Sliding wear of cold sprayed Ti6Al4V coatings: Effect of porosity and normal load

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Abstract

Ti6Al4V coatings were made from spherical and irregular powders manufactured using plasma gas atomization and Armstrong processes, respectively. The coatings, made from the two different powders, were distinctly different in terms of porosity content and hardness. Sliding wear tests were performed at different normal loads on both Ti6Al4V coatings. Despite low porosity and high hardness, irregular powder (IP) deposited coatings showed higher wear rates compared to spherical powder (SP) deposited coatings. In case of IP coatings, abrasive ploughing by the wear debris led to high wear rates whereas presence of porosity in SP coatings, entrapped the wear debris generated during sliding and decreased the wear rate. Increase in normal load led to a decrease in wear rate and CoF in both coatings. The decrease in wear rate was due to tribo-oxidation in IP coatings whereas the combined effect of entrapment of debris along with tribo-oxidation resulted in much lower wear rates in SP coatings. Transmission electron microscopy (TEM) analysis showed that the third bodies filled in the pores consisted of highly deformed material with ultrafine grain microstructure and micron sized particles from the counterface while the wear track had comparatively coarse grain microstructure. Results indicated that despite low hardness of SP Ti6Al4V coatings, presence of porosity facilitated for the entrapment of wear debris generated from first bodies which inhibited abrasive ploughing and contributed to low wear rates.

Keywords: Cold spray; Ti alloys; Porosity; Sliding wear; Third bodies; Subsurface microstructure
1. Introduction

Due to its high strength-to-weight ratio, high temperature thermal stability and excellent corrosion resistance Ti alloys especially Ti6Al4V is widely used in automobile, aerospace and marine applications [1–3]. However, the high costs and complex steps involved in manufacturing Ti parts due to its high reactivity and poor machinability requires alternate processes [4]. Recently cold spray (CS) or cold gas dynamic spraying is being used to deposit Ti and its alloys both as bulk and coatings [2,3,5,6]. In case of CS, micron sized particles are accelerated to supersonic velocities (600 to 1200 m/s) to impact on to a substrate and plastically deform. Since the coating formation occurs through plastic deformation of particles rather than melting, there are no phase transformations, minimal oxidation and tensile residual stresses in the final deposits [7]. Due to the versatility of the process and high deposition rates, CS is being widely used to deposit metals, composites and nanostructures coatings on to various substrates [8,9].

Despite having numerous advantages, deposition of high yield strength materials like Ti6Al4V using nitrogen as propellant gas remained challenging in terms of achieving low porosity levels (< 2 %). Recently, Ti6Al4V powders of irregular morphology with porous structure manufactured using Armstrong process resulted in extremely dense deposits compared to conventional gas atomized powders. The formation of dense coatings was attributed to the irregular morphology that led to high particle velocities, and equi-axed microstructure that facilitated for the particle deformation upon impact. In contrast, the hard-martensitic lath microstructure of the spherical powders inhibited their deformation and resulted in high porosity in the coatings. Although the coating characteristics and mechanical properties of the Ti6Al4V coatings deposited using the Armstrong and PGA powders are studied but their tribological properties are not yet fully explored. It is well known that the tribological properties of a coating material depend on several factors including microstructure, cohesion strength between the particles and hardness [10–13]. In case of pure metals or alloys, during dry sliding under the influence of a normal load, tribo-oxidation leads to the formation of continuous or islands of oxide films. The presence of oxide layer prevents metal-to-metal contact and changes the friction and wear behavour of the tribo-pair. The oxide films grow in thickness as the sliding progresses and after reaching a critical thickness (~1 – 5 µm for metals) they undergo fragmentation. The break down of the oxide films exposes the fresh metal underneath while the fragmented oxide particles act as abrasives resulting in ploughing and high
wear rates [11,14–18]. While these mechanisms are observed broadly, the presence of porosity, tribo-chemical reactions, localized temperature etc., effect the third bodies generation, chemical compositions and their flow inside the tribological circuit and change the friction and wear mechanisms [19–21].

Previously Dubrujeaud et al. observed that the volume fraction of porosity in the material influences its tribological behaviour [13]. Their results showed that increase in porosity (< 20 vol.%) initially decreased the wear rates due to entrapment of wear debris into the pores while high porosity levels (> 20 vol.%) decreased mechanical strength resulting in excessive plastic deformation and high wear rates. A similar decrease in wear rates due to the presence of optimum porosity were reported by Lim et al. and Straelini et al. [12,22]. However, Ceschini et al. illustrated that apart from porosity volume fraction, shape of the pore also has a considerable effect on the wear resistance of the material [23]. They found that sharp pores acted as stress concentration sites and led to the nucleation of microcracks that subsequently accelerated the material removal and increased the wear rates.

Li et al. found that in case of Ti alloys increase in sliding velocity and contact pressure results in tribo-oxidation and formation of an oxide rich tribolayer that changed the wear mechanisms from severe to mild wear [18]. Similarly, Farokhzadeh et al. reported transition in wear mechanisms from severe to mild in Ti alloys due to increase in normal load that led to greater rate of oxidation, formation of tribolayers and decreased the wear rate [11]. A summary of these studies indicates that localized features, coating characteristics and interfacial temperatures, normal load change the third bodies activities and intern change the friction and wear mechanisms.

