

Influence of microstructure and mechanical properties on the tribological behavior of reactive arc deposited Zr-Si-N coatings at room and high temperature

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Abstract

Varying the Si-content in Zr-Si-N coatings from 0.2 to 6.3 at. % causes microstructural changes from columnar to nanocomposite structure and a hardness drop from 37 to 26 GPa, where the softer nanocomposite also displays lower fracture resistance. The influence of microstructure and mechanical property variation on the tribological response of the coatings are investigated under different contact conditions both at room temperature and high temperature. Tribo-oxidation is the dominant wear mechanism at room temperature, where the nanocomposite coatings display the lowest wear rate of $6.4 \times 10^{-6} \text{ mm}^3/\text{Nm}$, by forming Si enriched W containing Zr oxide diffusion barrier layer above the coatings. When the test temperature and contact stress are increased, coatings display a transition in their wear mechanism from tribo-oxidation to micro-ploughing causing significantly higher coefficient of friction of 1.4, where the columnar structure display lowest wear rate of $1.05 \times 10^{-6} \text{ mm}^3/\text{Nm}$.

⁴ mm^3/Nm by virtue of their higher hardness. When the coatings are subjected to microscopic wear test in a contact-induced dominant elastic stress field, the coatings display wedge formation and pileup by the accumulation of the dislocation-induced plastic deformation similar to a fatigue process, where the nanocomposite coatings display lowest wear rate of $5.59 \times 10^{-11} \text{mm}^3/\text{Nm}$, by constraining the dislocation motion.

1. Introduction

ZrN based coatings are interesting candidate materials for the wear resistant applications with several unique features, such as superior cutting performance [1], high thermal stability [2], and fracture resistance enhancement by stress induced-transformation toughening [3]. However, the primary limitation to the ZrN based coatings is their poor oxidation resistance. The alloying of Si was shown to be very effective to improve oxidation resistance and mechanical properties of TiN [4–7]. Motivated by these results, Zr-Si-N system was investigated by several researchers, and the results indicate that the coating with Si concentration of 6 - 7 at. % display a transition in microstructure from columnar to nanocomposite structure, which leads to a systematic variation in hardness and improved oxidation resistance [8–11]. Previous studies of Zr-Si-N mainly focused on investigating the microstructure and mechanical property variation [9,12], and the tribological response of these coatings are relatively less studied, which motivates further studies in this area.

Though it is commonly agreed that the wear properties of the coating are dependent on the mechanical properties [13,14], the specific mechanisms are material dependent. Previous studies indicate that the wear rate of Zr-Si-N coatings vary as a function of Si concentration, where the nanocomposite Zr-Si-N coating with 7.6 at. % Si, display higher wear resistance in spite of its lower hardness, and the detailed wear mechanisms are not known [15]. It is not

known how the variation in contact conditions such as stress, sliding velocity and temperature influence the tribological response of Zr-Si-N coatings. In summary, the fundamental knowledge is lacking for Zr-Si-N coating, how the microstructure and mechanical property variation effects the tribological response under different contact situations. In addition, there is a growing interest in the nitride coatings for MEMs applications [16], where the microscale tribological response of the coatings becomes important, which is relatively unexplored.

In this work, the tribological response of Zr-Si-N coatings are investigated as a function of microstructure and mechanical property variation under varied tribological contact conditions, by altering the contact force, temperature and test configuration, both at high temperature and room temperature in a macro and micro-scale sliding contact. Furthermore, the underlying governing mechanisms how the structure-property variation influence the tribological response of the coating is established here by the TEM examination of thin lamellae extracted from the wear track. This fundamental knowledge is essential for the development of future wear resistant coatings.

2. Experimental procedure

2.1 Deposition of coatings

Seven different Zr-Si-N coatings with Si concentration varying between 0.2 and 6.3 at. % were grown on mirror finished WC-10 wt. % Co substrates in a Sulzer/Metaplas MZR-323 cathodic arc deposition system. The average surface roughness (R_a) of the coatings was measured between 0.2 and 0.3 μm with a thickness of $4 \pm 1 \mu\text{m}$. Detailed microstructural variation of the coating as a function of Si concentration is reported in reference [17].

