Harnessing nano oil reservoir network for generating low friction and wear in self-mating alumina

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HIGHLIGHTS
• Fomblin® Y25/6 oil is an excellent lubricant for self-mating nanoporous alumina.
• 90% Al2O3 relative density is the optimal in the range of 70–99.5% for achieving best tribological properties.
• Friction coefficients decreased with increase in normal loads (10–220 N) and sliding frequencies (1–24 Hz).
• Lowest friction coefficient of 0.025 was recorded for 95% dense self-mating lubricated Al2O3.
• Wear occurred by intergranular fracture in 70–90% dense Al2O3 and transgranular fracture in 95–99.5% dense Al2O3.

ABSTRACT
This study unleashes the potential of nanoporous connected networks as excellent oil reservoirs for reducing friction and wear in Al2O3-Al2O3 tribo-pairs. Alumina were fabricated via slip casting and sintering to generate wide-ranging densifications (70–99.5%) and slid in a reciprocating flat-on-flat configuration. Friction coefficients (FCs) lie between 0.025 and 0.37 which decreased with an increase in normal load (10–220 N), lubricant’s viscosity (19, 289 mPa·s) and sliding frequency (6, 12, 24 Hz). A central finding is that FCs of infused specimens are smaller than those of surface lubricated. Wear rates decreased from 10−5 to <10−8 mm³·N−1·m−1 for an increase in Al2O3 density. Wear occurred predominantly via intergranular and transgranular fracture modes as revealed by the electron microscopy studies.

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1. Introduction
Alumina is an abundant advanced ceramic that possesses excellent thermal properties, high compression strength, high hardness as well as excellent bio-compatibility [1,2]. Thus, Al2O3 is one of the extensively studied tribological materials for applications in wide ranging environments namely watch bearings [3], hip implants [4], dental implants [5], cutting tools [6], mechanical face seals [7], valve seats [8], ultrasonic motors [9] and armour plates [10].

The friction and wear properties of dry and lubricated fully dense Al2O3 systems are well-studied [11–25]. Different configurations were employed such as cylinder on plate [19], ball on disc [20–22], pin on disc [26] and flat on flat [24]. Various lubricants were utilized namely water [21], paraffin oil [27], hexadecane [28], iso-octane [19], polyacrylic acid [23] and liquid nitrogen...

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Friction coefficients (FCs) and wear rates were shown to depend on several parameters namely lubricant’s physicochemical properties, solid surface roughnesses [29,19], their grain sizes [29,30], environmental conditions [15,17], sliding speeds/frequencies [22,31], normal pressures [22] and residual stresses [32]. Typically, such FCs in Al2O3-Al2O3 tribo-pairs lie in between 0.15 and 1, while the wear rates reveal mild and severe wear.

Lubricants can significantly reduce the solid–solid contacts as in the mixed and hydrodynamic regimes of the Striebeck curve [33], thereby yielding low FCs and low wear rates. In order to keep low FCs and wear rates for extended periods in practise, it is essential to continuously replenish the surfaces with the lubricants. At this juncture, surface microtexturing is an outstanding approach that offers as a viable solution by providing lubricant reservoirs which enhances hydrodynamic lift-off thereby decreasing the friction and wear [34–36,37]. Various textures namely circular dimples/pores, oval dimples, linear grooves, triangle dimples have been fabricated on steels, polydimethylsiloxanes (PDMS), Si3N4, Ti-6Al-4V, Co-Cr-Mo alloy, Si single crystals etc. For example, a reduction in FC from 0.8 (flat) to 0.1 (textured) in nitriding steel was observed for micrometer circular dimples [38]. Furthermore, the striebec curve was shown to shift downwards and left side in steels demonstrating early transition to the hydrodynamic regime and yielding lower FCs [39]. Also, decreased wear-rates have been reported as those textures act as debris trappers [34]. Such microtextured surfaces have already been applied in piston rings, cutting tools and automotive components [37,40,41].

In spite of these exceptional capabilities of surface microtexturing and micro-porosity, there are no studies conducted to explore their potential in self-mating Al2O3 tribo-pairs. Thus we propose the utilization of connected nanoporous network in the bulk α-Al2O3 that acts as lubricant’s reservoir. This concept will continuously replenish the oil to the dry surfaces in the events of evaporation or shear-assisted drainage. Thus, this new approach may outperform the conventional surface microtexturing which only provides isolated reservoirs. Additionally, in this study, the ultrafine grain microstructures are proposed instead of micrograins employed by earlier researchers as the former would decrease the FCs [42]. Also nanoporous reservoirs are proposed instead of microtextures as the former will provide high capillary forces aiding in the enhanced self-replenishment process during long service hours.

