In the present work, the fretting wear (mode I, linear relative tangential displacement, constant normal load) of a newly developed nanocomposite is investigated with varying load (2–10 N) and test duration (10 000–100 000 cycles). A detailed morphological investigation of worn surface is carried out using a Stylus surface profilometer, optical microscope, SEM, and electron probe microanalyser (EPMA). A clear transition in friction and wear behavior with load is observed. Based on the worn surface topography and wear debris analysis, the wear mechanisms are proposed. The extremely low wear rate (10⁻⁸ mm²/N·m) along with low wear depth (< 1 μm) indicates high wear resistance of nanocomposite composites. The high fretting wear resistance of the nanocomposites as well as the observed tribological properties are discussed in terms of material properties, abrasion, and tribochemical wear phenomenon.

I. Introduction

In the last few decades, nanoceramic composites received greater attention of researchers in the materials community. Nanocrystalline materials/or nanocomposites are defined as materials with one of the phases having the dimension in the range of nanometers. Although the consolidation of nanocrystalline composite without excessive grain growth is commonly accomplished by spark plasma sintering (SPS), other sintering routes are also reported. The major advantage of the SPS process is that the sintering temperature is typically around 200 °C lower than in conventional sintering. A rapid rate of densification, fast heating rate, lower sintering time, and retention of finer grained microstructure are the other significant characteristics of SPS.

The dispersion of nanograined secondary phase particles within the matrix or along the grain boundary of the micron and/or submicron-sized matrix material leads to significant improvement in strength and fracture toughness by the order of two to four times than a conventional composite material. Following the early work of Niihara and Niihara et al., on the structural nanoceramic composites, research works have been carried out in alumina- and silica-based nanoceramic composites. Mukherjee and co-workers have recently developed alumina nanocomposites reinforced with carbon nanotubes and measured three times higher toughness (9.7 MPa·m¹/²) compared with that of conventional alumina. Also, in one of our recent works, the development of Y-TZP nanocomposites with high hardness (~ 14 GPa) and better wear resistance is reported. Improvements in mechanical property of nanocomposite composites make them promising candidates for various structural and wear resistance applications.

Recent literature reports also indicate the potential of ceramic nanocomposites in machining and tribological applications. For example, the Si₃N₄/BN nanocomposites, when compared with the microcomposite, have higher fracture strength and better machinability, as exhibited by the superior surface finish of the machined component. Also, nanocrystalline WC-Co composites are reported to have four times higher wear resistance, and more than double the lifetime in cutting applications than conventional coarse-grained composites. This is due to superior mechanical properties (hardness, toughness).

From the above, it should be clear that considerable work has been carried out to develop nanoceramics and their composites along with a few reports on the evaluation of their potential in engineering applications. However, research work to understand the tribological properties of the nanocomposites is rather limited. Recently, the tribological behavior of Al₂O₃/TiO₂/SiC and Si₃N₄/SiC nanocomposites has been reported in the literature. Dusza et al. investigated the friction and wear behavior of Si₃N₄/SiC nanoceramic composites against Si₃N₄ ball using a pin-on-disc wear tester. The friction coefficient varied between 0.4 and 0.6 under the experimental conditions of varying load (10, 15, and 20 N), sliding distance (600, 900, and 1200 m) and sliding speed (0.1, 0.2, and 0.3 m/s). The erosive wear behavior of Al₂O₃/SiC nanocomposites (against Al₂O₃) was investigated by Davidge et al. The dispersion of secondary SiC nanoparticles in polycrystalline alumina significantly reduced the wear rate, and smooth transgranular fracture paths were observed in the worn nanocomposites. Rodriguez et al. studied the sliding wear properties of Al₂O₃/SiC nanocomposites by varying the grain size of SiC. Intergranular fracture followed by grain pull-out are noted to be the dominant wear mechanisms. The tribological behavior of the Al₂O₃/TiO₂ nanocomposites against Si₃N₄ was carried out using a ball-on-disc tribometer. The highest wear resistance was noted for 10 mol% of TiO₂ reinforcement and the governing wear mechanisms were abrasive and plastic deformation.

In the above perspective, the present work is carried out to understand the friction and wear properties of WC–6 wt% ZrO₂ nanocomposites, processed by SPS. The details of the processing and mechanical properties of this nanoceramic composite are reported elsewhere.