2.2 Wear tests

Room temperature (RT) reciprocating sliding wear tests were performed using a tribometer TRM 1000 from Wazau GmbH with ball-on-disc configuration, where reciprocating ball

slides against the lower static specimen. During a sliding distance of 100 m a contact force of 5 N, stroke length of 4 mm and an average velocity of 0.06 m/s were maintained.

High temperature (HT) tribology tests were performed using a similar ball-on-disc configuration in a SRV Optimal wear test machine equipped with sample heating stage, which was maintained at 500 °C during the test. During the sliding distance of 3.6 m, a contact force of 10 N, stroke length of 1 mm and an average velocity of 0.02 m/s were used. Both these machines are equipped with computerized control and data acquisition system enabling control over stroke length, frequency, and contact force. For both RT and HT sliding wear tests, WC-8 wt. % Co balls of 10 mm diameter (Fritsch) with a hardness of 1600 HV₁₀ were used as a counter material.

Before the tests, the ball and the coatings were ultrasonically cleaned with acetone, ethanol, and blow-dried with N₂. The wear tests were conducted under dry sliding conditions in air with relative humidity of 60%. After the test, the depth of the wear track was measured with a Veeco Dektak 150 profilometer and observed in SEM.

2.3 Electron microscopy

Scanning Electron Microscopy (SEM) images of the coating and wear tracks were taken in a LEO 1550 FEG scanning electron microscope (SEM) operated at 5 kV with a working distance of 10 mm. Cross-sectional TEM foils were prepared under the wear track by the lift out technique using a focused ion beam (FIB) Zeiss Neon 40 dual-beam workstation [17]. Transmission electron microscopy (TEM) and scanning (S) TEM of foils under the wear track was performed using a FEI Tecnai G2 TF 20 UT FEG microscope operated at 200 kV, equipped with an energy- dispersive X-ray analysis spectrometer (EDX). For STEM analysis, a high angular annular dark field (HAADF) detector with a camera length of 160 mm was used.

Microwear tests were performed at ambient temperature of 25 °C, on a polished coating surface using a diamond conical indenter with a nominal tip radius of 5 μm in a Triboindenter® TI-950 from Hysitron in a multipass nanoscratch test configuration, equipped with *in situ* scanning probe imaging. During the sliding distance of 10 mm, a normal force of 10 mN is applied with a stroke length of 10 μm at a sliding velocity of 0.002 μm/s. Wear volume is calculated from the 3D cross-sectional profile of scanning probe image of the wear track.

Hardness (H) and elastic modulus (E) of the tribo-layer of the coatings were evaluated in a nanoindenter equipped with a Berkovich diamond tip and using the Oliver and Pharr method [18]. The continuous stiffness measurement (CSM) module was activated to log the contact stiffness (S) during the entire loading portion of load (P) - depth (h) curve. The tip area function was calibrated using a fused silica reference, and the measurements were corrected for the load frame compliance and thermal drift.

2.4 Oxidation test

Oxidation tests were done on 0.2, 1.8 and 6.3 at. % Si coating materials removed from the substrates. In this case, the coatings were grown on Fe substrates and using identical deposition conditions as for the WC-Co substrates. The Fe substrates were removed through mechanical polishing and subsequent dissolution in a diluted H₂SO₄ acid at a temperature of 90 °C. The resulting powder of the coating material was then rinsed with deionized water and dried in an oven at 150 °C overnight. Oxidation tests of the powder were conducted by heating at a rate of 5 °C/min up to 1000 °C in air at atmospheric pressure while measuring the sample mass in a Netzsch STA 410 instrument. Coated WC-Co substrates were also soaked at 800 °C for 1 hr in air, followed by SEM examination of fractured cross-section.

