Intermediate temperature tribological behavior of carbon nanotube reinforced plasma sprayed aluminum oxide coating

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Tribological behavior of plasma sprayed carbon nanotube (CNT) reinforced aluminum oxide (Al2O3) composite coatings was examined at room temperature, 573 K and 873 K using tungsten carbide (WC) ball-on-disk tribometer. The weight loss due to wear of Al2O3 coating was found to be increasing with the temperature while Al2O3-CNT coating showed a decreasing trend in the weight loss with the temperature. Relative improvement in the wear resistance of Al2O3-CNT coating compared to Al2O3 coating was found to be 12% at room temperature which gradually increased to ~56% at 573 K and ~82% at 873 K. Protective layer as a result of tribo-chemical reaction was observed on the wear track of both of the coatings. The improvement in the wear resistance of Al2O3-CNT coating was attributed to three phenomena viz. (i) higher hardness at the elevated temperature as compared to Al2O3 coating, (ii) larger area coverage by protective film on the wear surface at the elevated temperature and (iii) CNT bridging between splats. The coefficient of friction (COF) of Al2O3 coating was nearly constant at room and elevated temperature whereas COF for Al2O3-CNT coating decreased at the elevated temperature (873 K).

1. Introduction

Carbon nanotubes (CNTs) have attracted much attention as a potential reinforcement for the enhancement of toughness [1–6] and wear resistance [7–10] of the ceramic matrix due to their remarkable mechanical [11–15] and thermal properties [16,17]. In the past, researchers have addressed the tribological behavior of CNT reinforced aluminum oxide (Al2O3) composite [7–10]. An et al. [8] studied the effect of 4 wt.% CNT addition on tribological behavior of hot pressed Al2O3 and observed that relative wear weight loss decreased by 45% with CNT addition. However, the wear resistance of the composite significantly decreased with the addition of 10 wt.% CNT which was attributed to inhomogeneous dispersion of the CNT and poor cohesion between CNT and Al2O3 matrix. Another study on tribological performance of Al2O3-CNT by Lim et al. [10] showed that wear weight loss continuously decreased with an increase in CNT content up to 12 wt.%. This was attributed to the enhanced dispersion of CNT in Al2O3 composite which was achieved by tape casting followed by lamination and hot pressing. Balani et al. [9] reported an improvement of 49 times in the sliding wear resistance by the addition of 8 wt.% CNT to Al2O3. Such improvement was attributed to a uniform dispersion of nanotubes, CNT bridging between the splats and enhanced densification by CNTs. All these studies investigated tribological behavior of the Al2O3-CNT coating at room temperature. However, no attempt has been made to study the tribological behavior of CNT-reinforced ceramic composites at elevated temperature; though there are some studies [18,19] that provide an insight into the tribological characteristics of Al2O3 without CNT reinforcement at the elevated temperature.

Ouyang et al. [19] studied the tribological characteristics of low-pressure plasma sprayed Al2O3 coating from room temperature to 800 °C and found a transition from mild to severe wear with the increasing temperature. At room temperature, Al2O3 coating exhibited low friction (0.17) and wear rate (1.07×10⁻⁵ mm³/Nm) when sliding against Al2O3 ball. However, when temperature is increased above 400 °C, coefficient of friction (COF) and wear of the Al2O3 coating increased rapidly and reached a maximum (COF: 1.52, wear rate: 2.97×10⁻⁵ mm³/Nm) at 800 °C. Similar result was found by Lin et al. [18] who studied the tribological behavior of Al2O3–3 wt.% TiO2 coating against silicon nitride (Si3N4) ball from room temperature to 873 K. They found that wear rate of coating was too small to be measured accurately at the room temperature which increased (~5.5×10⁻⁵ mm³/Nm) with the increase in the temperature. Improved wear resistance at room temperature was attributed to the formation of protective silicon oxide (SiO2) layer on the wear track. This protective SiO2 layer was the result of the oxidation of Si3N4 (counter body) ball in the presence of the moisture. It was observed
that, with the increasing temperature, the absorption tendency of moisture on the worn surface decreased and there was no more protective SiO\textsubscript{2} layer resulting in higher wear of the coating. Formation of the protective layer between the ball and the coating occurs due to tribo-chemical reaction which is caused by the moisture/oxygen absorption from the atmosphere [20].