In the present study, the tribological behaviour of cold sprayed Ti6Al4V coatings deposited using spherical and irregular powders are investigated. The influence of coating properties and normal load on the friction and wear behaviour of the coatings are studied in detail. Electron channeling contrast imaging (ECCI) of the wear track cross-sections were done to characterize the subsurface microstructures. TEM analysis was done at specific locations on the wear track to compare the subsurface microstructures and understand the chemical composition of the third bodies. Nanoindentation was performed to determine the mechanical properties of the third bodies.
2. Experimental procedure

Ti6Al4V coatings were deposited using spherical Ti6Al4V powders (AP&C, Canada) and irregular Ti6Al4V powders (Cristal metals, USA) of size ranges 15 – 45 µm and 0 – 45 µm respectively. The spherical powders were manufactured using plasma gas atomization process while the irregular powders were manufactured using Armstrong process. The size distribution and the average particle diameter of the powders were presented in our previous publication [6]. Coatings were deposited on mild steel plates of dimensions 75 x 75 x 3 mm³. Prior to deposition the substrates were degreased, and grit blasted using alumina to enhance the coating-substrate bonding. Cold sprayed coatings were deposited using a PCS 800 cold spray system (Plasma Giken, Japan) with nitrogen as propellant gas. The gas stagnation pressure and temperature were 4 MPa and 800ºC respectively. The standoff distance between the nozzle exit and the substrate was 40 mm and the gun traverse speed was 200 mm.s⁻¹.

After deposition the coatings were cross-sectioned and cold mounted. The mounted specimens were polished using SiC abrasive papers of grit 320 to 1200 and using 9 to 1 µm polycrystalline diamond suspension and finally using 0.05 µm colloidal silica suspension solution. The polished coatings cross-sections were examined under a scanning electron microscope (SEM) SU3500 (Hitachi, Japan) fitted with a back scattered electron (BSE) detector. BSE images were taken at fifteen different locations and uploaded into ImageJ software to determine the porosity and average pore diameter. The porosity in the coatings was calculated by measuring the pixels associated with the differences in contrast. To determine the hardness, indentation was performed on the polished top surface of the coatings using a microhardness tester (Buehler, USA) equipped with a Vickers diamond indenter. Indentation was performed at 5 kg load with a hold time of 15 seconds.

Sliding wear tests were performed using a custom built ball-on flat reciprocating tribometer. WC-Co balls of diameter 6.35 mm were used as counterparts. Prior to wear testing, the top surface of the coatings was polished in a similar procedure as that of the cross-sections until the final polishing step using 0.05 µm colloidal silica suspension solution. All tests were performed in dry air environment (relative humidity < 2%) and at normal loads 0.5 N, 2.5 N and 5 N. At least 3 tests were performed at each load. The sliding speed was fixed at 3 mm.s⁻¹, and tests were run for a total sliding distance of 10 m. The coefficient of friction (CoF) was determined by dividing the frictional force with normal force and was continuously recorded during the entire test duration. To calculate
the wear rate, the worn samples at the end of the test were analyzed using a non-contact optical profilometer (Zygo Corporation, USA) and profiles were generated across the wear tracks. At least 35 profiles were generated across the wear track and wear area was determined by integrating the profiles above and below the unworn surface (selected as reference surface). This was multiplied by the track length to obtain wear volume (mm³) and was normalized with load (N) and total sliding distance (m) to calculate the wear rate (mm³ N⁻¹ m⁻¹).

To understand the wear mechanisms, the worn coatings and counterfaces were examined under the SEM SU3500 equipped with BSE and energy disperse X-ray spectroscopy (EDS) detectors. BSE images of the wear tracks were taken and exported into ImageJ software and the pixels associated with the contrast of the tribolayers (formed on the wear tracks) were calculated, to determine the wear track area covered with tribolayers. In addition, to determine the chemical composition of the third bodies, Raman analysis was performed using an inVia Raman spectrometer (Renishaw, UK) with Ar⁺ laser source of λ = 514.5 nm. To characterize the third bodies and subsurface microstructures, ECCI was performed on the polished wear track cross-sections using FE-SEM SU8230 (Hitachi, Japan) equipped with annular photo diode backscattered electron (PDBSE) and FlatQUAD EDS (Bruker, USA) detectors. The ECCI images were exported into ImageJ software and the size of the grains was determined. At least 60 to 100 grains were measured in each region and averaged, to determine the average grain size. Nanoindentation was performed using a Triboindendor (Hysitron Corporation, USA) at a peak load of 5 mN on the wear track cross-sections to determine the mechanical properties of third bodies. The hardness and elastic modulus were determined by analyzing the load-displacement curves using Oliver and Pharr method [24]. At least 10 indents were performed on each feature to calculate the respective average values. Indentation was performed in a grit pattern starting from the unworn coating up till the worn surface. To determine the hardness of a particular feature, imaging of the residual indents was done using FE-SEM SU8230 and were subsequently matched to the corresponding load-displacement curves. TEM analysis was performed on the wear track of spherical Ti6Al4V coating at different locations to compare the subsurface microstructures. To achieve this, thin lamellae were cut using focused ion beam (FIB) (FEI Helios Nanolab 660, Thermo Fisher Scientific, USA) and were examined under a cryo-transmission electron microscope (TEM) (FEI Tecnai G2 F20, Thermo Fisher Scientific, USA).
3. Results