In this work, slip casting followed by the sintering process are employed to fabricate specimens with a wide ranging porosity fractions of 0% to 30%. The sintering was carried out at different temperatures to either partially or fully densify the porous materials which is also accompanied by a grain growth. Due to the nature of synthesis route, the grain sizes are interlinked with the pore sizes and pore fractions. Here, the larger open porosity fraction provides more lubricant and high self-replenishment efficiency thus lowering the FCs. On the contrary, smoother surfaces, higher hardness and better wear-resistance will be achieved for small open porosity and total porosity fractions. Similarly, resultant grain morphologies in the sintering process can influence the friction and wear of these materials. Thus, this study aims at designing and tuning all the influencing microstructural parameters such as open porosity (OP), closed porosity (CP), total porosity (TP) fractions, as well as the pore sizes and grain sizes to be able to achieve low friction coefficients, high wear-resistance together with optimal self-replenishment of the lubricant. The chosen lubricant for this study is Fomblin® Y 25/6 oil, a high viscosity perfluoropolyether, due to its proven ability in retaining the molecular scale thin films for extended service duration thus yielding low FCs [43,44]. The developed porous lubricant infused surfaces could be used in dewetting [43,45], anti Fouling [46], anti-corrosive [47], and water harvesting [48] applications.

2. Experimental section

2.1. Nanoporous Al2O3 synthesis

Nanoporous α-Al2O3 bulk green compacts were synthesized by slip casting process. Basically, an Al2O3 colloidal suspension was poured into impermeable hollow silicone molds supported by a plaster of paris base at the bottom for enabling vertical drying in one dimension [49]. The silicone molds were fabricated by curing a two-component mixture (9:1 ratio) of Elastosil® 622 RT A/B (Aneba AB, Switzerland) at 100 °C for 20 min. α-Al2O3 (99.5% purity) ultrafine powders were procured from BMA 15, Baikowski, France and were reported to have specific surface area of 14900 m²·kg⁻¹ as measured via nitrogen gas adsorption–desorption method. The powder granules have spherical or polygonal shapes with diameters in the range of 10–100 μm as observed in an electron microscope and presented earlier [49]. These granules are composed of smaller particles/grains which need to be dispersed before casting. Particle size distributions of homogeneously dispersed Al2O3 suspension were measured with a disc centrifuge (CPS disc centrifuge, CPS Instruments, Europe, The Netherlands) thrice to ensure a high reproducibility. The individual particles/grains have their diameters between 90 nm and 220 nm while the median diameter d₅₀ is 150 nm implying that 50 vol% of particles have diameters smaller than 150 nm as previously reported [49].

To achieve homogeneous dispersion of Al2O3 particles/grains, they were mixed with 2 wt% polyacrylic acid (PAA) + 98 wt% water solution and pH of the resultant was maintained at 10 by adding a few drops of NH₄OH. The required 2 wt% PAA was made by diluting the commercially available 65 wt% solution possessing molecular weight (MW) = 2000 (Sigma-Aldrich, Switzerland). The slurries obtained were given mechanical energy to break the agglomerates. The dispersion procedure commences by ultrasonicating 40–55 cm³ amounts of slurry with a UP200Ht ultrasonicator horn using 50 W power, 26 kHz frequency for about 15 min. Following that, 3–5 drops (i.e. 5–10 μl) of 1-Octanol (Sigma-Aldrich, Switzerland) were added to the slurry to act as a surfactant which aids in efficient degassing in the later steps. In the next stage ~ 1 mm diameter Al2O3 beads were added to the slurry to perform low energy milling in a SRT 9D roller (Stuart, Switzerland) for 24 h at 60 rpm. Finally, the slurry was degassed at 200 mbar for 10–15 min to remove the air bubbles.

Subsequently, the dynamic viscosity of the slurries were measured with a Thermo/HAAKE RheoStress RS100 Rheometer (USA) and lie between 7 mPa·s and 30 mPa·s for varying solid content from 20 vol% to 37 vol%. The viscosity measurements were repeated thrice per each solid content and display high reproducibility. For an efficient deagglomeration as well as to minimize the sedimentation effects, a trade-off of 25 vol% Al2O3 was found to be an optimum solid content. This optimized ceramic slurry was cast into the silicone molds and dried at 25 ± 2 °C for 24 h each firstly at 90% relative humidity (RH) and then later at 45% RH. As a result of drying, tribo-pairs comprising of cuboidal (24 × 12 × 10 mm³) and cylindrical (7.5 mm diameter, 17 mm thick) shaped green compacts were formed. Elaborate details about the slip casting setup, granulated powders, slurry rheology and drying mechanisms can be found elsewhere [49–51].