In the present study, the tribological behavior of plasma sprayed Al\textsubscript{2}O\textsubscript{3}–1.5 wt.% CNT coatings is investigated at elevated temperature (from room temperature to 873 K) using ball-on-disk tribometer. Wear and friction behavior of the Al\textsubscript{2}O\textsubscript{3}–CNT composite coating against a tungsten carbide (WC) ball at temperature ranging from room temperature to 873 K is investigated.

2. Experimental procedure

2.1. Powder and coating synthesis

Chemical vapor deposition (CVD) technique was employed for uniform growth and dispersion of CNTs on dense Al\textsubscript{2}O\textsubscript{3} powder (ALO 101, Praxair Inc., Danbury, CT) [21]. The size range of dense Al\textsubscript{2}O\textsubscript{3} powder was between 15–45 μm and the original phase of dense Al\textsubscript{2}O\textsubscript{3} powder was α-Al\textsubscript{2}O\textsubscript{3}. More details of in situ grown CNT reinforced Al\textsubscript{2}O\textsubscript{3} composite powders are displayed in Section 3.1. Al\textsubscript{2}O\textsubscript{3}–1.5 wt.% CNT composite powder (referred as ICP-1 powder) was plasma sprayed using SG 100 gun (Praxair Surface Technology, Danbury, CT) on an AISI 1020 steel substrate (100 mm×19 mm×3.2 mm) to synthesize Al\textsubscript{2}O\textsubscript{3}–CNT composite coating (ICP-1 coating). The plasma processing parameters are tabulated in Table 1. Al\textsubscript{2}O\textsubscript{3} powder (ALO 101 powder without CNTs) was also plasma sprayed as the reference coating. The details of powder processing and coating synthesis are published elsewhere [21].

2.2. Tribological properties

High temperature ball-on-disk tribometer (Nanovea, Micro Photonics Inc., CA, USA) was used to evaluate the wear resistance of the composite coatings at room and elevated temperature. Wear tests were carried out at 250 rpm and at normal loads of 30 N with a stationary tungsten carbide (WC) ball and the rotating sample. The wear test was conducted for 60 min resulting in 15,000 revolutions which correspond to 565 m linear distance. A 3 mm diameter WC ball was used to slide against the coating surface. The composition of the tungsten carbide ball was WC–6 wt.% Co. The hardness of the WC–6 wt.% Co ball was 90–92 HRC (~24–27 GPa).

Surface of the plasma sprayed coatings was polished prior to wear tests. Surface roughness of the coating was measured using surface roughness analyzer TR 200 (Micro Photonics Inc., CA, USA). The average roughness value (R\textsubscript{a}) of the Al\textsubscript{2}O\textsubscript{3} coating was 1.43 ± 0.38 μm and peak to valley height (R\textsubscript{pk}) was 4.68 ± 0.96 μm. For CNT reinforced Al\textsubscript{2}O\textsubscript{3} coating, R\textsubscript{a} and R\textsubscript{pk} were 1.83 ± 0.38 μm and 5.98 ± 1.01 μm respectively. Wear tests were conducted at room temperature, 573 K and at 873 K. Two or three wear tests were conducted for each condition in order to see the consistency of the wear weight loss as well as the coefficient of friction (COF) of the coatings. The weight change (averaged from two or three tests) in the coating sample was measured after the wear test using Ohaus digital balance with an accuracy of 10\textsuperscript{−5} g. Also, to maintain the accuracy in weight measurement process, wear weight loss has been measured three times and the average value of the measurement is reported. Wear weight loss was calculated based upon these measurements. The frictional force between the WC ball and the coating was recorded for room temperature and 873 K. The data was acquired at a rate of 1000 data points per minute.