3.1. Coatings and their characteristics

The properties of the coatings deposited using irregular and spherical Ti6Al4V powders are summarized in Table 1. Irregular powder (IP) deposited Ti6Al4V coatings were dense with negligible porosity while the spherical powder (SP) coatings were porous (see Fig. 1). The high porosity in SP coatings was mainly due to the inherently hard martensitic microstructure of the particles that resulted in their poor deformability upon impact [6]. The irregular powders had more deformable equiaxed microstructures and their irregular morphology accelerated them to much higher velocities due to greater drag force compared to spherical powders for similar spray conditions [25] leading to extremely dense deposits. The microhardness of the IP coatings was higher compared to the SP coatings due to lower porosity and better cohesive strength between the splats [6]. Contrarily, the nanohardness of IP coatings was lower compared to SP coatings. This was due to the equi-axed microstructure of the IP coatings in contrast to the hard martensitic lath microstructure of SP coatings [6].

![SEM images of (a) IP and (b) SP Ti6Al4V coating.](image)

**Fig. 1:** SEM images of (a) IP and (b) SP Ti6Al4V coating.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Porosity (%)</th>
<th>Average pore diameter (µm)</th>
<th>Microhardness (HV5 kg)</th>
<th>Nanohardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP Ti6Al4V</td>
<td>0.3 ± 0.1</td>
<td>---</td>
<td>191 ± 12</td>
<td>4.8 ± 0.4</td>
</tr>
<tr>
<td>SP Ti6Al4V</td>
<td>13.0 ± 2.0</td>
<td>25</td>
<td>174 ± 8</td>
<td>5.7 ± 0.3</td>
</tr>
</tbody>
</table>

**Table 1.** Coatings properties.
3.2. Sliding wear tests

3.2.1. Friction and wear

The CoF versus the cycle number plotted for both coatings at corresponding normal loads is shown in Fig. 2. The average CoF calculated by averaging the CoF over the entire sliding distance is summarized in Table 2. For a given load, the average CoF for the coatings was found to be largely similar and there was a trend of decrease in CoF with an increase in normal load. In both Ti6Al4V coatings, the CoF curve at 0.5 N load was found to be high and largely fluctuating between 0.45-0.70. As the normal load increased the CoF showed fewer fluctuations. At 2.5 N, the CoF was found to be varying between 0.35 – 0.45 and at 5 N load between 0.35 – 0.42 in both the coatings. The CoF in IP coatings at 2.5 and 5 N appeared to be less fluctuating compared to SP coatings, however, there was no significant difference in their average CoF.

The wear rate of the coatings at the end of 1000 cycles at different normal loads is shown in Fig. 3. SP Ti6Al4V coatings showed lower wear rates compared to IP coatings at all the tested normal loads. An increase in normal load from 0.5 N to 2.5 N decreased the wear rate in IP coatings, and beyond 2.5 N the wear rate was almost constant. Contrarily, in case of SP Ti6Al4V coatings, there was a steady decrease in wear rate with increase in normal load from 0.5 N to 5 N.

Fig. 2: Coefficient of friction versus sliding distance for (a) IP and (b) SP deposited Ti6Al4V coatings at different normal loads.
3.3. Characterization of the worn surfaces

3.3.1. Wear track

To understand the wear mechanisms, wear tracks were characterized using an SEM and are shown in Fig. 4 and 5. SEM images of the worn surfaces of both spherical and irregular powder coatings showed abrasive wear along with the presence of ploughing marks in the sliding direction (see Fig. 4a-e and 5a-e). The abrasive grooves were formed due to the entrapment of the wear debris between the two sliding surfaces or due to the scoring action of the counterface. Furthermore, presence of small tribolayers surrounded by wear debris were observed on the wear tracks of both coatings (see Fig. 4a,c,e and 5a,c,e). BSE images showed darker contrast at these locations compared to the wear track (see Fig. 4b,d,f and 5f) and EDS analysis performed at these locations

<table>
<thead>
<tr>
<th>Coating</th>
<th>0.5 N</th>
<th>2.5 N</th>
<th>5 N</th>
</tr>
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<tbody>
<tr>
<td>IP Ti6Al4V</td>
<td>0.56 ± 0.05</td>
<td>0.40 ± 0.02</td>
<td>0.38 ± 0.02</td>
</tr>
<tr>
<td>SP Ti6Al4V</td>
<td>0.59 ± 0.05</td>
<td>0.41 ± 0.03</td>
<td>0.38 ± 0.02</td>
</tr>
</tbody>
</table>

Table 2. Average CoF of the coatings at different normal loads.

