ON IMPROVEMENT OF TRIBOLOGICAL PERFORMANCE OF PULSED DC CFUBM SPUTTERED WS$_2$ SOLID LUBRICANT COATING THROUGH ADDITION OF Ti OR TiN

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ABSTRACT

The present work reports on the structural, mechanical and tribological properties of WS$_2$ based solid lubricant coatings. The films were deposited by pulsed DC closed field unbalanced magnetron (CFUBM) sputtering. The deposited films were characterized by Field Emission Scanning Electron Microscopy, Grazing Incidence X-Ray Diffraction, Scratch Adhesion test, Nanoindentation test and Pin-on-disc tribological test. Pure WS$_2$ coating showed poor tribological performance because of its high susceptibility to atmospheric moisture and oxidation and poor adhesion to the substrate. Addition of Ti to the WS$_2$ film in the order of 12% densified the coating microstructure, improved the film hardness as well as adhesion of the film to the substrate which was reflected in its improved tribological performance. TiN is a well known hard, wear resistant coating which has been used for decades for combating wear on cutting tools and different sliding surfaces. However, the friction coefficient of TiN against counter-bodies like steel is on the higher side which does not qualify TiN as an ideal solid lubricant. Addition of tailored amount of soft, lubricious WS$_2$ phase to the hard, wear resistant matrix of TiN resulted in a composite coating which not only outperformed WS$_2$, WS$_2$-Ti but also TiN in terms of durability and wear resistance in tribological tests because of combination of properties like hardness and lubricity in a single matrix.

Keywords: WS$_2$-Ti, TiN-WS$_2$, Wear, Coatings

1. Introduction

WS$_2$ and MoS$_2$ are lamellar solids which are well known for their solid lubricating behaviour. Sliney (1982) demonstrated that the mass loss rate for WS$_2$ was lower as compared to MoS$_2$ at higher temperatures and it could maintain its lubricating action up to temperatures approximately 200°C higher as compared to MoS$_2$. The crystal structure of WS$_2$ consists of a layer of tungsten atoms hexagonally packed within two sulphur layers. The bonding between tungsten and sulphur atoms is covalent while the sulphur layers from adjacent lamella are bonded together by weak Van der Waals forces which get easily sheared during sliding thereby exhibiting very less friction coefficient. However, it has recently been reported that the Coulombic repulsion between the sulphur layers plays the major role in providing low friction co-efficient. The major drawback of lamellar solids like MoS$_2$ and WS$_2$ is their inability to provide low friction co-efficient for longer duration when operated under humid air and elevated temperatures because of rapid oxidation of the edge planes and moisture penetration through the coating thickness resulting in formation of oxidation products like MoO$_3$ or WO$_3$. Renevier et al. (2000) and Efeoglu et al. (2008) showed that such susceptibility to moisture and temperature can be significantly reduced through addition of calculated amount of metal like Ti. Other metals like Cr, Ag, Au, Nb etc are also reported to induce such improvement. The improvement occurs because of several intertwined factors like densification of coating microstructure, improved retention of the (002) basal plane parallel to the substrate, both of which act as a barrier for oxygen and moisture penetration through the film. The mechanical properties like film hardness, Young’s Modulus, adhesion of the film to the substrate also improves because of such addition.

Although addition of different metals to MoS$_2$ or WS$_2$ matrix improves the properties of the film like hardness and adhesion, yet there remains a concern about its utility in severe mechanical application domains like dry machining where the coating should
possess high abrasion resistance as well as high temperature stability. TiN, TiAIN etc are successful industrial coatings for cutting tool applications. However, these materials are not generally considered as ideal solid lubricants as they exhibit relatively higher friction coefficient against materials like steel in the order of 0.4 to 0.8 depending upon the tribological test conditions. Different research groups have therefore concentrated their efforts to prepare and characterize composite coatings where a hard wear resistant matrix like TiN, TiB$_2$, CrN contain a dispersion of soft lubricant phase like MoS$_2$ or WS$_2$. The idea is to maintain a continuous supply of solid lubricant during the tribological tests or similar applications like dry machining while maintaining the significant high hardness of the coating. The presence of lubricious phase is expected to promote easier sliding of the counter body while the hard matrix will prevent the abrasive wear of the coating. However, it may be emphasized that, the amount of lubricating phase should be judiciously controlled in order to have a notably high abrasive wear resistance along with appreciably low value of friction coefficient. Goller et al. (1999) and Gangopadhyay et al. (2009) showed that addition of MoS$_2$ to a hard TiN matrix makes the composite coating hard as well as lubricious.