2.3. Microstructural characterization

A JEOL JSM 6330 F field emission scanning electron microscope (FE-SEM) was used to investigate the microstructural and topographical features of worn surface of plasma sprayed Al\textsubscript{2}O\textsubscript{3}–CNT coatings. X-ray mapping was performed using a JEOL JSM 5910LV scanning electron microscope (SEM) operating at 15 kV and 16 frames in a matrix of 1024 × 800 pixels taking 50 μs per square pixel, each pixel of dimensions 0.336 μm in the x and y equally. Micro-Raman spectroscopy (spatial resolution: 5 μm) was used to study the CNT structure in ICP-1 powder as well as in plasma sprayed ICP-1 coating. A titanium (Ti)-sapphire crystal target with a laser wavelength of 785 nm was used and the laser was produced using a source from Spectra Physics (Model 3900 S, CA, USA) with the detector (spectral resolution: 4 cm\textsuperscript{−1}) from Kaiser optical system, Inc. (MI, USA).

2.4. X-ray photoelectron spectroscopy (XPS) analysis of wear surface

The wear tracks of the Al\textsubscript{2}O\textsubscript{3} and ICP-1 coating after high temperature testing (873 K) were characterized using Physical Electronics (PHI 5400) ESCA X-ray photoelectron spectroscopy (XPS). Non-monochromatic X-ray radiation from MgK\textalpha source of 300 W was used for the analysis. The survey spectra, and multiplex spectra were recorded with pass energies of 35.7 and 17.9 eV, respectively to achieve better resolution. The spectrometer was calibrated using a metallic gold
standard (Au 4f\(_{7/2}\) = 84.07 ± 0.1 eV). The peaks shift due to charging produced by the specimen was removed by using a binding energy scale referred to that of C(1 s) of the hydrocarbon part of the adventitious carbon line at 284.6 eV. The nonlinear least-squares curve fitting was carried out using a Gaussian–Lorentzian distribution. Curve fitting was accomplished by first smoothing the data using a Savitsky–Golay routine and then fitting this smoothed data by assuming a 100% Gaussian peak shape. All data smoothing and curve fitting were performed using Peak Fit software (version 4.05, SPSS Inc., Chicago, Illinois, USA) with modified fit routine.

3. Results and discussion

3.1. Background of plasma sprayed Al\(_2\)O\(_3\) and ICP-1 coatings

A brief background of the powder processing and coating synthesis is provided here for the sake of completeness. The details are published elsewhere [21]. Multi-walled carbon nanotubes were grown on the dense Al\(_2\)O\(_3\) powder particle (as shown in Fig. 1 (a)) via chemical vapor deposition (CVD). Fig. 1 (b) shows the high magnification image of CNTs which shows the entanglement of long nanotubes and the length of the CNTs is in the range of 0.6–2 µm. Uniform dispersion of the CNTs on the entire powder surface was successfully achieved.

Al\(_2\)O\(_3\) coating and Al\(_2\)O\(_3\)–CNT composite coating (referred as ICP-1) were synthesized by plasma spraying of Al\(_2\)O\(_3\) powder and ICP-1 powder respectively. Fig. 2 (a) and (b) shows the cross-sectional view of plasma sprayed Al\(_2\)O\(_3\) and ICP-1 coatings, respectively. Table 2 shows the thickness, density and microhardness of both the coatings. Coatings have a uniform thickness of 400 µm with a theoretical density of 94% for Al\(_2\)O\(_3\) coating and 96% for ICP-1 coating, as measured by the water immersion technique. The microhardness of both the coatings was measured at ∼39.2 N load for dwell time of 30 s. The microhardness of the plasma sprayed ICP-1 coating was 553.2 ± 91.2 VHN (5.42 GPa) whereas Al\(_2\)O\(_3\) coating had a hardness of 481.3 ± 35.9 VHN (4.71 GPa). The 15% increase in the microhardness value of ICP-1 coating is due to the enhanced indentation resistance by CNT reinforcement. An increase in 24% in relative fracture toughness of ICP-1 coating was observed with the addition of 1.5 wt% in situ grown CNTs in starting dense Al\(_2\)O\(_3\) powder. Relative improvement in the fracture toughness of ICP-1 coating is attributed to the following toughening mechanisms: (i) crack bridging by CNT, (ii) crack deflection at CNT interface and (iii) strong CNT-Al\(_2\)O\(_3\) interface [21].