Fig. 3: Wear rate of the coatings at the end of the 1000 cycles.
showed higher amount of oxygen content compared to other regions of the wear track (not shown here). At 0.5 N normal load, the wear track area covered with tribolayers was ~20% and increase to ~32% at 2.5 N and to ~40% at 5 N in both the coatings. Raman analysis on the tribolayers and wear debris showed characteristic peaks corresponding to the rutile and anatase phases of TiO₂ while on the wear track no active Raman peaks were observed as shown in Fig. 6.

Comparing the wear track morphologies at similar normal loads, abrasive wear marks were found to be continuous over the entire wear track in IP coatings while in SP coatings, these were discontinuous indicating displacement of the wear debris from the sliding interface. Higher magnification SEM images of the wear tracks of SP coatings showed filling of pores with wear debris along with the presence of large volumes of debris around them (at higher loads) (Fig. 5b, d and g). Furthermore, with an increase in normal load, the pore filling for SP coatings was found to be higher and at a greater number of locations on the wear track compared to lower loads. At 2.5 N and 5 N, in addition to wear debris, portions of highly deformed material was found to be dislodged and contributed to the pore filling as shown in Fig. 5d and g. This indicated that at higher loads, the material adjacent to the pores underwent significant plastic deformation and as the sliding progressed, the deformed material dislodged itself from the wear track (see Fig. 5h) and fell into the pores along with wear debris.
Fig. 4: Secondary electron (SE) images of the wear track of IP deposited coatings tested at normal loads (a) 0.5 N (c) 2.5 N (e) 5 N and (b), (d), (f) corresponding BSE images; Inset image in (f) shows higher magnification image of region marked with red box in (f); White arrows show tribolayers.
Fig. 5: SE images of the wear track of SP deposited coatings tested at normal loads (a) 0.5 N (c) 2.5 N (e) 5 N and (b), (d), (g) corresponding high magnification images of the wear tracks showing pore filling; (f) and (h) BSE images corresponding to (e) and (g). Red box shows dislodged worn material inside the pore.
3.3.2. Counterface

Figure 7a-c shows the SEM images of the counterfaces after the completion of the sliding tests at 5 N load. Both the counterfaces show the presence of thick transfer film at the contact surface along with high volume of wear debris circumscribing them. Higher magnification images of the transfer film showed layered structure along with the presence of cracks (Fig. 7b). The formation of thick transfer film indicated the plastic flow and material transfer from the coating, whereas the presence of cracks indicates oxidation and subsequent detachment during sliding resulting in the formation of wear debris. Similar features were observed on the counterspheres at other lower loads (not shown here).

Raman analysis was performed at different locations on the countersphere to understand the chemical compositions of the corresponding features. Raman spectra of the wear debris on both
counterspheres showed characteristic peaks corresponding to the rutile and anatase phases of TiO$_2$ as shown in Fig. 7d. This was similar to the Raman spectra of wear debris formed on the wear track. However, no active Raman peak was found on the thick transfer film indicating that it was composed of metallic Ti6Al4V (see Fig. 7e) transferred from the wear track on to the counterface during wear process.

3.4. Subsurface microstructure characterization and mechanical properties

To observe the subsurface deformed microstructures, ECCI of the wear track cross-sections were performed and are shown in Figs. 8 and 9. Interparticle de-bonding was found below the wear track in both the coatings at all the normal loads. Particle de-bonding was more clearly visible in case of IP coatings (see 8a) due to their dense as-sprayed microstructures while the presence of initial porosity in the SP coatings inhibited the direct observation of particle de-bonding. Furthermore, formation of ultrafine grains (UFGs) were found beneath the wear tracks followed by a combination of fine grains (FGs) as well as heavily deformed grains and finally the initial
microstructure. The thickness of the UFG region was found to be discontinuous and depended on the normal load, presence of tribolayer, and on the coating microstructure.

Wear track cross-section of IP coatings, at 0.5 N load showed the presence of UFGs below the wear track up to a distance of ~ 3 µm, followed by highly deformed grains (see Fig. 8b-c) and finally the initial coating microstructure. The UFGs below the wear track had an average grain size of ~ 68 ± 27 nm. Furthermore, no evidence of tribolayer on the surface was seen, which was due to its low area coverage on the wear track. At 2.5 N, formation of a thin and localized tribolayer was found on the surface of the wear track and underneath the tribolayer, UFGs of average size ~ 72 ± 20 nm were observed up to a depth of ~ 6.2 µm (not shown here). Wear track cross-section of the coatings tested at 5 N showed the presence of tribolayer of thickness ~ 2.4 µm followed by a UFG region ~ 6 µm comprising of grains of average size ~ 95 ± 24 nm (see Fig. 9e-f). Higher magnification images of the tribolayer showed differences in contrast along with the presence of thin cracks and small pores (Fig. 8e). To understand the distribution of different elements inside the tribolayer, EDS mapping was performed at two different accelerating voltages and are shown in Fig. 8g-h. EDS at lower accelerating voltage (3 keV) accurately showed the distribution of oxygen while the distribution of titanium was better observed at higher accelerating voltage (8 keV). EDS mapping of the tribolayer showed the presence of oxygen rich regions corresponding to darker contrast while the brighter contrast showed the presence of high amount of Ti.