2.2. Sintering and density measurements

In order to remove the PAA binder and other organics, Al2O3 green compacts were pre-sintered in air by heating to 600 °C at a rate of 1 °C·min⁻¹ followed by isothermal holding for 1 h. The compacts were then finally furnace cooled. Subsequently, they underwent sintering in a tubular furnace in air at different
temperatures varying between 1150 °C and 1500 °C at a heating rate of 10 °C/min⁻¹. This was followed by a 1 h isothermal step and furnace cooling to yield relative densities of 70%, 80%, 90%, 95% and 99.5%. The densities were measured via Archimedes principle at 23 ± 2 °C and 35 ± 10% RH conditions where water was the suspending liquid. Water impregnates into the open connected porous networks and therefore the wet weight (weight of alumina + water in open porosity in air medium) will be measured along with dry weight (weight of alumina in air medium) and immersed weight (weight of alumina + water in open porosity suspended in water medium). Thus, the OP and the relative density (RD) were estimated using Eqs. (1) and (2), respectively.

\[
OP = \frac{ww - dw}{ww - iw} \times 100
\]

\[
RD = \frac{dw \times \rho_{\text{water}}}{(ww - iw) \times \rho_{\text{Al}_2\text{O}_3}} \times 100
\]

where, \(dw\) is the dry weight of the specimen measured in air, \(iw\) is the immersed weight of the specimen when suspended in the liquid (water here), and \(ww\) is the wet weight of the specimen measured in air after immersion in liquid. \(\rho_{\text{water}}\) and \(\rho_{\text{Al}_2\text{O}_3}\) are densities of water and Al₂O₃ and are 1000 kg m⁻³ and 3987 kg m⁻³ respectively.

2.3. Surface finishing and optical profilometry

The sintered porous \(\text{Al}_2\text{O}_3\) were embedded in a two-component methacrylate based epoxy (Technovit 5071, Naas Werkstoffprüfung, Switzerland) to accomplish surface polishing. Firstly, coarse grinding was conducted using 40 μm and 20 μm diamond blades and sequentially treated with 15 μm, 6 μm, 3 μm, 1 μm and 0.25 μm diamond slurries (Struers MD Dur®), Switzerland for a finer finish. The demolded \(\text{Al}_2\text{O}_3\) polished specimens were ultrasonicated in isopropanol for 30 min and heated in an oven to 200 °C for drying. The flatness, waviness and roughness of polished surfaces were probed using a white light optical AltiProfi Optic® profilometer according to the standard DIN EN ISO 4288, ASME B46.1. To study the surface finish at different locations, three to five measurements were taken on each specimen. Typically, at least three specimens were taken from each densification to obtain surface roughness and flatness profiles. The results indicate that there are no strong topological undulations over such large specimen areas indicating that polishing procedure is highly reproducible.

2.4. Oil infusion/lubrication and tribological tests

Fomblin® Y25/6 oil (MW = 3300 a.m.u., dynamic viscosity = 28 9 mPa·s at 30 °C), a perfluoropolyether having the structural formula (CF₃O)[–CF(CF₃)CF₂O–][–CF₂O–]n[–CF₂O–]CF₂) was procured from Sigma-Aldrich, Switzerland for liquid infusion/lubrication purposes. The polished specimens containing open porous network were infused while the rest of them were surface lubricated by submerging them in an oil bath at 150 °C for 2 h. The excess oil on the surfaces were blown with Ar gas to obtain sub-millimeter films. Reference single crystal sapphire discs (20 mm diameter) were procured from Stettler Sapphire S.A (Switzerland), 1 mm thick diamond is coated on tungsten carbide (WC) cylinders (4 mm diameter) by a chemical vapor deposition (CVD) process and obtained from Diamond Materials (Germany) for serving as sapphire’s counter bodies.

The reciprocating sliding frictional tests were conducted in a SRV® III tribometer (Optimol Instruments Prüftechnik GmbH, Germany) in a flat-on-flat configuration. This geometry enables providing large worn areas (up to 42 mm² in this study). Such areas are essential to characterize the wetting, biofouling, anti-icing properties post wear. Such wear-resistant self-healable slippery surfaces are useful in paint industries, medical implants, medical devices and sewage applications. It was already showcased that perfluoropolyether impregnated alumina composites demonstrate excellent non-wetting properties towards water, acrylic based paints, hexadecane and dodecane [43-52]. Such liquid impregnated surfaces (referred to as LIS) or slippery liquid impregnated porous surfaces (referred to as SLIPS) have already shown exceptional anti-sticking [45], anti-fouling [53], anti-icing [54] properties.