3.2. High temperature tribological behavior of the coatings

3.2.1. Wear behavior vs. temperature

Fig. 3 shows the wear weight loss of Al\(_2\)O\(_3\) and ICP-1 coatings at different temperatures. The weight loss increases with the temperature for Al\(_2\)O\(_3\) coating while it decreases for ICP-1 coating. At room temperature, relative improvement in the wear resistance of ICP-1 coating was found to be 12% while at 573 K and at 873 K, relative increases in the wear resistance of ICP-1 coating were found to be 56% and 82%, respectively. This clearly indicates that temperature has a strong effect on the wear behavior of both plasma sprayed coatings against WC counter body. Wear surfaces of both coatings have been analyzed carefully to understand the high temperature tribological behavior of the coatings.

Fig. 4 (a) (b) and (c) shows the micrographs of the wear surfaces of the Al\(_2\)O\(_3\) coating sliding against the WC ball at room temperatures, 573 K and at 873 K respectively. Similarly, Fig. 4 (d), (e) and (f) are the micrographs of the wear surface of the ICP-1 coating at room temperatures, 573 K and 873 K respectively. SEM images show that mild wear occurs in both coatings at room temperature (Fig. 4 (a) and (d))

![Fig. 2. SEM image showing cross-sectional view of plasma sprayed (a) Al\(_2\)O\(_3\) coating and (b) ICP-1 coating.](image)

Table 2

Properties of Al\(_2\)O\(_3\) and ICP-1 coatings.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Thickness of the coating</th>
<th>Density of the coatings</th>
<th>Hardness of the coatings</th>
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<tbody>
<tr>
<td>Al(_2)O(_3) coating</td>
<td>~400 µm</td>
<td>~94% of theoretical density</td>
<td>481.3 ± 35.9 VHN (4.71 GPa)</td>
</tr>
<tr>
<td>ICP-1 coating</td>
<td>~400 µm</td>
<td>~96% of theoretical density</td>
<td>553.2 ± 91.2 VHN (5.42 GPa)</td>
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![Fig. 3. Wear weight loss of Al\(_2\)O\(_3\) coating and ICP-1 coating at room temperature (RT), 573 K and at 873 K. At room temperature, relative improvement in wear resistance of ICP-1 coating was 12% while at 573 K and at 873 K, relative increases in the wear resistance of ICP-1 coating were 56% and 82% respectively.](image)
resulting in smoother wear surface. Occasional pull out of the coating was also observed in the case of mild wear at room temperature. In contrast, wear surface had rough surface and was covered with discontinuous smooth thin film at the elevated temperature, as shown in Fig. 4 (b), (c), (e), and (f). Rough wear surface indicates the phenomena of severe wear while the discontinuous smooth thin film results very likely from the tribo-chemical reaction at the elevated temperature. Similar, wear phenomena has been observed for counter body (WC ball). Fig. 5 (a) and (b) shows the unworn and worn surfaces of the ball. Compare to the unworn surface, worn surface has a rough region (Fig. 5 (b)) indicating the severe wear phenomena. Also, a discontinuous thin film was observed at the worn surface (Fig. 5 (b)) which is attributed to the tribo-chemical reaction. Tribo-chemical reaction is considered to be an important factor that affects the wear behavior of ceramic materials at elevated temperature [20]. Formation of a smooth thin film or protective layer on the wear surface as result of tribo-chemical reaction can reduce damage to coating surface during sliding [18,20]. The formation of tribo-chemical layer is explained in Section 3.2.2.