Worn cross-sections of SP coatings at 0.5 N (Fig. 9a) showed the presence of UFGs of average size ~ 70 ± 20 nm that extended into the wear track up to a distance of ~ 5 µm (as shown in Fig. 9b). This was followed by fine and elongated grains (see Fig. 9c) and finally the initial martensitic lath microstructure of the coating (see Fig. 9d). At 2.5 N and 5 N, formation of tribolayers of thickness ~ 2.2 µm and 1.4 µm (see Fig. 9f) respectively, was found on the wear tracks. At 2.5 N (not shown here), beneath the tribolayer UFGs of average size ~ 86 ± 27 nm were observed that extended up to a distance of ~ 4.3 µm. This was followed by a mixture of fine and elongated grains and finally the initial microstructure. At 5 N, below the tribolayer the UFG region had a thickness of ~ 8.2 µm and grains of average size ~ 105 ± 32 nm (see Fig. 9g). This was followed by fine and elongated grains as shown in Fig. 9h and finally, the coating microstructure (shown in Fig. 9i). Higher magnification images of the tribolayers at both loads showed the presence of cracks and small holes similar to that of the tribolayer formed in IP coatings. EDS mapping of the tribolayer
formed at 5 N load showed the presence of oxygen and titanium rich regions corresponding to the dark and bright contrasts as shown in Fig. 9j-k.

**Fig. 8:** ECCI of the wear track cross-section of IP coatings (a) 0.5 N - subsurface (b) 0.5 N - near wear track (c) 0.5 N - away from wear track (d) 5 N - subsurface (e) 5 N - tribolayer formed on the wear track (f) 5 N - below the tribolayer; (g) & (h) EDS map showing distribution of O and Ti in the tribo layer (red box). White boxes show specific location where the ECCI was done. – indicates sliding direction.
Fig. 9: ECCI of the wear track cross-section of SP coatings tested at normal loads (a) 0.5 N - subsurface (b) 0.5 N - near the wear track (c) 0.5 N – below the wear track (d) 0.5 N – away from the wear track (e) 5 N - subsurface (f) 5 N - tribolayer formed wear track (g) 5 N - below the tribolayer (h) 5 N – below the UFG region; 5 N – away from the wear track; (j) & (k) EDS map showing distribution of O and Ti in the tribolayer (red box). – indicates sliding direction.
Nanoindentation was performed on the wear track cross-sections and a hardness profile as a function of the distance from the worn surface to the coating was obtained and is shown in Fig. 10. The surface hardness of the wear track was found to be higher compared to the coating at all normal loads. A trend of decrease in hardness with distance from the worn surface was observed. In both coatings, the near surface hardness of the wear tracks with tribolayer was greater than the wear tracks that did not show tribolayer presence. Comparing the hardness of the tribolayers formed on spherical and IP coating wear tracks, no significant difference in hardness values were observed at corresponding normal loads which could be due to their similar chemical composition (i.e. mostly TiO$_2$). In addition to hardness (H), the elastic modulus (E) of the tribolayer and the near surface of the wear track (in the absence of tribolayers) was determined. The elastic modulus of the tribolayer was $\sim 130 \pm 16$ GPa while for the UFG region (for wear tracks without tribolayers) it was $\sim 148 \pm 13$ GPa. The ratio of hardness to elastic modulus (H/E) termed as “plasticity index” indicates the resistance of a surface to plastic flow [26]. From Table 3, tribolayers exhibited higher H/E values compared to worn surfaces where there was no tribolayer formation. This was mainly due to the higher hardness of tribolayers compared to worn surface of the wear tracks without tribolayers.

Fig. 10: Profile showing the variation of hardness from the worn surface (i.e. tribolayer in IP - 5 N and, SP - 2.5 N and 5 N whereas UFG region in IP – 0.5 N and 2.5 N, and SP – 0.5 N) down till the initial coating of the worn (a) IP and (b) SP coatings.
3.5. TEM analysis of the third bodies and worn surfaces

The worn surface of SP coatings showed two different morphologies, one being the pore filled region and another being the bare wear track. To compare the microstructures of the material inside the pore and the worn surface (away from the pore filled region), TEM analysis was performed (shown in Fig. 11 and 12) on the cross-sectioned thin foils obtained from respective locations using FIB. The specific locations on the wear track selected for performing the thin foils are shown in Figs. 11a and 12a. TEM images of the material inside the pores showed the presence of UFG region and FG region (Fig. 11b). Furthermore, significant cracking was observed which could be due to its poor ductility or stresses generated during reciprocating sliding (see Fig. 11b). The UFG region (see Fig. 11c-d) appeared mostly near the worn surface and near the regions where cracks were observed. The UFG region was followed by FG region (Fig. 11h). Selected area electron diffraction (SAED) pattern obtained around the UFG region (Fig. 11c-d) showed distinct circular rings (see Fig. 11e) indicating the grains were nanocrystalline while the SAED pattern in the FG region (Fig. 11i) also showed circular rings but were less continuous compared to the UFG region. This indicated that the FG region had coarser grains compared to UFG region. The d-spacing determined from the SAED patterns matched with the corresponding d-spacing of the TiO$_2$ standard reflections obtained from the JCPDS card no: 021-1276 and 021-1272 and with Ti$_3$O$_{17}$ standard reflections obtained from the JCPDS card no: 050-0791 and α-Ti standard reflections from JCPDS card no: 044-1294. This indicated that the pore filled material mainly comprised of nanocrystalline oxides of Ti and α-Ti. Higher magnification images of the regions close to the wear track showed the presence of small micron sized fragmented particles embedded inside the pore filled material as seen in Fig. 11f. EDS analysis on the wear debris revealed characteristic peaks