II. Experimental Procedure

(1) Materials

SPS-processed WC–6 wt% ZrO₂ nanocomposite is used as the flat material in our experiments. A commercial bearing grade (SAE 52100) steel ball, 8 mm in diameter with mirror finish (surface roughness 0.02 μm, according to supplier), was used as a counterbody material. The details of the flat and counterbody are mentioned in Table I. The commercially available co-precipitated ZrO₂ (Tosoh grade TZ-3Y, starting particle size of 27 nm) and commercial WC powder (99.5% pure, particle size around 0.2 μm, H.C. Starck, Germany) were used as starting powders. The SPS experiments were carried out under a vacuum of 50–60 mtorr at 1300 °C for 5 min under a pressure of 30 MPa to obtain a final density of 98–99% of the theoretical density. The nanocomposite exhibits ultrahigh hardness (~ 23 GPa) and moderate toughness (~ 5 MPa·m¹/²). XRD investigation on the WC–6 wt% ZrO₂ nanocomposite indicated the predominant presence of tetragonal ZrO₂ and WC. No reaction product is detected. An
SEM image of WC–6 wt% ZrO2 nanoceramic is illustrated in Fig. 1. The microstructure is characterized by dispersion of nanosized ZrO2 in submicron WC matrix.

(2) Tribological Tests
The tribological behavior of the nanoceramic composite was studied using a ball-on-flat-type fretting wear tester. Among various modes of fretting tests, Mode I is commonly used for the simulation of the fretting in the laboratory scale. Mode I fretting wear tester is characterized by small amplitude, linear relative tangential displacement at constant normal load and commonly referred to as tangential displacement fretting. The displacement stroke, normal load, frequency, and number of fretting cycles are the external variables associated with the aforementioned tribosystem. Essentially, the tester having an oscillating base (achieved by stepping motor) is equipped with an inductive transducer to monitor the displacement of the flat (sample). The piezoelectric transducer attached to the loading arm records the friction force. The details of the wear tester are shown in Fig. 2(a).

The WC–6 wt% ZrO2 nanoceramic composites were used as a flat sample and held mechanically on a translation table, which oscillates with the preset displacement and frequency. Prior to each test, the ultrasonic cleaning of both flat as well as steel ball is carried out in acetone. The fretting wear experiments have been conducted over constant frequency (8 Hz) and constant displacement stroke (50 μm) by having load and cycles as the external variables of the tribosystem. The load and cycles were varied from 2 to 10 N and 10 000 to 100 000 cycles respectively (Fig. 2(b)). The average sliding velocity is around 0.008 m/s. The contact displacement in fretting mode I establishes gross slip sliding between mating surface that occurs across the whole contact area under the selected experimental conditions.

(3) Characterization of the Worn Surface
In order to understand the wear mechanisms, worn surfaces were investigated using SEM (JEOL-JSM840, JEOL, Tokyo, Japan) and EPMA (JEOL-JXA8600). The depth of the wear scars on the ultrasonically cleaned worn surfaces was evaluated using a stylus surface profilometer (Tencor z-Step-100™, USA). Initially, the wear scars on the nanoceramic composites were observed under a Zeiss optical microscope in order to characterize the topographical features and to measure the diameter of the wear scars in the direction perpendicular to the sliding direction. From the transverse wear scar diameter, the wear volume of flat sample is calculated according to Klaffke’s formula. Justifying that the normalized diameter is greater by the order of 2, i.e., the wear scar diameter is greater that twice the Hertzian contact diameter, our calculation provides an error less than 8% as was in our experiments.

III. Results
(1) Frictional Behavior
The influence of varying load (2, 5, and 10 N) on the frictional behavior of WC–6 wt% ZrO2 nanoceramic composites fretted against steel for 100 000 cycles is illustrated in Fig. 3. From Fig. 3, it is clear that the evolution of frictional behavior is strongly dependent on normal load as well as fretting cycles. Under the lowest load of 2 N coefficient of friction (COF) increases from a low value to 0.1 in the initial 500 cycles and a steady-state COF of 0.1 is maintained throughout the entire test period of 100 000 cycles. A distinct transition in the frictional behavior is observed with an increase in load from 2 to 5 N. In the case of 5 N load, the steady-state COF of ~0.1 to 0.15 is maintained up to 20 000 cycles and subsequently a slow increase

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**Table I. The Density and Mechanical Properties of the Tribocouple Used in our Experiment**