Fig. 6 shows the elemental X-ray maps of wear track of Al2O3 coating at 873 K. Fig. 6 (a) is the back scattered image of the wear track and Fig. 6 (b) and (c) confirms the formation of a thin film containing large amount of tungsten with traces of cobalt respectively. The presence of tungsten and cobalt in the wear track suggests that tungsten carbide ball was oxidized at the elevated temperature and a layer was transferred to the wear surface of the coatings. Fig. 6 (d) and (e) showed the signature of aluminum (Al) and oxygen (O) respectively which has come from the Al2O3 matrix while Fig. 6 (f) showed the presence of carbon (C) which might have come from protective film of WC. Fig. 7 is the elemental X-ray map of the wear track of ICP-1 coating at 873 K. Fig. 7 (a) is the back scattered image of the wear track and Fig. 7 (b) and (c) confirms the presence of tungsten and cobalt respectively in the wear track which is as a result of transferred oxidation product of tungsten carbide ball. Similar to the wear track of the Al2O3 coating, the wear track of the ICP-1 coating also gave the signature of Al (Fig. 7 (d)), O (Fig. 7 (e)), and C (Fig. 7 (f)). Similar phenomenon was observed at 573 K but only 873 K results are presented for the sake of brevity.
The formation of $\text{WO}_3$ film was experimentally validated by performing XPS analyses of the wear surface of the coatings at elevated temperature (873 K). XPS technique allowed the measurement of the oxidation state of a very thin layer on the wear track. Energy dispersive spectroscopy (EDS) results also confirmed the presence of the W, Co and Al in the wear track. The XPS analysis on the worn surfaces (873 K) of Al$_2$O$_3$ and ICP-1 coatings reveals the presence of tungsten 6+ valence state as shown in survey and multiplex XPS data (Fig. 8 (a) and (b)). The major peak of $\text{W}^{6+}$ (4f7/2) was observed near 35.4 eV which is in good agreement with the reported literature value [24]. Because the tungsten is most stable in its 6+ oxidation state this confirm the formation of thin oxide layer of $\text{WO}_3$. It has been reported that the WC-Co has shown excellent wear resistant at ambient temperature and has poor high temperature oxidation resistant and degrades by forming an oxide [25,26]. A similar behavior is observed in the present study where WC degraded at 873 K to form a transfer layer on the coating.

The percentage of area covered by the transferred thin film ($\text{WO}_3$ and traces of Co) on the wear track of coating was measured from three or more wear track images using Image J software (http://rsbweb.nih.gov/ij/index.html). Table 3 shows the fraction of the area coverage of the transferred $\text{WO}_3$ film on Al$_2$O$_3$ and ICP-1 coatings at different temperatures. From Table 3, it can be concluded that the amount of transfer layer on the wear track increases with the increasing temperature for both coatings indicating the higher rate of tribo-oxidation reaction at elevated temperature. Further, higher transfer of $\text{WO}_3$ containing film in case of ICP-1 coating is attributed to the higher hardness of ICP-1 coating which leads to more intense wear of WC ball. It is well known that transferred thin film to the wear track acts as a protective layer and can protect the surface effectively against further wear of the coating [18,20]. This phenomenon dominates in the ICP-1 coating which shows the higher area fraction of the transfer film at 873 K and hence least wear (Fig. 3).

Increasing weight loss of Al$_2$O$_3$ coating with temperature (as seen in Fig. 3) can be understood in terms of two competing phenomenon: (i) hardness of Al$_2$O$_3$ coating which decrease with the temperature increase and (ii) the presence of protective layer at the elevated temperature. Evans and Marshall [27] have proposed the wear of ceramic material at room temperature which is based on the fracture toughness and is represented in Eq. (5):

$$V = P_n^{1.25} K_c^{-0.5} H^{-0.625} \left( \frac{E}{\pi S} \right)^{0.8}$$  \hspace{1cm} (5)

