.95</td>
<td>31.68</td>
<td>3.0</td>
<td>0.10</td>
<td>2959</td>
</tr>
<tr>
<td>TiBCN-2</td>
<td>20/30</td>
<td>40.82</td>
<td>12.89</td>
<td>4.75</td>
<td>41.54</td>
<td>4.1</td>
<td>0.16</td>
<td>3061</td>
</tr>
</tbody>
</table>

Fig. 3 shows the friction coefficients of the coatings deposited on WC-Co substrates against 6 mm soda lime glass ball after 2500 rotation cycles. The TiBCN coatings showed stable lower friction coefficient as the C content increased. The friction coefficient of TiBCN coatings displayed an initial of 0.27 followed by a drop to 0.1 after a short run-in period. However, the TiBN coating exhibits a gradual increase of friction coefficient from initial period. During tests, steady-state friction coefficient values between approximately 0.37 were recorded for TiN and TiBN coatings. However, the friction coefficient decreased down to 0.10 as the carbon content was raised up to 40 at.%. This low value is considerably similar with the DLC coatings reported elsewhere [14,15].
In 1M H$_2$SO$_4$ solution, potentiodynamic measurements generated polarization curves of potential (E$_{corr}$) relative to SCE. vs. current density (I$_{corr}$), as presented in Fig. 4(a). Clearly, in comparison with the TiN and TiBN coated stainless steels, TiBCN coated substrate possessed higher value of E$_{corr}$ reaching from -0.3V of TiN and TiBN coated stainless steels to -0.18V of TiBCN-1 coated substrate by applying the B or C contents. This increase voltage represents nobler electrode potential being achieved, thus indicating the improvement of corrosion resistance. Corrosion current density is commonly utilized as an important parameter to evaluate the kinetics of corrosion reactions. The corrosion rate is normally proportional to the corrosion current density measured through polarization test [17]. From the Fig. 4(a), The TiN coated stainless steel was corroded far more quickly than TiBN and TiBCN coated substrates once the corrosion potential had been surpassed, and finally remained stable current density. This can be attributed to the more dense structure by adding B and C in the TiBN and TiBCN coatings. As expected, a pitting corrosion on the TiBCN-1 coated substrate was occurred by applying SEM observation on the corroded coatings (Fig. 4(b)). This may suggest that the passive behavior of TiN, TiBN and TiBCN coatings. However, limited number of pinholes was decreased by adding B and C in the TiBN and TiBCN coatings, preventing transport of acid solution to the stainless steel.
4. Conclusion

Synthesis of TiBN and TiBCN coatings were conducted by using cathodic arc deposition with Ti_{60}B_{5} alloy target and mixture of C_{2}H_{2} and N_{2} gases. By applying B and C elements into the TiN coating can improve the properties of the coating. The hardness of the coatings was decreased in a series of TiBN, TiBCN, TiN. However, the roughness of the coatings is trade-off in an increased series of TiBCN, TiBN, TiN, respectively. The friction coefficients of the TiBCN coating deposited on WC-Co substrates against 6 mm soda lime glass ball was as low as 0.1 due to the B and C content increased. The passive behavior of TiBCN coating was obtained due to the limited number of pinholes by adding B and C in the coatings, preventing transport of acid solution to the stainless steel.

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References