In this study, the tribological properties of these novel class of materials are focused which pave a new research direction for further exploration.

Fig. 1a presents the setup of a tribo-pair inside a tribometer wherein the holder for the counter body is the central focus. This holder is specially designed to aid at better self-alignment between two sliding surfaces to ensure excellent flatness. For this, this holder was given a small degree of linear movement in X-direction and a few degrees of rotation about X-axis (X-Y-Z axes are indicated in Fig. 1a). The optical profilometry measurements on the polished \(\text{Al}_2\text{O}_3\) specimens reveal a flatness difference of only 10 μm for a stroke length of 4 mm which can be easily accommodated by this counterbody holder. Further, a pre-load of 20 N is applied for 15-45 min prior to the test to enable better alignment of the contacting surfaces. A sketch showcasing the tribo-pair and parameters (normal load, frequency and geometry) is presented in Fig. 1b. The infused (<94% density) and lubricated (≥95% density) cases are also shown in Fig. 1c and d respectively.

The kinetic friction coefficient or simply referred to as FC in this study is the ratio of applied normal force to the frictional shear force acting on the moving contacting surfaces. The temporal FCs are measured at regular time intervals of 0.16 s. The normal load varied from 10 N to 220 N in the increasing steps of 10 N. The equivalent normal pressures are 0.2 MPa to 6 MPa. The sliding frequency was fixed at 6 Hz in majority of the experiments. In one case, sliding frequencies of 1 Hz, 6 Hz, 12 Hz, 18 Hz and 24 Hz are employed to investigate their influence on the FC. The stroke was fixed at 4 mm and thus the estimated average sliding speeds (\(x \times \text{frequency} \times \text{stroke}\)) are 0.008 m s⁻¹, 0.048 m s⁻¹, 0.096 m s⁻¹, 0.144 m s⁻¹ and 0.192 m s⁻¹ respectively. The maximum sliding speeds \((V_{\text{max}})\) in the sinusoidal movement are estimated using the equation \(V_{\text{max}} = \pi \times \text{frequency} \times \text{stroke}\) and are 0.012 m s⁻¹, 0.075 m s⁻¹, 0.15 m s⁻¹, 0.226 m s⁻¹, 0.301 m s⁻¹ respectively.

The friction tests were conducted in a controlled environment (RH = 30 ± 5%, temperature = 30 ± 2 °C). To estimate the wear rates, the specimens were weighed prior and post sliding tests using a precision balance (precision of 10⁻⁴ g). Friction and wear tests were repeated on two to three specimens from each densification for as-sintered and polished \(\text{Al}_2\text{O}_3\).

2.5. Microstructural characterizations

The pore neck diameters and their distributions were estimated using mercury porosimetry. Hg was intruded into the open porous networks of cylindrical shaped \(\text{Al}_2\text{O}_3\) specimens by increasing the pressure from 0 MPa to 200 MPa in a Pascal 440 (Germany) porosimeter. These measurements were repeated for three specimens from each density displaying excellent reproducibility. Scanning electron microscope (SEM) (Hitachi S4800) was used to characterize the microstructures of the sintered, polished and
worn specimens in secondary electron (SE) mode with 1.5 kV voltage, 10 μA beam current and working distance of 4–5 mm. These morphological investigations were carried out on at least five specimens for each densification and show high reproducibility. The miller indices of sapphire single crystal discs were obtained from Electron Back Scattered Diffraction (EBSD) measurements by employing 15 keV energy and a specimen tilt of 70° on three regions of the specimen. The hardness values were measured with a Vickers indenter by employing 0.1 kgf load for a dwell time of 30 s. To realize the scatter, hardness tests were conducted on ten locations of each specimen and three specimens from each density.

3. Results and discussion

3.1. Pore network and surface microstructures

The optimized sintering temperatures were 1150 ± 5 °C, 1205 ± 5 °C, 1250 ± 5 °C, 1320 ± 10 °C and 1500 ± 10 °C to yield relative densities of 70 ± 3%, 80 ± 3%, 90 ± 3%, 95 ± 1% and 99.5 ± 0.5% respectively. A graphical presentation of the same is shown in Fig. 2 a wherein the relative density increases (i.e. porosity fraction decreases) continuously up to ~1300 °C, and beyond that only a sluggish change was observed. The total RD, OP and CP are listed for each density in Table 1 and are also plotted in Fig. 2 b.