<table>
<thead>
<tr>
<th>Material</th>
<th>Density ρ (gm/cc)</th>
<th>Hardness (GPa)</th>
<th>Fracture toughness Kx (MPa m^{1/2})</th>
<th>Elastic modulus E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat (Sample)</td>
<td>WC-6 wt.% ZrO₂</td>
<td>14.25</td>
<td>23.6 ± 0.3</td>
<td>5.9 ± 0.1</td>
</tr>
<tr>
<td>Ball (Counterbody)</td>
<td>Steel (SAE 52100 grade)</td>
<td>7.8</td>
<td>~7</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. SEM image of the fracture surface of the WC–6 wt% ZrO₂ (3Y) material densified using SPS at 1300°C, 5 min.

Fig. 2. Schematic representation of fretting (mode I) ball-on-flat type setup (a) and the experimental parameters (b) used in the present investigation.
in COF from 0.15 to 0.50 is observed between 20 000 and 45 000 fretting cycles. Further, a steep increase in COF from 0.15 to 0.5 is recorded between 45 000 and 55 000 fretting cycles and a steady-state COF of 0.5 is maintained beyond 60 000 cycles. At the highest load of 10 N, the transition to higher COF of 0.5 takes place at an early stage of around 20 000 cycles. Beyond 40 000 fretting cycles, steady-state COF of 0.5 is maintained throughout the fretting test.

(2) Wear Data

Based on the measurement of the transverse diameter of wear scars, wear volume is measured following Klaffke’s formula, as also mentioned in section 2.3. The wear volume is normalized with respect to load and total sliding distance (number of cycles × displacement stroke × 2) in order to obtain normalized wear rate. The wear rate after different testing time (10 000–100 000 fretting cycles) is plotted against normal load in Fig. 4(a). The wear rate is quite low and in the order of \(10^{-8} \text{mm}^3/\text{N} \cdot \text{m}\). It can be noted here that dense WC–6 wt% ZrO2 composite, pressureless sintered at 1600°C, exhibits a wear rate in the order of \(10^{-6} \text{mm}^3/\text{N} \cdot \text{m}\). After fretting for 10 000 cycles, the wear rate measured on the worn flats is low and does not vary much with normal load. The wear rate, measured after 50 000 cycles, increases as load increases from 2 to 5 N, but no further increase is noted at the highest load of 10 N. The measured wear rate after 100 000 fretting cycles shows a monotonic increase with normal load, varied between 2 and 10 N.

The maximum depth of the wear scar is measured on the ultrasonically cleaned worn surfaces using a Stylus profilometer, and the representative profilometer traces for different fretting conditions are shown in Fig. 5. The wear depth data are plotted against fretting variable in Fig. 4(b). At the lowest load of 2 N, the scar depth is not measurable after 10 000 and 50 000 cycles. The wear depth is around 0.15 \(\mu\)m after fretting for 100 000 cycles at 2 N load. The increase in wear depth from \(\sim 0.20 \rightarrow 0.24 \mu\)m with increasing fretting cycles (10 000–100 000 cycles) at an intermediate load of 5 N is noted. However, this increase is considerable at the highest load of 10 N. A maximum depth of \(\sim 0.55 \mu\)m is recorded after fretting for 100 000 cycles at 10 N load. Summarizing, the wear data clearly reveal that the severity of the wear of the investigated ceramic nanocomposites, i.e., the amount of material removal at the fretting contacts, increases with an increase in load and test duration.

(3) Topographical Observations of Worn Surfaces Using SEM

The topography and details of the wear scar on the nanocomposite after fretting at 2 N for 100 000 cycles are shown in Fig. 6.

The smooth appearance of the wear scar correlates well with the measured wear depth (Fig. 6(a)). The observation of mild abrasive scratches is also indicative of mild wear at low load (Fig. 6(b)). It can be noted here that the topographical observation correlates well with the profilometer trace of the worn scar.

The formation of the tribochemical layer is only observed when the normal load is increased to 5 N and above. Considering the difference in contrast between the tribolayer and the underlying worn surface of the nanocomposite, it is clear that the tribochemical layer (dark contrast) is rich with transferred iron oxide (see Fig. 7(a)). The smeared transfer layer (white contrast) is WO3, which is heavier than WC (gray contrast). It is quite probable that WC is oxidized at the fretting contacts, as also observed in our earlier work on wear of TiCN–(WC)–Ni cermets (similar fretting conditions). The formation of WO3, as a result of tribo-oxidation of WC, was confirmed by Raman spectroscopy. However, the severe cracking of the tribolayer indicates the non-protective nature and justifies the higher wear loss. The severity of cracking and subsequent spalling of tribo-layer is much more pronounced at a higher load 10 N after 100 000 fretting cycles.