3. Results

3.1 Microstructure and mechanical property variation as a function of Si

The focus of the current paper is wear and oxidation behavior of Si-alloyed ZrN coatings. A detailed study of the microstructure and mechanical properties of the coatings used for these tests have already been reported [17]. Here, as a background, we summarize the most relevant results. Si forms a substitutional solid solution up to 1.8 at. %, on the metallic sublattice of ZrN. Additional Si causes precipitation of an amorphous-SiN_x phase on the growth front and a breakdown of the columnar structure. At ~ 6.3 at. % Si the coatings have an equiaxed nanocomposite structure. Figure 1 shows SEM micrographs of fractured cross-sections to visualize these microstructural changes. The hardness and elastic modulus are listed in Table 1 (from [17]). The hardness of the columnar structured coatings is found to increase with Si up to 1.8 at. % (~ 37 GPa), due to solid solution hardening. Strain localization caused by the grain boundary mediated deformation causes a considerably lower hardness (~ 26 GPa) of the nanocomposite structure. The fracture resistance of these coatings was found to be highest for the columnar structure with 0.2 at. % Si and lowest for the nanocomposite coating with 6.3 at. % Si.

3.2 Room temperature wear tests

Wear rates of the coatings recorded at RT using a contact force of 5 N (Hertzian contact stress of 1200 MPa) are shown in Fig. 2, which results in a. The wear rate is calculated by dividing the wear volume [mm³] by the normal force [N] and the sliding distance [m]. The wear rate shows a systematic increase up to a Si concentration of 1.8 at. %, with a maximum of 1.4×10^{-5} mm³/Nm. Further Si additions reduces the wear rate to the lowest value of 6.4×10^{-6} mm³/Nm for coatings with 6.3 at. % Si, i.e. the soft and brittle nanocomposite coatings exhibit a wear resistance enhancement of 120 % compared to the hard columnar structured coating. The coefficient of friction (COF) was measured to be between 0.5 and 0.6 for all the coatings. The inset image in Fig. 2 shows the cross-section profiles of the wear track of 0.2 and 6.3 at.

% Si containing coatings. We observe a deep and rough profile for the 1.8 at. % Si coating while the wear tracks of 6.3 at. % Si coating show shallow and smooth profiles.

Figure 3 shows SEM micrographs of plan view and FIB prepared cross-sections of the wear tracks. They reveal a bilayer in the wear track with contrast variations for the columnar structured coatings containing 0.2 and 1.8 at. % Si (Fig. 3 a, b and c, d). Cross-sectional micrographs reveal formation of a discontinuous thick tribo-layer for the columnar structured coatings, which suggests delamination during the test. In contrast, the nanocomposite coating (6.3% at Si) displays fine tracks in the sliding direction (Fig. 3e and f).

The thickness of the residual coatings is measured to be 2.0 and 0.6 μm , whereas the tribo-layer are 0.9 and 0.7 μm for 0.2 at. % Si and 1.8 at. % Si coatings, respectively. The lower thickness of both the coating and the tribo-layer, indicate that 1.8 at. % Si coatings are more prone to delamination, compared to 0.2 at. % Si coating. This observation can also explain the appearance of more discontinuous wear track of 1.8 at. % Si more clearly observed in the overview micrograph. The coatings with 6.3 at. % Si display thin tribo-layers with fine tracks in the sliding direction. These tracks were attributed to micro-ploughing of the tribo-layer by wear debris.

BF-TEM micrographs of lamellas extracted under the wear track formed in columnar and nanocomposite coating are shown in Fig. 4 a and e, respectively. No signs of sliding induced plastic deformation nor cracks are observed in the coatings and, the virgin microstructures are retained for both columnar and nanocomposite structures. The coating with 1.8 at. % Si shows a thick tribo-layer on top of the columnar structure with sub surface voids, cracks and delamination from the coating. The voids are likely generated by the accumulation of lattice defects induced by the sliding contact. STEM image (Fig. 4b) shows a homogeneous tribo-layer with a bright contrast region of ~ 10 nm, near the delaminated interface. Comparing EDX-spectra recorded from the tribo-layer and the coatings show higher concentration of O,

Zr, and W in the tribo-layer, which suggests it to predominantly be a tungsten containing zirconium oxide. The EDX spectra also reveal enrichment of W and Co at the delaminated interface between the tribo-layer and the coating giving the bright contrast region in the STEM image.