It is clearly evident from Table 1 that for 70%, 80% and 90% dense specimens, the OP fraction decreases with an increase in the densification while similar CP fractions are observed, thereby decreasing the ratio of \( \frac{OP}{CP} \) with increase in density. However, for 95% dense specimens, the amount of CP is significantly increased as compared to that of low dense specimens and is also much higher than its own OP fraction. This means that there is a significant transformation in the microstructures beyond 1300 °C. The SEM images of the sintered specimens are presented in Fig. 2d-h for varying alumina densities to showcase decreasing porosity fractions and increased grain diameters. Specimens with 70–90% density possess open porous networks as well as ultrafine grains and narrow grain size distributions. On the other hand, 94–99.5% dense specimens do not have significant connected porous networks and have larger grain diameters. In 95% dense specimens, the grains remain equiaxed while in 99.5% dense specimens, the grains exhibited anisotropic growth and have rod like structures.

The average grain diameters for 70–99.5% dense as-sintered alumina specimens obtained from the statistical treatment of several SE-SEM images (measured for 100 grains) are plotted in Fig. 2i along with the starting primary particle size in the alumina powders. The average grain sizes for 70%, 80% and 90% dense specimens are 150 ± 50 nm, 107 ± 25 nm, 134 ± 36 nm respectively revealing no major grain growth. However, an increase in the grain size can be observed for 94% dense specimens to 330 ± 140 nm. Further, grain growth becomes pronounced in 99.5% dense specimens and the grains are no longer ultrafine as they exhibit an average grain size of 1005 ± 805 nm. Such grain growth is common in sintered alumina and often reported in literature [55–57].

In order to estimate the pore neck diameters (\( d_p \)) and their distributions, Lucas-Washburn’s equation (Eq. (3)) [58] was employed. We assume cylindrical porous channels and the estimated distributions of pore diameters are presented in Fig. 2c for 70%, 80% and 90% dense Al₂O₃. For higher densities, Hg could not be intruded as the OP fraction is very limited. The pore size distributions are unimodal and narrow. The average pore neck diameters are 47 ± 12 nm, 34 ± 10 nm and 25 ± 7 nm for 70%, 80% and 90% dense specimens respectively.

\[
d_p = \frac{4\gamma_l \cos \theta}{P}
\]

where \( P \) is the intrusion pressure, \( \gamma_l \) is the surface tension of Hg (485 mN·m⁻¹) and \( \theta \) is the contact angle of Hg with Al₂O₃ (140°).
Prior to carrying out the sliding friction tests, all the specimens and their counter bodies were finely polished as described in the Section 2.3. The microstructures of the 70–99.5% dense polished Al₂O₃ specimens are presented in Fig. 3 (a-e). For 70–90% dense specimens, the microstructures look very similar. They comprise of relatively flat regions (referred to as debris compacted regions) which seem to be homogeneously distributed all over the surface. These debris compacted regions seem to be a resultant of polishing process which is an abrasive type of wear. This is similar to a tribo-sintering process wherein the produced debris may have been compacted and sintered to the surface. In some cases, it is only partially sintered leaving extremely small pores (<5 nm) as evident from debris compacted regions in Fig. 3 b. This partial sintering is not specific to 80% density specimens but also observed in 70% and 90% densifications at different locations. On the other hand, for 95% dense specimens, surface pores are seen occasionally but majorly appear polished. Further in 99.5% dense, the surfaces are highly polished throughout and no pores were observed.

Since the surface porosity can significantly influence the frictional and wear properties, quantification of the surface porosity was carried out. The area fractions of debris compacted regions were estimated for 70%, 80% and 90% dense specimens from several SEM images using Image J software. The observed mean area fraction is 0.7 for all three densifications. The rest of the surface, i.e. 30% area is not occupied with debris compacted regions. These regions will have surface porosity same as that of their bulk assuming isotropic microstructure implying 9%, 6% and 3% surface nanoporosities for 70%, 80% and 90% dense specimens respectively.

The arithmetic mean roughness (Ra), root mean square roughness (Rq), maximum profile peak height (Rp), maximum profile peak depth (Rv), and average maximum height of the profile (Rz) of 70–99.5% dense polished specimens are measured and graphically presented in Fig. S1, supplementary material. All the roughness parameters indicate a decreasing trend with an increase in the Al₂O₃ density and the lowest values are shown by single crystal sapphire. The ranges of Ra, Rq, Rp, Rv, and Rz are 9–88 nm, 12–115 nm, 27–330 nm, 27–260 nm and 55–760 nm respectively. The Ra and Rq values are in the same range and similarly Rp and Rv values are in the same range. Overall, the roughness values indicate that the surfaces are having nano roughness and are homogeneously polished. Fig. 3f presents a Kikuchi pattern of monocristalline sapphire with major directions indexed. The miller indices are found to be (1 2 11).