<table>
<thead>
<tr>
<th>Coating worn surface</th>
<th>IP Ti6Al4V</th>
<th>SP Ti6Al4V</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>0.044 ± 0.002</td>
<td>0.060 ± 0.011</td>
</tr>
<tr>
<td>H/E</td>
<td>0.043 ± 0.007</td>
<td>0.060 ± 0.012</td>
</tr>
<tr>
<td></td>
<td>0.057 ± 0.017</td>
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</table>

Table 3. Ratio of hardness (H) to elastic modulus (E) of the worn surfaces.
corresponding to W (Fig. 11g), which indicates the transfer of WC fragments from the counterface to the sliding interface and subsequently into the pores during wear process.

TEM analysis on the wear track (away from the pore filling region) showed the presence of a continuous layer of UFGs of thickness ~ 3.7 µm (see Fig. 12b). SAED pattern obtained over the UFG region showed continuous ring formation indicating the grains were nanocrystalline and the d-spacing calculated from these reflections matched well with the standard reflections of α-Ti obtained from JCPDS card no. 044-1294 (see 12c-d). The UFGs were followed by a region comprising of fine and large elongated grains as shown in 12e-f. SAED pattern obtained over the FG region (Fig. 12d) showed less continuous rings indicating that these grains were coarser compared to the UFG (Fig. 12f). Furthermore, under the wear track, unlike the pore filling region, no subsurface cracking nor embedding of WC particles were observed. Comparing Figs. 12c and 11c, the grains in the UFG region of the wear track appeared coarser compared to the UFGs observed in the pore filled region. This indicated that the pore filled material was highly deformed between the two sliding bodies before being transported into the pores.
Fig. 11: (a) FIB cut location on the wear track; TEM images of the (b) pore filling region subsurface (c) BF image of the region near the worn surface (d) DF image of the region near the worn surface (e) SAED pattern taken at location ‘c’ (f) subsurface showing the embedding of micron sized particles (g) EDS point analysis performed on the particles (h) recrystallized region near the worn surface (i) showing SAED pattern taken at location ‘h’. Red boxes show the locations where higher magnification images were taken; White arrows show WC particles. A – Anatase phase (TiO₂), R – Rutile phase (TiO₂).
4. Discussion

The physical characteristics like porosity, second phase reinforcement, near surface microstructure of a bulk or coating material significantly influence its friction and wear behaviour [11,27,28]. These features alter the localized stresses or provide resistance to plastic shearing and in turn improve or degrade the overall tribological performance. Furthermore, the quantity or volume fraction, of these features change the third bodies activities which in turn alter the friction and wear mechanisms [13,22,28–30]. For example: Studies have shown that increase in porosity up to an optimum percentage decreases the wear rates due to decrease in abrasion, whereas high porosity levels reduce the mechanical strength of the material and lead to significant plastic deformation and high wear rates [13]. In addition to these, the physical conditions like the normal load, localized temperature, ambient conditions favour the formation of tribolayers which provide...
localized resistance to normal and shear stresses, and improve the tribological performance of the material [14,20,31,32]. In the present study, cold sprayed Ti6Al4V coatings with distinct properties showed different tribological behaviour during sliding. As it will be discussed in this section, differences in porosity in the coatings changed the third bodies generation, flow at the tribo-pair interface which in turn changed the wear mechanisms.