The present work reports on the comparative study of the different physical, mechanical and tribological properties of solid lubricant based composite coatings of WS$_2$-Ti and TiN-WS$_2$. Pure WS$_2$ and pure TiN coatings are also included in the study for the purpose of analysis of the results and realizing the improvements which occurred due to the synthesis of such composites.

2. Experimental details

2.1 Coating deposition

Pulsed DC Closed Field Unbalanced Magnetron (CFUBM) sputtering was employed for the deposition of the films. Four different coating architectures viz. WS$_2$ (A1), WS$_2$-Ti (A2), TiN (A3) and TiN-WS$_2$ (A4) were deposited on AISI 1040 steel discs (25mm diameter and 8mm thickness) and M2 grade HSS blocks (10mm × 10mm × 20mm). The coated steel discs were used for tribological tests while the coated HSS blocks were used for other physical and mechanical characterizations. The substrates were initially polished to obtain a surface finish of R$_a$ = 50 nm or better. This was followed by ultrasonically degreasing with 1N NaOH solution and dehumidification with isopropyl alcohol and finally drying with hot air blast. After loading the substrates into the deposition chamber, the system was pumped down to a base pressure of approximately 8 × 10$^{-6}$ Torr and heated to 200$^\circ$C along with substrate rotation with 4 rpm. Argon was used as the sputtering gas for all the coating architectures and nitrogen was used as the reactive gas during deposition of TiN and TiN-WS$_2$ composite coatings. Before deposition of the different coating architectures, a thin Ti adhesion layer (200-300 nm) was deposited on to the substrates to promote adhesion of the coating to the substrate and minimization of residual stress. The values of pulsing frequencies and duty cycles were determined on the basis of literature survey and preliminary experiments. Table I shows the flow rates of Ar and N$_2$, the different cathode currents as well as the bias voltage employed during deposition of the coatings.

<table>
<thead>
<tr>
<th>Deposition parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar:N$_2$ sccm</td>
<td>15:11.5</td>
</tr>
<tr>
<td>WS$_2$ cathode current (A)</td>
<td>0.5</td>
</tr>
<tr>
<td>(i) For A1, A2</td>
<td>0.1</td>
</tr>
<tr>
<td>(ii) For A4</td>
<td></td>
</tr>
<tr>
<td>Ti cathode current (A)</td>
<td>0.1</td>
</tr>
<tr>
<td>(i) For A2</td>
<td>5.0</td>
</tr>
<tr>
<td>(ii) For A3 and A4</td>
<td></td>
</tr>
<tr>
<td>Bias Voltage (V)</td>
<td>-50</td>
</tr>
</tbody>
</table>

2.2 Coating analysis

The morphology and cross sectional structure of the coatings were examined through Field Emission Gun Scanning Electron Microscope (FEG-SEM). The composition of the coatings was tested through energy dispersive X-ray microanalysis (EDAX) in terms of atomic percent of the constituent elements i.e. the number of atoms of an element per hundred atoms representative of the coating material. The EDAX was operated at 20 keV. The crystalline structure of the coatings was investigated through high resolution Philips, PANalytical PW 3040/60 XPert PRO instrument in grazing incidence X-ray diffraction (GIXRD) mode using Cu Kα radiation of wavelength 0.15418 nm at an incident angle of 2°.

2.3 Scratch adhesion test

A TR101-M5 DUCOM scratch tester was employed to evaluate the adhesion of the different coatings deposited on M2 grade HSS substrates. The scratch adhesion tester consisted of a Rockwell C diamond stylus of 0.2 mm tip radius, which was initially pressed on the sample with a preloading of 10N and then moved over the sample with a velocity of 12mm/min and a loading rate of 5N/mm up to a final load of 80N. The associated software WINDUCOM 2004 coupled with the device recorded the variation of friction force and hence co-efficient of friction with the variation of the normal load. The total failure of the coating was determined by a sudden increase in the friction force at a particular value of normal load and that value of normal load was considered as the critical load (L$_c$) of failure for the coating. However, for verifying the exact location and mode of failure of the coating as well as for confirming the critical load,
the scratch tracks were later observed through optical microscopy.