### Table 1

| Relative density (RD) (%) | Open porosity (OP) (%) | Closed porosity (CP) (%) |
|--------------------------|-----------------------|--------------------------|
| 70 ± 3                   | 28.7 ± 2.2            | 0.98 ± 0.2               |
| 80 ± 3                   | 19.1 ± 2.1            | 1.0 ± 0.3                |
| 90 ± 3                   | 8.6 ± 1.6             | 0.9 ± 0.5                |
| 95 ± 1                   | 0.9 ± 0.2             | 2.7 ± 0.2                |
| 99.5 ± 0.5               | 0                     | 0.5                      |
| 100 (sapphire)           | 0                     | 0                        |

3.2. Friction coefficients for varying loads and Al₂O₃ densifications

Firstly, temporal FCs were measured for fully dense (99.5% density) polished Al₂O₃ in dry and lubricated conditions for varying
normal loads between 10 N and 220 N (0.2 to 6 MPa), each for 15 min. They are presented in Fig. 4a to evaluate the lubricant’s efficacy. For dry tribo-pair, FC slightly decreases with increase in normal load and reaches a steady state value of 0.185. A two to five fold decrease in FC was observed as compared to those reported in literature (FCs of 0.4 [59] and > 0.9 [60]) owing to five times larger grain diameters in literature (5–10 μm) as compared to the present study (~1 μm, see Fig. 2i). As compared to the dry tribo-pair, lubricated specimens yielded three times lower FC values of 0.07. Similarly, FCs of as-sintered 70% dense dry and oil infused specimens show a decrease from 1.6 (dry) to 0.4 (oil infused) for 60 N normal load (see Fig. S2, supplementary material). Both these studies indicate that Fomblin® oil is an excellent lubricant in reducing the FC of both as-sintered as well as polished Al2O3.

The FCs of lubricated fully dense Al2O3 lie between 0.15 and 1 as reported in literature [19,21–23,27]. Typical lubricants utilized were water (in different modes), isocyanate, polyacrylic acid, liquid nitrogen, paraffin oil and others. The sliding frequencies, normal loads employed are 10–30 Hz and 10–100 N respectively which are comparable to the present study. A comparison of FCs (0.05–0.175) in lubricated specimens from present work with those from literature suggests that Fomblin® oil outperforms all the conventional lubricants.

In order to evaluate the effects of running-in stage on FC in these tribological systems, the sliding wear tests were conducted by applying constant loads of 50 N or 80 N or 200 N for the entire duration of sliding (1 h or 3 h). Fig. 4b displays a FC curve of 70% dense as-sintered specimen for an applied normal load of 80 N. A pre-load of 20 N is applied for 15 mins to aid the alignment of surfaces in motion. FC exhibits a constant value of 0.26 for the total 3 h sliding time. This indicates a very small running-in stage (typically < 5 mins). To further verify, we performed two tests with sister specimens (90% dense, as-sintered) where one is subjected to regular step-wise increase in load (10 to 100 N) and another is treated with step-wise decrease in load (100 to 10 N). The corresponding FC curves are presented in Fig. 4c. They reveal an excellent overlap for all the varying loads except for 10 N.

Such a precise reproducibility of the FCs has encouraged us to conduct sliding tests by steadily varying the normal load (10 N to 220 N) to inquire its influence on FC. These are crucial as normal load was reported to play a pronounced role in affecting the FC of lubricated systems [27,31]. The counter bodies for these experiments are polycrystalline Al2O3 with the same density as that of the bottom specimen but kept dry i.e. un lubricated/uninfused (see Fig. 1c-d). On the other hand, dry diamond was utilized as a counter body for monocrystalline sapphire. A pre-load of 20 N was applied for 15–45 mins for better alignment of the surfaces (FC data excluded). The sliding frequency and stroke are fixed at 6 Hz and 4 mm respectively resulting in an average sliding speed of 0.048 m.s⁻¹ and sliding distance (2 × frequency × stroke × time) of 0.95 km.