A schematic showing the different wear mechanisms that occur in the two coatings are shown in Fig. 13a-b. Ti6Al4V coatings deposited using spherical and irregular powders showed abrasive wear, with characteristics of ploughing by wear debris and scoring by the counterface (Fig. 4 and 5). Furthermore, formation of an adhesive transfer film at the contact surface surrounded by wear debris was observed on the counterface at all loads (Fig. 7a and c). The formation of adhesive transfer on the counterface sliding against Ti and its alloys was previously reported by many researchers [16,29]. This is due to the low d-bond character of Ti and its alloys that results in adhesive bonding with the counterface material. Higher magnification images of the transfer film showed the presence of brittle cracks inside them (Fig. 7b). This indicated that loosening, detachment of the transfer film, transfer into the sliding interface, oxidation and fragmentation occurred during the wear process. These fragments along with the worn material generated from the coating essentially constituted the wear debris. Raman analysis showed that these wear debris were predominantly TiO2 particles (Fig. 6c). The high reactivity of Ti results in the formation of oxide on its surface, while its high “Pilling-Bedworth ratio”, mismatch of coefficient of thermal expansion with the underlying metal results in fragmentation during sliding [20,32,33]. These fragments get further added to the wear debris and result in three-body abrasion and high wear rates. Similarly, researchers have reported that the non-protective nature of surface oxides result in abrasive ploughing and high wear rates in Ti alloys [14,15,18,20]. Despite having dense microstructures and higher hardness, IP Ti6Al4V coating showed higher wear rates compared to SP coating at all tested normal loads (Fig. 3). The dense microstructure of IP coatings supported abrasive ploughing by the wear debris (Fig. 13a) and scoring by the counterface. In contrast, SP coatings had internal porosity which acted as a reservoir and captured the debris during wear process (Fig. 13b). This decreased the possible agglomeration and intensity of abrasive ploughing caused by the wear debris thereby decreasing the overall wear rates. As the normal load increased, greater formation of the wear debris led to greater ploughing in IP coatings (Fig. 4) whereas in SP coatings, high volume fraction of porosity led to greater entrapment of the wear debris (Fig. 5b,d
and g). Studies from literature have reported that in case of porous materials the pore size, shape and volume fraction play an important role in determining the wear behaviour of the material [12,13,22,28]. Dubrujeaud et al. previously observed that low porosity levels (< 10 vol.%) with a mean pore size of < 10 µm makes it difficult to entrap the debris and the pores often get closed due to plastic deformation during the wear process [13]. Contrarily, high volume of porosity > 20 vol.% leads to poor mechanical strength, inhibits complete pore filling due to excessive plastic deformation and results in high wear rates. They concluded that an optimum volume fraction of 10 – 20 vol.% porosity with a mean pore size > 12 µm ideally facilitates wear debris capture and decreases the wear rate. Here in the present study, SP Ti6Al4V coatings had an average porosity of ~ 13% and mean pore size (diameter) of ~ 25 µm that favoured the pore filling mechanism and led to lower wear rates compared to dense IP Ti6Al4V coatings at all loads. Additionally, presence of porosity increases the real contact area between the two surfaces and decreases the contact stress [13]. Hence for the same normal load, lower contact stress is evident in case of SP coatings due to the presence of higher volume fraction of porosity compared to IP coatings. To determine the initial maximum Hertzian contact stress, the elastic modulus of the SP Ti6Al4V coatings was calculated using an empirical expression proposed by Bert [34] which accounted for the reduction in elastic modulus due to the presence of porosity. The elastic modulus determined from the expression matched well with the experimental value reported by Garrido et al. [35] for cold sprayed Ti6Al4V coatings (with similar porosity volume fraction) deposited using spherical gas atomized powders at similar spray conditions. The initial static maximum Hertzian contact stress in case of IP coatings at 0.5, 2.5 and 5 N normal load was ~ 0.44, 0.75 and 0.94 GPa whereas in SP coatings it was ~ 0.41, 0.71 and 0.89 GPa. In general, decrease in contact stress decreases plastic deformation and subsequently material removal. However, in the present study the decrease contact stress due to porosity was only between ~ 5% - 7% at all the tested normal loads. While the decrease in contact stress could have led to lower wear of the SP coatings during the initial cycles, as the test progressed, wear debris formation and pore filling would have a more significant effect in decreasing the wear rates in SP coating.

Researchers have indicated that the entrapment of debris which are mostly hard oxide particles into the base material i.e. pores at the near surface of the wear track, make the localized surface to act as a composite and increase its resistance to localized shear deformation [12,13]. In the present study, TEM analysis of the pore filled material (SP -Ti6Al4V coating) showed the presence of
TiO₂ along with few micro-sized particles of WC embedded into the matrix (see Fig. 11c and f) while the remaining wear track did not show any presence of second phase material (Fig. 12b-c). This indicated that the pores acted as a sink for oxides (from the coating) and few hard particles from the counterface during the wear process. Contrarily, in case of IP coatings, absence of porosity led to the continuous abrasive ploughing by the oxides and hard particles from the counterface, until being ejected out of the sliding interface or wear track, thus contributing to higher wear rates. In both coatings, increase in normal load led to an increase in the wear track area covered with tribolayers due to tribo-oxidation. The formation of tribolayers due to the compaction of debris between the sliding surfaces increased the near surface hardness (Fig. 10) and provided localized resistance to plastic shearing thereby resulting in a decrease in the wear rate in both the coatings. However, the decrease was higher in case of SP coating compared to IP coating. This indicated that at higher loads, while tribo-oxidation would have an influence in improving the wear resistance, specifically in SP coatings, the additional pore filling mechanism also had a profound effect in decreasing the wear rates.