where, $V$ is the wear volume ($\text{m}^3$), $P_n$ is applied load (MPa), $K_c$ is fracture toughness, $H$ is the hardness, $E$ is the elastic modulus (GPa) and $S$ is the sliding distance (m). Eq. (5) clearly indicates that high fracture toughness of the material will result in enhanced wear resistance of the coating at room temperature. However, with the increase in temperature, elastic modulus and hardness both changes and can affect the wear property of the material. Gonzalez et al. [28] mentioned that the elastic modulus of Al$_2$O$_3$ decreases very slowly up to about 600 °C (873 K) and decreases more sharply above this temperature. Wang et al. [29] studied the temperature dependence of ceramic hardness and found that the hardness of Al$_2$O$_3$ exponentially decreases with the increasing temperature (Eq. (6))

$$H = H_0 e^{-\alpha T}$$  \hspace{1cm} (6)

where, $H_0$ and $\alpha$ are the constants determined from the experimental data, and $T$ is the test temperature (°C). The hardness of Al$_2$O$_3$ reduces by ~29% at 300 °C and 67% at 600 °C [29]. Based on this fact, it is
expected that hardness of Al₂O₃ coating decreases with the elevated temperature which will ultimately lead to high wear rate of the coating. Since, the small area (20%) of the wear surface of Al₂O₃ coating is covered with the protective layer at 573 K, severe wear occurs at the unprotected area due to reduced hardness. Ultimately, severe wear of the unprotected surface dominates over the protective layer and hence total wear loss of the Al₂O₃ coating increased at 573 K in comparison to room temperature. In case of 873 K, even if the wear surface of Al₂O₃ coating is half (∼52%) covered with the protective layer, it is expected that there is a drastic reduction (∼67%) in hot hardness of Al₂O₃ coating at 873 K leading to severe wear in the unprotected area. The degree of material removal is more intense in the case of 873 K than 573 K due to the very low hardness of Al₂O₃ coating at 873 K. Hence, the highest wear loss is observed for Al₂O₃ coating at 873 K.

In contrast, wear loss of ICP-1 coating shows a decreasing trend with increasing temperature. Fig. 9(a) shows the CNT bridging in the wear track of ICP-1 coating at 573 K. CNT bridges that hold the splat together increase the adhesion between splats to reduce the wear loss. Even if the hardness of ICP-1 coating decreases at 573 K, ICP-1 coating has higher hardness (∼15%) and higher elastic modulus than Al₂O₃ coating and relatively large part (27%) of the wear surface is covered with the protective layer. CNT bridging was also observed in the wear track of ICP-1 coating at 873 K (Fig. 9(b)). Further, 72% of the wear surface is covered with the protective layer in the ICP-1 coating at 873 K. These two mechanisms dominate over the wear of the ICP-1 coating due to lower hardness at 873 K and hence overall wear resistance of the ICP-1 coating increased at 873 K. Also, relative higher transfer of the protective layer in the wear track of ICP-1 coating at the elevated temperature contributes towards the weight gain of the ICP-1 coating and hence shows lower wear loss.

3.2.3. Thermal stability of carbon nanotube reinforcement

The stability of the CNT structure at elevated temperatures has been debated by several researchers. CNT oxidation at the elevated temperature can significantly degrade its mechanical properties [30].
Researchers have different opinions on the oxidation behavior of CNTs at elevated temperature [31–34]. Osswald et al. [33] monitored the oxidation of multi-walled carbon nanotubes (MWCNTs) by Raman spectroscopy and concluded that oxidation of CNT occurs above 440 °C with a severe oxidation at 550 °C–600 °C. Li et al. [32], also concluded that oxidation of MWCNTs occurs in the temperature range of 480 °C–750 °C in air. Zhang et al. [34] mentioned that oxidation resistance of CNTs depends on the degree of graphitization, content of the metallic catalyst particle, surface group and the local heat effects. Purified MWCNTs exhibit higher activation energy for oxidation [34] (activation energy for oxidation of as-received MWCNT: 166.38 kJ/mol, activation energy for oxidation of purified MWCNT: 287.13 kJ/mol) resulting in improved oxidation resistance in air than as-received MWCNT [34]. Similar finding was observed by Huang et al. [31], who mentioned that purified MWCNT is more stable towards oxidative destruction than the raw MWCNTs.