2.4 Nanoindentation test

The hardness of the coatings with different architectures was evaluated through nanoindentation technique carried on a TI950 Tribo-nanoindenter (Hysitron Inc., Minnesota, MN, USA). A Berkovich probe was used for making the indentations with a maximum indentation load of 8 mN with loading and unloading time of 10 s each. The hardness was calculated automatically by the associated software from the loading-unloading curves through Oliver-Pharr Method. Fifteen indentations were made on each sample and the average hardness for each coating architecture is reported here.

2.5 Pin-on-disc test

The tribological properties of the coatings deposited on AISI 1040 steel discs were evaluated using a tribometer in pin-on-disc configuration. A bearing steel ball (6mm diameter) was used as the counter body. The tests were operated with a normal load of 5N, sliding velocity of 10 cm/s under room temperature and relative humidity of 50±5%. The wear track on the coated discs was later examined through optical microscopy. The cross-sectional profile of the wear tracks were later scanned with a surface profilometer for the purpose of estimation of wear coefficients.

3. Results and Discussion

3.1 Chemical composition

The chemical composition of the different coating architectures obtained through EDAX analysis are presented in Table II. It may be observed from Table II that coating (A1) suffered from severe sulphur loss thereby yielding a S/W ratio of only 0.65. Such loss of sulphur from the growing film can be attributed to the film synthesis method during which the positively charged Ar+ ions bombards the negatively biased substrate resulting in preferential re-sputtering of sulphur from the growing film. Application of pulsed substrate biasing in the present work further augmented the sulphur re-sputtering because of its capability to draw higher ion-current as compared to pure DC biasing. Such re-sputtering of sulphur has been observed by many researchers for sputter deposited MoS2 and WS2 coatings. From the literature review, it has been found out that addition of Ti in the range of 5-20 % resulted in improvement of the mechanical and tribological performance of MoS2 and WS2 films. In the present work, approximately 12 % Ti were added to the WS2 coating. It has been observed that addition of Ti improved the S/W ratio in the film to 1.5. The reason may be attributed to the increased plasma density because of addition of Ti ions and neutrals into the plasma volume which resulted in a shorter molecular mean free path of the Ar+ ions which lost some of their energy due to enhanced re-scattering thereby reducing the re-sputtering of sulphur. The TiN coating was almost stoichiometric as revealed from the EDAX data. However, co-deposition of WS2 with TiN again resulted in severe loss of S from the film. Similar observations have been reported by Nossa et. al. (2001) for W-S-N coatings where it has been pointed out that formation of W-N bonds restricts the bonding of W and S resulting in low S/W ratio.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>W %</th>
<th>S %</th>
<th>O %</th>
<th>Ti %</th>
<th>N %</th>
<th>S/W ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>49</td>
<td>32</td>
<td>19</td>
<td>0</td>
<td>0</td>
<td>0.65</td>
</tr>
<tr>
<td>A2</td>
<td>30</td>
<td>45</td>
<td>13</td>
<td>12</td>
<td>0</td>
<td>1.50</td>
</tr>
<tr>
<td>A3</td>
<td>0</td>
<td>0</td>
<td>51</td>
<td>49</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>3</td>
<td>1</td>
<td>49</td>
<td>47</td>
<td>0.33</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Structure and morphology

3.2.1 Structure

The GIXRD spectra obtained for coatings with different architectures deposited on HSS substrates are presented in Fig. 1. It may be observed that coatings A1, A2 and A4 showed prominent orientation of the (002) basal plane parallel to the substrate which is significant for obtaining good tribological properties. The broad peak pertaining to (002) basal plane suggested the formation of a nanocrystalline structure. A broad hump occurring approximately at 2θ = 40° refers to the turbostratic stacking of the 10L (L= 0, 1, 2, . . .) planes of the WS2 crystal lattice. With addition of Ti, the (101) edge plane got suppressed as compared to that of pure WS2 coating and it is beneficial for good tribological properties. For the TiN coating (A3) different crystalline planes viz. (111), (200), (220) and (311) may be observed. The TiN-WS2 composite coating (A4) showed the co-existence of phases of both (002) peak of WS2 phase and (111), (200), (220) and (311) peaks of TiN phases suggesting the coexistence of TiN and WS2 in a single matrix.