The morphology of the wear debris after fretting at low (2 N) and high (10 N) load is presented in Fig. 8. A striking difference
in wear debris particles is clearly noted. After fretting at 2 N load, the debris particles are largely submicron in size and spherical in nature. Occasionally, agglomerated wear debris of size up to 2 \( \mu \text{m} \) are observed. At the highest load of 10 N, the formation of a large fraction of sheet/platelet-like wear debris particles is observed. The typical size of the wear debris is around 50–100 \( \mu \text{m} \). A smaller fraction of submicron-sized debris particle is also seen.

In order to obtain qualitative and semi-quantitative composition of the tribolayer, X-ray mapping had been carried out using EPMA on the worn surfaces and the results are presented in Fig. 9. The accumulated wear debris around the edges of the wear pit is primarily iron rich and no significant transfer of oxidized steel onto the flat worn surfaces is recorded (see Fig. 9(b)). The distribution of Zr is quite homogeneous as no part of the tribolayer shows clustering of Zr-rich region. Additionally, the X-ray image presented in Fig. 9(c) closely matches the composition of the nanocomposite reinforced with 6 wt% ZrO\(_2\). Fig. 9(d) reveals that the transfer layer on the flat worn surface is primarily W-rich, indicative of extensive formation of WO\(_3\). The results of the semiquantitative analysis of the tribolayer, as analyzed using EPMA, are plotted in Fig. 10. The average of the point analysis, carried out at different spots (at least 10 points), is shown in Fig. 10 and the error bar indicates the standard deviation of different spot analysis data. It is quite evident that the transfer of Fe from steel ball is limited up to 10 wt% and the transfer layer is predominantly W-rich under the investigated fretting conditions.

### IV. Discussion

One of the important aspects of tribology research is to establish the wear mechanisms. In the case of ceramic nanocomposites, two important issues need to be addressed: (a) Whether the improved hardness leads to any appreciable improvement in wear resistance? (b) What would be the role of a finer microstructure in the process of material removal from contacting interfaces?

Based on our experimental results, it is evident that the influence of higher hardness leading to lower COF and wear is only realized at a low load of 2 N. Additionally, the observation of lower wear depth (<1 \( \mu \text{m} \)) can be correlated with higher hardness of the nanocomposite. It also indicates that the wear-induced material damage of the nanocomposite is limited to the submicron region below the tribological surface. With an increase in normal load from 2 to 5 N, a transition in friction and wear of the WC–6 wt% ZrO\(_2\) nanocomposite occurs, while mild wear coupled with low friction is observed at the lowest load of 2 N and high COF as well as severe wear is observed at an intermediate load of 5 N with more severe wear at the highest load of 10 N. At higher load (5 N or more), the tribochemical wear is the predominant mechanism for material removal.

Observing the smooth worn surfaces and extremely finer wear debris (brighter contrast), it is quite probable that WC grains are pulled out from the tribological interface following the intergranular fracture caused by repeated fretting strokes. WC grains, once pulled from the matrix, become oxidized to WO\(_3\) and subsequently the debris particles are ejected from the worn surface. Hence, mild oxidative wear is proposed to be the major wear mechanism. This physico-chemical process, involved in wear at a low load of 2 N, is highly likely and supported by the fact that the wear debris particles are of similar size as WC grains. It can be noted here that a similar wear mechanism, i.e., intergranular fracture followed by grain pull-out, is also...
reported for Al2O3/SiC nanoceramic composite and nanocrystalline Y-TZP.

At a higher load of 5 N or more, the wear of the nanocomposite is determined by the formation and behavior of the tribochemical layer at the contacting interface. The oxidized WC wear debris is agglomerated at a higher load and this forms the tribochemical layer incorporating iron oxide transferred from the worn steel ball. Once the tribochemical layer spreads over the worn surface, contact is established between the worn steel ball (iron-oxide layer) and the tribolayer on the flat. This explains the transition in friction leading to a higher COF of 0.5, maintained at high load regime (5 N or more). It can be noted here that the transition from mild to severe wear is not observed in Cu–TiB2 nanocomposites, when tested against steel on a pin-on-disk tribometer with varying loads (20–140 N). The dominant mechanism of material removal is the plastic deformations with flake-like wear debris formation.