For the 6.3 at. % Si coating consisting nanocomposite structure, the observed oxide layer is thin (~ 80 nm), continuous, and well adhered to the coating (Fig 4e and g). The tribo-layer consists of oxides of Si and Zr, with traces of W. The Si is enriched, while the Zr is depleted in the tribo-layer compared to the coating. Lattice resolved TEM images (Fig. 4d and h) show that the tribo-layer is dominated by an amorphous structure with isolated nano-crystalline regions for both the columnar and nanocomposite structure.

Hardness and elastic modulus of the tribo-oxide layer were found to be comparable for all the coatings with values of 4 ± 1 GPa and 80 ± 10 GPa, respectively. To further explore the mechanism of superior tribo-oxidation resistance of the nanocomposite coatings, static oxidation tests were performed.

3.3 Oxidation studies

Figure 5 shows SEM micrograph of Zr-Si-N coatings after being subjected to oxidation. The oxide layer thickness is about 3, 2, and 1 μm for the coating with 0.2, 1.8 and 6.3 at. % Si, respectively, suggesting an increased oxidation resistance of ZrN coating with Si addition. We also note a change of the oxide layer's morphology as the Si-content is increased.

Figure 6a shows the relative mass change of the powder extracted from the coatings when oxidized in air. The onset temperature of oxidation was measured to be 590, 620, and 640 $^{\circ}\text{C}$ for 0.2, 1.8 and 6.3 at. % Si respectively. Thereafter, the coatings display a constant mass gain rate as a function of temperature with a value of 0.12 %, 0.11% and 0.06% for 0.2, 1.8 and 6.3 at. % Si respectively. The oxidation behavior is rather similar when comparing samples with 0.2 and 1.8 at. % Si, while the data indicates a 40% reduction in the oxide growth rate of the

6.3 at. % Si coating with a nanocomposite structure compared to the one with 0.2 at. % Si with columnar structure. The x-ray diffractograms in Fig. 6 only display a monoclinic (m) ZrO_2 phase for 0.2 and 1.8 at. % Si coatings, while coatings with 6.3 at. % Si displays also a tetragonal (t) -ZrSiO_4 phase. This indicates that higher oxidation resistance of the coatings with Si addition is related to the formation of t- ZrSiO_4 phase. However, the reduction in oxidation rate with Si-content is too low to completely explain the reduced wear rate observed for the nanocomposite structure.

3.4 High temperature wear test

Figure 7 shows the wear rate of the coatings tested at 500 °C, and using a contact force of 10 N, which corresponds to a Hertzian contact pressure of 1600 MPa. The inset shows cross-sectional profiles of the wear track where the sample with 6.3 at. % Si exhibits the deepest track, less for 0.2 at. % Si, and the most shallow for 1.8 at. % Si. Wear rate of the coatings decreases with increasing Si content up to 1.8 at. % with a minimum value of $1.05 \times 10^{-4} \text{ mm}^3/\text{Nm}$. Further Si additions increase the wear rate and a value of $6.1 \times 10^{-4} \text{ mm}^3/\text{Nm}$ is recorded for the sample with 6.3 at. % Si. That is, samples with a columnar microstructure have a lower wear rate than the ones with a nanocomposite microstructure. Furthermore coatings with high hardness shows high wear resistance, which is the opposite to the RT tribological response, see section 3.2. All the coatings display a steady state coefficient of friction between 1.4 and 1.5, which is significantly higher compared to the RT tests.