![Figure 1 GIXRD spectra for the coatings with different architectures](image-url)
3.2.2 Morphology and cross-section of the coatings

The surface morphology and cross-section of the different coatings are presented in Fig. 2. The thickness of all the coating architectures were in the range of 1.7 to 2 µm. All the coatings showed a Ti adhesion layer of 250-300 nm. Pure WS₂ coating deposited through pulsed DC sputtering showed a granular morphology which is different from the 'acicular' porous structure generally obtained through DC and RF sputtering. Such a morphology also supported the GIXRD spectra which showed prominent orientation of the (002) basal plane. The cross-section of the WS₂ coating showed a fibrous structure with some porosity. With addition of Ti, the morphology acquired a typical ‘cauliflower’ like appearance and such change in structure of pure WS₂ coating with different metal addition like Ag, Cr, Ti has been reported by other researchers. Schaarf et. al (2009) attributed such change in microstructure to the influence of the metal dopants in restricting the crystalline growth of WS₂. The fractured cross section of the WS₂-Ti composite coating showed a more compact columnar structure as compared to that of pure WS₂ coating. The TiN coating (A3) showed agglomerated grain morphology with compact columnar cross-sectional structure. With addition of WS₂ to the TiN matrix, the morphology changed to a ‘globular’ appearance. The cross section of the TiN-WS₂ coating (A4) also showed a columnar structure but the width of the columns were finer as compared to that of TiN coating. Such refinement in structure may be attributed to a competitive growth of the TiN and WS₂ phases and is consistent with the results obtained for TiN-MoS₂ composite coatings.

3.3 Scratch Adhesion test

The critical loads of the coatings with different architectures are presented in Table III while the optical micrographs of the scratch tracks near the failure zone for different coatings are shown in Fig. 3. The failure zone of pure WS₂ coating A1 showed severe lateral spallation along the two edges of the scratch tracks which resulted from the release of the elastic energy stored because of the compressive stresses at the tip of the moving stylus. The stored elastic energy was utilized in opening up large areas on the two sides of the scratch tracks as explained by Bull et. al. (1991). Addition of Ti to the WS₂ matrix helped in restricting the lateral spallation to a large extent and it only exhibited some buckling at the edges. The hard and brittle TiN coating showed some brittle flaking at the edges of the scratch track which significantly reduced on addition of WS₂ to the TiN matrix. The presence of soft WS₂ phase within the TiN matrix possible restricted the propagation of brittle cracks within the film and thereby reduced the flaking of the coating along the edges. Such improvement in adhesion with addition of calculated amount of MoS₂ to hard TiN or CrB₂ matrix has been reported in the literature. A comparative analysis of the optical micrographs of the failure zones of WS₂-Ti and TiN-WS₂ composite coatings in Fig. 3 as well as their critical loads clearly indicates the superior capability of the TiN-WS₂ system over WS₂-Ti system in resisting the lateral flaking and improvement in coating adhesion.

![Figure 2 Surface morphology and cross section of the coatings with different architectures](image)

![Figure 3 Optical images of the failure zones of the scratch tracks on coatings with different architectures](image)
3.4 Nanoindentation test

The nanohardness values of the coatings with different architectures are presented in Table III and the corresponding representative loading-unloading plots obtained from nanoindentation measurements are plotted in Fig. 4. Pure WS$_2$ coating showed a nanohardness of 5.4 GPa which is higher than that of RF sputtered WS$_2$ which exhibited a nanohardness of 1.5 GPa. The nanohardness of WS$_2$ obtained in the present work coincided with the nanohardness values of pulsed DC sputtered MoS$_2$ and WS$_2$.

### Table III: Adhesion and hardness of the coatings with different architectures

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Critical Load ($L_c$), N</th>
<th>Nanohardness, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS$_2$ (A1)</td>
<td>48±5</td>
<td>5.4±2.5</td>
</tr>
<tr>
<td>WS$_2$-Ti (A2)</td>
<td>60±4</td>
<td>8.6±1.5</td>
</tr>
<tr>
<td>TiN (A3)</td>
<td>65±5</td>
<td>28.5±4</td>
</tr>
<tr>
<td>TiN-WS$_2$</td>
<td>68±4</td>
<td>20.5±3</td>
</tr>
</tbody>
</table>

Application of pulsed DC along with pulsed substrate bias increases the flux of ions impinging the growing film thereby increasing its compactness and hardness. Addition of Ti to WS$_2$ increased the hardness to 8.6 GPa because of solid-solution hardening effect. The nanohardness of TiN was 28.5 GPa which conformed well to the mostly reported values in the literature. The TiN-WS$_2$ composite coating showed a reduction in hardness as compared to that of TiN because of the presence of soft WS$_2$ phase within the hard TiN matrix.