A sliding tribological contact led to the particle debonding and dynamic recrystallization resulting in the formation of fine, coarse and highly deformed microstructures (Fig. 8 and 9). However, the extent of grain refinement was found to be dependent on the near surface hardness of the wear tracks. Wear tracks that showed significant coverage of the worn area with tribolayers had higher near surface hardness, resulting in the formation of coarser UFGs compared to the wear tracks without tribolayers. This indicated that presence of tribolayers increased the load bearing capacity and transferred less stress to the subsurface. Furthermore, the H/E values of the wear tracks covered with tribolayers were marginally higher compared to the uncovered wear tracks (Table 3). Higher H/E values of the tribolayers indicates that these surfaces were more resistant to plastic deformation compared to the wear tracks not covered with tribolayers. According to Irwin–Orowan fracture model [36], the fracture toughness of a material can be improved by increasing the critical stress required to fracture (i.e. increasing the hardness) and by decreasing the elastic modulus [26]. This signifies that, a material with high H/E ratio will be more resistant to fracture, compared a material with lower H/E value. Here in the present study, a comparatively higher H/E value of the tribolayers indicates that these worn surfaces were more resistant to cracking compared to wear tracks without tribolayers which could have also contributed to their lower wear rates.
Increase in normal load from 0.5 N to 5 N decreased the CoF in both coatings due to the increased coverage on the wear track area (~ 20% to 40%) with oxygen rich tribolayers. Raman analysis on the tribolayers showed peaks mostly corresponding to the rutile phase of TiO$_2$ while TEM analysis (SAED pattern in Fig. 11e) indicated that they were crystalline in nature. Studies performed by researchers have shown that the during wear of Ti and its alloys, tribo-oxidation due to high interfacial temperatures lead to the formation of non-stoichiometric phases or Magnéli phases of TiO$_2$ [37–39]. In the present study, SAED patterns (Fig. 11e) showed the presence of Magnéli phases in the tribolayer (Note: Pore filled region shown in Fig. 11a was in the tribolayer). However, a significant overlap between the diffraction patterns of the Magnéli phases, and the anatase phase of TiO$_2$ and $\alpha$-Ti were observed. Hence, a complete confirmation regarding the presence of the Magnéli phases couldn’t be made in the present work. However, similar formation of Magnéli phases during wear of Ti was observed previously by Woydt et al., Gardos et al. and Erdemir et al. [37,38,40,41]. Literature studies illustrate that, localized high temperatures during tribological processes or bombardment of the surface with high energy ions lead to oxygen deficiency on the surface along with the formation and diffusion of anion vacancies resulting in Magnéli phases [39]. These Magnéli phases have low lattice energy crystallographic shear planes that result in low shear strength [41]. It is well known from the classical theory of Bowden and Tabor that to reduce the adhesion component of the friction, a hard material with soft skin can be used to minimize the shear strength and increase the contact pressure at the tribo-pair contact interface [29,42]. The formation of islands of tribolayers comprising of low shear strength Magnéli phases on wear track would have acted like a soft skin on hard material and decreased the CoF. Furthermore, SEM images of the worn surfaces at different loads indicate an increase in wear track width with increase in normal load (Figs. 4a-e and 5a-e). This would have led to higher contact area between the sliding surfaces which reduces the frictional force between the tribo-pair at higher loads. Thus, the combined effect of formation of low shear strength tribo-chemical oxides and increase in contact area between the tribo-pair resulted in less fluctuating and low CoF in both the coatings at higher loads.
Ti6Al4V (IP) coatings

(a)

Ti6Al4V coating

Wear debris (TiO₂)
Transfer film
WC-Co

(b)

Ti6Al4V (SP) coatings

Pore filled with debris

Pore filled with debris
Wear debris (TiO₂)

Fig. 13: A schematic summarizing the wear mechanisms in Ti6Al4V coatings deposited using (a) irregular and (b) spherical powders.
5. Summary and conclusions

The tribological behaviour of cold sprayed Ti6Al4V coatings deposited using powders with different morphology and microstructure, were studied at different normal loads. SP Ti6Al4V coatings, despite high porosity and lower hardness compared to IP coatings showed lower wear rates at all test loads. Abrasive ploughing by the wear debris led to high wear rates in IP coatings, whereas entrapment of wear debris into the pores reduced the ploughing resulting in low wear rates in SP coatings. Increase in normal load from 0.5 N to 2.5 N decreased the wear rate in both the coatings, and with further increase in normal load to 5 N, no significant change in wear rate was found in IP coating, whereas in SP coatings a further decrease in wear rate was observed. The decrease in wear rate in IP coatings was due to the tribo-oxidation that led to the greater coverage of wear track area with tribolayers, whereas the combined effect of both tribo-oxidation and higher entrapment of wear debris led to a more significant drop in the wear rates of SP coatings. These results indicate that the improvement in wear resistance imparted by tribo-oxidation was limited and was effective only up to a normal load of 2.5 N. Contrarily, in case of SP coatings similar increase in wear track area covered with tribolayers was observed, whereas the wear rate continuously decreased with increase in normal load from 0.5 N to 5 N due to greater filling of pores with debris. This indicates that, although porosity is detrimental to the mechanical strength of the coatings, from a tribological point of view, their presence helped to reduce the abrasive ploughing by wear debris and subsequently wear rates. Thus, the wear resistance of the Ti alloys can be improved by incorporating optimum porosity in the coatings.

Tribolayers formed on the wear tracks were mostly composed of rutile TiO₂ (crystalline) which essentially were low shear strength Magnéli phases. The formation and significant coverage of wear track area with tribolayers helped in reducing the CoF at higher loads. The average CoF in both coatings was not significantly different at similar loads. This signifies that the CoF remained unaffected by the presence of porosity and the formation of tribo-oxides helped in reducing the CoF in both the coatings.
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References