Fig. 10 shows the Raman spectra for the ICP-1 powder and ICP-coating. $I_D/I_G$ ratio was calculated for the ICP-1 powder and for ICP-1 coating which has been tabulated in Table 4. The $I_D/I_G$ ratio for starting ICP-1 powder is 1.56 which decreased to 0.98 for plasma sprayed ICP-1 coating. Reduction in $I_D/I_G$ ratio indicates the lower defect content and high purity of CNTs in the ICP-1 coating. Several studies have confirmed the purification and graphitization of CNTs at high temperature [31,35–37]. Huang et al. [31] performed high temperature (2000 °C) annealing of CNT and found that the purity of CNT increased resulting in higher degree of graphitization. High temperature annealing of CNTs leads to the refinement of the graphene shell structure [36] by (a) reducing the interlayer spacing between CNTs.
walls and (b) by eliminating the catalyst particle embedded in CNT i.e. by sublimation of catalyst particle. It is envisaged that higher degrees of graphitization and purification of CNT also contribute towards the enhanced oxidation resistance of CNTs in ICP-1 coating.

3.2.4. Friction behavior of coatings

Coefficient of friction (COF) for both coatings was measured at the room temperature and 873 K. Fig. 11 shows the COF of Al₂O₃ and ICP-1 coatings as a function of sliding distance at room temperature (Fig. 11 (a)) and at 873 K (Fig. 11 (b)). Coefficient of friction is almost similar (∼0.7) for Al₂O₃ coating at room and elevated temperatures. It is recalled that wear surface at room temperature was smooth (Fig. 4 (a) and (d)) due to mild wear. Higher spikes and fluctuations were observed for COF of Al₂O₃ coating at 873 K (as seen in Fig. 11 (b)) which are attributed to the debris generation during severe wear condition. The large amount of wear debris dominates the protective film formation and hence results in higher fluctuations in COF for Al₂O₃ coating at 873 K. In contrast, ICP-1 coating has relatively large area (∼72%) of wear surface covered with protective layer at 873 K. Hence, coatings as a function of sliding distance at room temperature (Fig. 11 (a)) and at 873 K (Fig. 11 (b)).

Table 3

<table>
<thead>
<tr>
<th>Wear track of Al₂O₃ coating</th>
<th>Wear track of ICP-1 coating</th>
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<tbody>
<tr>
<td>0.20</td>
<td>0.27</td>
</tr>
<tr>
<td>0.52</td>
<td>0.72</td>
</tr>
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</table>

Fig. 8. XPS spectra collected from (a) wear track of Al₂O₃ coating at 873 K and (b) wear track of ICP-1 coating at 873 K. Both the spectra show the major peak of W⁶⁺ (4f⁷/2) confirming the formation of thin WO₃ layer on the surface of the wear track.

Fig. 9. High magnification SEM image of wear track (WT) of (a) ICP-1 coating at 573 K and (b) ICP-1 coating at 873 K showing the CNT bridging between the splats.

Fig. 10. Raman spectrum of CVD CNT-Al₂O₃ powder and ICP-1 coating. Raman peaks suggest retention of CNTs and enhanced graphitization in the ICP-1 coating.
film formation dominates over wear debris generation leading to lesser fluctuation in COF value at 873 K (Fig. 11(b)).

4. Conclusion

Tribological behavior of plasma sprayed Al2O3 and Al2O3-CNT coating was evaluated at room temperature, 573 K, and at 873 K. The wear surface shows the formation of WO3 rich protective layer due to tribo-chemical reaction with WC ball at elevated temperature. Relative improvement in the wear resistance of Al2O3-CNT coating was found to be 12% at room temperature, 56% at 573 K and 82% at 873 K. Improved wear resistance of Al2O3-CNT coating was attributed to: (i) large area coverage by protective film at the elevated temperature, (ii) higher hardness than Al2O3 coating and (iii) CNT bridging between splats. COF for Al2O3 showed consistent results (∼0.7) at room and elevated temperatures while COF displayed a decreasing trend (0.75 to 0.55) for Al2O3-CNT coating at 873 K.

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