Based on the wear debris analysis, the transition from mild to severe wear mechanism can be discussed. We will first discuss the cause for submicron debris formation at low load. Based on the indentation fracture mechanics concepts, Roberts observed the minimum load required for fracture due to abrasion:

\[ P^* = \frac{54.47\beta}{\pi n^2 \theta^2} \left( \frac{K_{IC}}{H} \right)^3 K_{IC} \]  

(1)

where \( P^* \) is the minimum load required to produce fracture from a point contact (N), \( \beta \) is the constant relating hardness to diagonal (2.16 for Vickers Indentation), \( \theta \) is the geometrical constants (≈ 0.2), \( K_{IC} \) is the fracture toughness of the material indented (MPa m\(^{1/2}\)), and \( H \) is the hardness of the material indented (GPa).

Incorporating the material properties (see Table I) into Eq. (1), it has been found that a minimum of ~2.15 N load is required for abrasion-induced fracture of the investigated nanocomposites. Hence, it is quite plausible that the finer wear debris (≤2 μm) forms due to intergranular fracture of the nanocomposites even at such a low load (2 N). This finer debris particle, once formed, can get trapped between the mating counterfaces and some debris particle can eventually be ejected out to the edges of the wear pits. This explains that the low COF of ~0.15 and lower wear rate at 2 N load is primarily due to three-body abrasion, i.e., due to rolling of the finer debris particles.

However, the coarser wear debris, in the form of sheets, is typically observed at a higher load (> 5 N). Based on the adhesional theory of friction, Rabinowicz proposed that the average diameter of a wear debris particle is dependent on the work of adhesion:

\[ d = 60000 \frac{W_{ad}}{H} \]  

(2)

where \( W_{ad} \) is the work of adhesion, \( H \) is the hardness of the material, and \( d \) is the debris diameter.

From Eq. (2), it is clear that the size of wear debris particles, being directly proportional to the work of adhesion, should be
dependent on normal load and tangential force. In fact, COF linearly increases with $W_{ad}^{35,37}$. This can be rationalized from the fact that in order to maintain relative motion at frictional contact, higher frictional force is necessary to break the adherent bonds between interlocking asperities at higher loads. In our experiments, it is observed that COF increases with load and therefore a higher work of adhesion at the frictional contact should be expected. From the above discussion, it should now be evident that coarser debris formation is realistic at a higher load ($\geq 5$ N). Furthermore, higher COF at higher load ($\geq 5$ N) implicates the dissipation of more frictional energy. It is quite probable that more energy is expended to form and knock off coarser wear debris from the tribosurface. Another probable reason is that the tribochemical layer is non-protective (see Fig. 7(a)) and becomes fractured due to repeated fretting strokes. This leads to the formation of sheet-like wear debris, which is subsequently ejected around the wear scar (see Fig. 8(b)). Once the tribolayer is removed, a similar process occurs during the fretting tests. Since the size of the wear debris is also a reflection of the wear rate, the observation of coarser wear debris indicates a higher wear rate of nanocomposites at higher loads ($\geq 5$ N).

V. Conclusions

(a) WC–ZrO$_2$ nanoceramic composites, processed via SPS, exhibit lower COF of 0.1 at a lower load of 2 N. A clear transition in frictional behavior leading to a high COF of 0.5 is recorded during fretting (100 000 cycles) at a higher load of 5 N.
At the highest load of 10 N, the frictional transition takes place earlier than that at 5 N load. This interesting observation also elucidates a transition from mild to severe wear at higher loads.

(b) Under the experimental fretting conditions, the newly developed WC–ZrO₂ nanocomposite exhibits low wear depth (maximum ~0.6 μm) and high wear resistance (wear rate ~10⁻⁸ mm³/N·m). This can be correlated with high hardness of the nanocomposite (~23 GPa).

(c) The formation of mild abrasive scratches along with finer (submicron sized) wear debris particles indicates higher wear resistance of the nanocomposite at lower load (2 N).

(d) Tribochemical wear is the predominant wear mechanism of the material removal at higher load (5 and 10 N). The observation of cracking induced spalling of non-protective tribolayer and the formation of sheet-like agglomerated wear debris is implicative of severe wear at high load.

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