Fig. 5a displays the temporal variation of the FC data of 70%, 80%, 90%, 95% polycrystalline oil infused/lubricated polished Al2O3 and monocrystalline sapphire as a function of load. The reproducibility of these tests were studied by using two or three tribo-pairs of the sister specimens and the FC data are presented in Section S4, supplementary material. In the majority of the cases, a very good reproducibility is shown. Nevertheless, in 90% dense specimens and sapphire, the FC values are not very reproducible. This is due to the lack of control on the oil film thickness on the specimen surfaces due to manually blowing away the excess using N2 gas (refer to Section 2.4). Additionally, the capillary forces that the oil gets subjected in different densifications are different as the pore fractions, pore diameters and surface roughness are different. This also led to different dynamic evolutions of film thicknesses during the sliding. Further studies are needed to precisely coat the film thickness on the porous surfaces. Focusing on Fig. 5a which presented lower FC curves, we can observe that FCs have continuously decreased and stayed constant with an increase in the normal load for 70%, 80% and 95% dense specimens. However, for both 90% dense oil infused Al2O3 and lubricated sapphire, FC initially decreased for increase in the load up to ~120 N followed by an increase for further increase in the load up to 220 N.

When load ≤110 N, the decreasing order of FC as a function of Al2O3 density is 70% > 80% ≈ sapphire > 95% > 90%. This is one of the key outcomes of this work which unleashes the high potential of nanoporous oil reservoirs in 90% dense specimens to yield the lowest FC (0.13) even smaller than that of sapphire (0.14). In turn, this outcome indicates that optimal frictional properties are obtained with infused specimens (90% dense) as compared to lubricated ones (95% dense Al2O3 and sapphire) discovering novel high impacting tribological systems for several applications. How-
ever, for normal loads of >110 N, sapphire and 90% dense specimens compete in yielding low FC.

Wear-resistance of unpolished and intrinsically rough surfaces are crucial for superhydrophobicity \[61\], anti-icing \[54\], anti-fouling \[53, 62\] and for mating parts in compressors \[63\]. Moreover, Fomblin® C210 oil molecules (width = 0.8 nm, length = 2–8 nm) \[64, 65\] may find it difficult to permeate through these very fine pores (≤5 nm) present in the debris compacted regimes of polished specimens (see Fig. 3b). This is because Fomblin® oil molecules approach the pore diameters and could slip at pore wall (unpublished data). Also, as quantified in Section 3.1, the effective amounts of surface nanoporosity are 9%, 6% and 3% only in 70%, 80% and 90% dense specimens. Consequently, polished specimens lose some effective oil reservoirs. Therefore, friction tests of as-sintered specimens were also performed in addition to polished ones and FCs curves are summarized in Fig. S3, supplementary material.

A comparison of the FCs of as-sintered specimens with their as-polished specimens reveal only minor differences. For instance the steady state FC of 80% dense as-sintered and as-polished

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**Fig. 4.** Temporal variation of the FCs of (a) dry and oil lubricated 99.5% dense polished Al₂O₃ specimens for varying normal load, (b) 70% dense oil infused Al₂O₃ at a constant load of 80 N with a 20 N pre-load, (c) 90% dense as-sintered oil infused specimens for increasing and decreasing normal loads.

**Fig. 5.** FC data of (a) oil infused/lubricated 70%, 80%, 90%, 95% dense polished Al₂O₃ and single crystal sapphire, (b) 90% as-sintered and polished specimens for a comparison, (c) self-mating 95% lubricated pair.
specimens are 0.25 and 0.21 (compare Fig. S3, supplementary material and Fig. 5a) respectively. Similarly, the FCs of 90% as-sintered and polished Al₂O₃ reveal a difference of only ~0.07 (see Fig. 5b). This is because 90% polished specimens have lower surface porosity (3%) as compared to their as-sintered specimens (10%, see Table 1). Also, the polished specimens have lower roughness as compared to their as-sintered specimens. This can imply that decreased surface roughness compensates to a greater extent the effect of diminished surface nanoporosity on the FCs.

For normal loads ≤ 80 N (<1 MPa), the trend for FC is 70% > 80% > sapphire > 90% ≈ 95% > 99.5% density in as-sintered specimens (see Fig. S3, supplementary material). It is highly promising that despite their high roughness, oil infused as-sintered 90% dense specimens have generated lower FC (0.2) than smooth lubricated sapphire discs (FC of 0.21). Nevertheless, 99.5% density is the optimum (FC of 0.19) owing to their lower roughness. Furthermore, for loads of 140–220 N (1.5–2 MPa), FC follows the order: 80% > 95% ≈ 99.5% > 90% > sapphire. Although, monocrystalline sapphire exhibited the lowest FC, 90% dense Al₂O₃ shows optimum among polycrystalline as-sintered ones.

The reasons that yield 90% density as an optimum are explained here. Among 70%, 80% and 90% densifications, the latter ones have lower surface roughness (Fig. S1, supplementary material), higher hardness (Fig. 7) due to increased grain to grain necking (compare Fig. 2e and f). Therefore, intuitively 90% dense specimens will have relatively lower FC values as compared to the two former ones. On the other hand, specimens with >90% density do not contain strong open pore network (Fig. 2b), which diminishes the continuous lubricant supply by capillarity. Also, grain growth is pronounced for densities >90% (Fig. 2i) and it is known that bigger grain sizes can lead to higher FCs [42].