Figure 8 a-c shows over view and magnified plan view SEM micrograph of the wear tracks displaying deep grooves in the sliding direction, indicating abrasive wear of the coatings. The wear track also shows discrete white particles, most clearly seen for 6.3 at. % Si coating. FIB prepared cross-sectional view (Fig 8d-f) reveal a higher residual thickness for 1.8 at. % Si, followed by 0.2 at. % Si and 6.3 at. % Si, which is in line with the measured wear rates. Also we note that nanocomposite coating shows uniformly embedded white particles under the

wear track, whereas the 1.8 at. % Si coating display embedded white particles under the wear track, along with the lateral crack in some locations.

Cross-sectional TEM micrograph of the lamellae extracted under the wear track of columnar (1.8 at% Si) and nanocomposite coating (6.3at%Si) are shown in Fig. 9. The coating with 1.8 at. % Si shows fine columnar structure with lateral cracks in the subsurface region (Fig. 9a). Above the coating, a thin tribo-layer with a thickness of ~ 200 nm is observed. STEM image (Fig. 9b) shows that the tribo-layer consists of uniformly distributed white particles. Also note that the lateral cracks are connected with the vertical and inclined cracks, where the tribo-layer penetrate in to the virgin coating. EDX line scan (Fig. 9c) along with the point scan (not shown here) indicate that the tribo-layer is an oxide of Zr, W and the white particles are WC from the counter surface. These observations suggest that the tribo-layer is formed by compacting the fine wear debris of coating and the counter material under the contact stress. For the nanocomposite coating (Fig. 9d), the cross-sectional micrograph shows only the tribo-layer attached to the substrate with the crack at the interface, indicating that the virgin coating is already consumed. These results suggest that the dominant wear mechanism at high temperature is the combination of deformation and crack formation in place of the tribo-oxidation observed at room temperature.

3.5 Microwear tests

The coatings display significantly lower wear rate under a microscale reciprocating sliding contact of a diamond tip at a normal force of 10 mN, which generates a Hertzian contact pressure of 19 GPa. The coatings display a monotonic decrease in the wear rate as a function of Si content up to 6.3 at. % with a minimum value of 5.59×10^{-11} mm³/Nm, i.e. nanocomposite coatings exhibit the highest wear resistance. The measured coefficients of friction in this test are significantly lower (0.15-0.17) for all of the coatings. 3D cross-

sectional profiles of the wear tracks (Fig. 11b and c) show deep grooves accompanied with pileup on the sides of the wear track for both the columnar and nanocomposite coatings. The columnar 0.2 at. % Si coating shows deeper groove and a larger material pile up compared to the nanocomposite structure with 6.3 at. % Si coating. The ratio of groove volume to material pile up was measured close to 1 for both the columnar and nanostructured coatings. No loose debris either inside or adjacent to the wear track was detected. Instead the material pile up is caused by material flow caused by the induced stress field under the sliding contact, similar to the situation during quasi-static indentation [17]. The inset $P-h$ (load-displacement) curves of a quasi-static spherical indentation at a force of 10 mN (Fig. 10a) shows limited plasticity with an elastic recovery of $\sim 90\%$. Hence, the formed groove and pileup is the result of accumulated plastic deformation over several repeated cycles.

4. Discussion

Macro- and microscale sliding wear tests performed on Zr-Si-N coatings yield different tribological response given the different contact situations. We note that the coating that displays highest wear resistance at room temperature, displays poor wear resistance at high temperature. The mechanisms governing the tribological response of the coatings as a function of microstructure and mechanical properties are discussed below.

For the RT macroscale tests, all the coatings are subjected to tribo-oxidation. Columnar structured coatings form thick tribo-oxide layer and suffer from delamination process which leads to a higher wear rate. In contrast, the nanocomposite coating (6.3% Si) forms a thin tribo-oxide layer which has a higher resistance to delamination, and results in lower wear rate. The cross-sectional electron micrograph of the wear track shows continuous tribo-layer without any interparticle boundaries or accumulation of debris and attaching to the coating. Instead, the tribo-oxide layer formation is attributed to the contact-induced oxidation process,

where the oxide layer thickness increases as the sliding continues. The transformation of ZrN to ZrO₂ is associated with an energy gain of 180 kcal.mol⁻¹ [19], providing the strong thermodynamic driving force for the oxidation process. Friction induced heating causes a higher local flash temperature providing the necessary energy, as the combination of thermal and mechanical energy in a tribo-system reduces the activation energy for the tribo-chemical reactions [20] which likely causes the tribo-oxidation of ZrN feasible at significantly lower temperatures similar to what has been observed for TiN [21,22].