3.5 Friction coefficient and wear behaviour

The variation of friction co-efficient with sliding distance for different coating architectures are presented in Fig. 5. Pure WS$_2$ coating (A1) showed the least wear life in thetribological test and failed only after 115 m. The early failure of pure WS$_2$ coating may be attributed to a combination of factors like rapid oxidation of the coating leading to products like WO$_3$, low hardness and low adhesion to the substrate. Addition of approximately 12% Ti to the WS$_2$ matrix reduced its susceptibility to atmospheric oxidation. Such addition also increased the hardness and adhesion of the coating to the substrate. All these factors led to the improvement in the tribological performance of the WS$_2$-Ti coating (A2) which was reflected in the steady friction co-efficient of 0.07 up to an increased sliding distance of 300 m. The TiN coating showed a steady state friction co-efficient of 0.45 which lied within the range of friction coefficient values of TiN in the literature under similar tribological test conditions. With addition of WS$_2$ to the TiN matrix the steady state friction could be lowered down to 0.25. The fluctuation of the friction coefficient also reduced on addition of WS$_2$ to TiN. Although the friction co-efficient of WS$_2$-Ti composite was lower as compared to that of TiN-WS$_2$ composite, yet the latter outperformed the former in terms of endurance of tribological run and did not fail up to maximum test limit of 700m.

In order to elucidate the wear behaviour of the different coating architectures, the morphologies of the wear track were observed through optical microscopy and the images are presented in Fig. 6. The wear track of pure WS$_2$ coating exhibited deep abrasive marks inside the track. The relatively low hardness of the WS$_2$ coating allowed the counter body to partially embed inside which caused ploughing and micro-scooping of the coating at high normal load leading to early failure of the coating. Some lateral spallation on two sides of the wear track could be also noticed which indicates poor adhesion of the coating to the substrate. The width of the wear track of WS$_2$-Ti composite coating was comparable to that of pure WS$_2$ but after 300m of sliding distance. The abrasion marks on the wear track were also finer as compared to that of pure WS$_2$ coating which resulted from increased coating hardness due to Ti addition. However, some brittle flaking could be seen along the edges of the wear track which might have resulted from increased hardness and accompanying brittleness.
because of Ti incorporation. The wear track on TiN coating showed signs of brittle fracture which indicates that the removal of the coating occurred in the form of chunks. However, addition of soft WS$_2$ phase to hard TiN matrix reduced the tendency of brittle fracture of the TiN-WS$_2$ composite coating in tribological test as evident from the relatively smoother appearance of the wear track when compared to that of pure TiN coating. The basally oriented soft WS$_2$ islands within the TiN matrix promoted easier sliding of the counter body which was reflected in reduced friction co-efficient of the TiN-WS$_2$ composite coating as compared to TiN.

Figure 6 Optical Images of the wear tracks for different coating architectures

The wear coefficients of the coatings with different architectures are presented in Table IV. Pure WS$_2$ coating (A1) showed the highest wear co-efficient i.e. the least wear resistance. Addition of Ti to the matrix improved the wear resistance of the WS$_2$-Ti composite coating. The TiN coating also showed a high wear resistance. However, The TiN-WS$_2$ composite coating outperformed all the other architectures and showed the highest wear resistance among all the coating architectures.

Table IV: Wear coefficient of the coatings with different architectures

<table>
<thead>
<tr>
<th>Coating Architecture</th>
<th>Wear Coefficient (× 10$^{-15}$), m$^3$/N-m</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1-WS$_2$</td>
<td>45</td>
</tr>
<tr>
<td>A2-(WS$_2$-Ti)</td>
<td>20</td>
</tr>
<tr>
<td>A3-TiN</td>
<td>10</td>
</tr>
<tr>
<td>A4-(TiN-WS$_2$)</td>
<td>7</td>
</tr>
</tbody>
</table>

4. Conclusion

The major conclusions of the present work are as follows:

(i) Pure WS$_2$ coating showed poor tribological performance because of high susceptibility to atmospheric moisture and oxidation as well as poor adhesion to the substrate.

(ii) Addition of Ti to the WS$_2$ matrix increased the hardness and adhesion as compared to pure WS$_2$ coating, which was reflected in improved wear resistance and longer tribological run.

(iii) Co-deposition of soft WS$_2$ phase with hard TiN phase resulted in a composite coating which outperformed WS$_2$, WS$_2$-Ti as well as TiN in terms of longevity in tribological run and wear resistance because of blend of properties like hardness and lubricity in a single film.

References