The volumetric mismatch between the tribo-oxide layer and the coating generates residual stress in the oxide layer, whose magnitude increases with the oxide layer thickness. A balance between tribo-layer elastic stress and the interface strength between the coating and the tribo-layer sets a critical thickness, beyond which, the tribo-layer delaminates. This explains why the thick tribo-layer for the columnar structured coating undergoes delamination, where the interface between the tribo-layer and the coating offers the preferential weak plane for the crack to nucleate and propagate (Fig. 4a).

The columnar structured coatings display increased wear rate between 0.2 and 1.8 at. % Si, despite of their increased static oxidation resistance. This anomaly is explained by the fact that the tribo-oxidation resistance is not only dependent on the oxide growth rate but also on the resistance to the delamination process. Compared to 0.2 at. % Si coating, the 1.8 at. % Si coating shows lower resistance to the delamination process, as observed from the lower critical thickness of the tribo-layer before it delaminates (Fig 3b and d). A possible explanation for the lower critical thickness of the tribo-layer is that the higher hardness difference between the tribo-layer and the coating for 1.8 at. % Si coating causes a lower interface strength compared to the softer 0.2 at. % Si coating, similar to what has been shown for the adhesive strength between the coating and substrate [23].

The tribo-oxide layer shows mostly amorphous structure for both the columnar and nanocomposite coating, which is not the case for the static oxidation. A low temperature oxidation process in a tribo-contact causes a lower diffusivity of the oxidizing species that is not adequate enough for the lattice reconstruction to yield a thermodynamically stable crystal structure. Similar amorphization of the tribo-oxide layer was reported previously for TiN based coatings in a sliding contact at room temperature [24]. The amorphous tribo-oxide-layer is has voids and cracks, which results in a lower hardness ($H \sim 4 \pm 1$ GPa) and elastic modulus ($E \sim 80 \pm 10$ GPa). The softer tribolayer is subjected to the microcutting process by the wear debris, more clearly seen for the nanocomposite coatings, which explains the ploughing tracks on the tribo-layer (Fig. 3c).

Even though 6.3 at. % Si coating with nanocomposite structure show higher resistance to both static and tribo-oxidation, the improvement is remarkably higher for the later case. In case of static oxidation, the higher oxidation resistance of higher Si containing nanostructured coating is related to formation of $t\text{-ZrSiO}_4$, which has relatively lower ionic conductivity for the diffusion of oxidizing species [25] compared to the $m\text{-ZrO}_2$ phase in the columnar structured coating with lower Si concentration. In case of tribo-oxidation, the nanocomposite structure displays a significantly higher oxidation resistance by forming amorphous structured, Si enriched W containing Zr oxide diffusion barrier layer.

In a high temperature wear test, the wear mechanism is dominated by deformation and fracture of the coating. Although it is expected that the high test temperature accelerates the tribo-oxidation, it is a diffusion-driven process and time-dependent phenomena. As a consequence, before the onset of tribo-oxidation, the coatings are subjected to a deformation-dominant wear process due to the combined action of higher contact stress and the thermal softening of the coating material. The two dominant wear mechanisms for the high temperature tests are, (a) micro-ploughing of the coating surface and (b) cracking observed

for the columnar structured coating. Micro-ploughing of the coating is caused by the abrasive action of the WC particles generated by the asperity breakage and transfer of the counter material. The high plastic strain associated with micro-ploughing of the coating leads to high COF with a value between 1.4 and 1.5, which causes the wear rate of the coatings to be higher by an order of magnitude compared to room temperature test. Previously, it was shown that the high COF causes higher tensile stresses at the trailing edge of the sliding contact [26], which is the most likely responsible mechanism for crack formation in the coating (Fig. 9b) in a high temperature wear test. Based on the postmortem electron microscopic investigation of the wear track, it is difficult to ascertain the individual contribution of these mechanisms precisely. The measured wear resistance of the coatings follow the hardness trend of the coating (Fig. 7), indicating that micro-ploughing is the dominant wear mechanism. This is also supported by overview cross-sectional micrograph indicating that the crack formation is confined to relatively small areas in the coating (Fig 8 e).

In the multipass microwear test, the sliding of the hard diamond tip causes formation of a deep wedge accompanied with material pile-up under a sliding contact- induced dominant elastic stress field (Fig. 10 b and c). This is attributed to the accumulation of plasticity over several repeated cycles. Higher hardness implies higher resistance to contact stress-induced deformation and therefore explains the continuous drop in the wear rate up to 1.8 at. % Si. Beyond this Si content the coating hardness reduces (table 1), as a consequence of strain localization by grain boundary mediated deformation mechanism for the nanocomposite structure, in contrast to the dislocation mediated homogeneous deformation for the columnar structured coating [17]. In the current study, the 3D cross-sectional profile of the microscale wear track does not display any shear bands besides the wear track of the nanocomposite coating. In addition, the comparable pile-up to wedge volume ratio between the columnar and nanocomposite coatings indicate that wedge formation is caused by dislocation mediated

deformation for both the coatings. The difference in the deformation mechanism of the nanocomposite coating between the sliding contact in the current study and the previous static indentation could be explained by the difference in the contact stress field, i.e. a dominant elastic stress field in the former case (inset Fig. 10 a) and a fully developed plastic zone in the later case. The limited plasticity in the sliding contact might not provide the necessary conditions to cause a collective atomic rearrangement that triggers grain boundary sliding. As a consequence, nanocomposite coating displays higher resistance to groove formation by constraining the dislocation motion which leads to higher wear resistance. The limited plasticity in the contact sliding keeps the ploughing-induced friction component to be low, and the counter surface of diamond tip is significantly hard and immiscible to the coating material, causing lower contribution of adhesion component. As a consequence, the microscale wear tests display significantly lower COF of 0.15 to 0.17, which reduces the wear rate by a factor 10^{-4} compared to the macroscale tribological sliding tests.

5. Conclusions

Zr-Si-N coatings were grown on WC-Co substrates by reactive cathodic arc deposition. Si content of the coatings was varied between 0.2 and 6.3 at. % Si to produce systematic changes in microstructure and mechanical properties. Tribological response of these coatings under a macro-and microscale wear test in a reciprocating dry sliding contact shows a transition in the dominant wear mechanism by varying the contact force and the test temperature.

In a macro scale wear test, when the sliding is performed at room temperature and lower contact stress, tribo-oxidation is the dominant wear mechanism. The columnar structured coatings form thick tribo-layer, which undergoes delamination that leads to higher wear rates. Whereas the nanocomposite coating form thin and strongly adhered oxide layers with a lowest wear rate of $6.4 \times 10^{-6} \text{ mm}^3/\text{Nm}$. The superior tribo-oxidation resistance of the nanocomposite coating is attributed to the formation of Si rich W containing Zr oxide diffusion barrier layer.

At higher temperature, the softening of coatings combined with the higher contact stress, makes them to undergo micro-ploughing caused by the abrasive action of WC particles from the counter surface, which leads to a high COF of 1.4 and higher wear rate. The hard columnar coatings display higher resistance to the surface deformation by micro-ploughing.

Microscale wear test of the coatings shows wedge formation accompanied with material pile-up, which is ascribed to the accumulation of dislocation mediated plasticity under the sliding contact-induced dominant elastic stress field over several repeated cycles. A dominant elastic stress field under the sliding contact has resulted a low COF of 0.16, while the dislocation confinement in the nanocomposite coating leads to a lowest wear rate of $5.59 \times 10^{-11} \text{ mm}^3/\text{Nm}$.

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