In addition to the above experiments where counter bodies are dry, selected measurements were performed in self-mating condition i.e. counter body is also lubricated. A lowest FC of 0.025 is demonstrated by oil lubricated 95% dense self-mating pair (see Fig. 5c). This FC is two times smaller than that of 99.5% dense tribo-pair (FC of 0.05, see Fig. 4a) due to difference in grain sizes and morphologies. Similarly, this is smaller than that exhibited by 90% dense tribo-pair (FC of 0.2, see Fig. S5). Also, FC of 0.025 is eight times smaller than the corresponding tribo-pair wherein only bottom specimen is lubricated (FC of 0.2, see Fig. 5a) as the lubricant film thickness could be relatively higher in the self-mating condition.

3.3. Influence of sliding frequency and oil viscosity on friction coefficients

It is well-known that variation in the sliding speed affects the FC [42,66]. From the earlier presented FC data, it was observed that 90% density is the optimum among all densifications. Therefore, the effect of sliding frequency (6 Hz and 24 Hz) on the frictional behavior was evaluated for 90% dense oil infused as-sintered Al₂O₃ and presented in Fig. 6a. One can conclude that an increase in the sliding frequency from 6 Hz to 24 Hz does not show a significant influence on the overall frictional behavior. Similarly, FCs were measured for 95% dense oil lubricated polished (instead of as-sintered) specimens wherein frequencies of 1 Hz, 6 Hz, 12 Hz, 18 Hz and 24 Hz (0.008, 0.048, 0.096, 0.144, 0.192 m s⁻¹ average sliding speeds) were employed for different loads of 50 N, 100 N and 200 N. The FCs for 6 Hz at 50 N, 100 N and 200 N loads are 0.212, 0.190 and 0.177 respectively (see Fig. 6b) and match closely to 0.204, 0.194 and 0.193 as reported in Fig. 5a (6 Hz) indicating a good reproducibility especially at lower loads. Overall, a decrease in the FC for increase in the sliding frequency is observed and this effect is more pronounced at higher loads. Both these experiments reveal that sliding frequencies tend to impact the FC strongly on smoother surfaces as compared to rougher surfaces.

In order to study the influence of viscosity on the FC, the bottom oil infused specimen in the tribo-pair has been heated to a higher temperature of 100 °C. The viscosity of the oil decreased from 289 mPa s (at 30 °C) to 19 mPa s (at 100 °C). A clear and constant increase (of 0.05) in the FC was observed (Fig. 6c) at almost all loads due to decrease in the film thickness at the moving surfaces thereby increasing the solid–solid contacts.

To identify the lubrication regime in these composites is non-trivial. Firstly, there are scratches on all the worn surfaces and their
counter bodies except for sapphire indicating that there are local solid–solid contacts. Secondly, the average sliding speeds are maximal of 0.2 m s\(^{-1}\) only and reduced FCS are observed for increase in the average sliding speed. Thirdly, FC decreased with an increase in the oil viscosity. These three reasons can hint that the contacting surfaces are in mixed lubrication regime of the Stribeck curve. On the other hand, FC majorly decreased with increase in the normal load for most specimens except for 90% dense Al\(_2\)O\(_3\) and sapphire, which is contrary to that expected in the mixed regime of Stribeck curve. Some reasons for such abnormal behaviour are explained as follows.

To begin with, such similar decrease in the FCs was reported for paraffin lubricated fully dense Al\(_2\)O\(_3\) but constant FC values were reported under water lubrication [31] with increase in the normal load. Fomblin\(^\text{®}\) oil is a long chain molecule with dimensions of 0.8 nm width and 8 nm length [64,65] while paraffin and water molecular dimensions are 0.4–1 nm [67] and 0.25 nm [68] respectively. The relative order of wetting/adhesion with Al\(_2\)O\(_3\) is Fomblin\(^\text{®}\)/C\(_2\)10 > paraffin > water. Therefore, the initial film thicknesses are in the order Fomblin\(^\text{®}\)/C\(_2\)10 > paraffin > water. Furthermore, the pressure – viscosity coefficient (\(a\)) values of Fomblin\(^\text{®}\) oil, paraffin and water are ~ 4.46 × 10\(^{-8}\) Pa\(^{-1}\) [69], 1.5 × 10\(^{-8}\) Pa\(^{-1}\) [69] and 0 Pa\(^{-1}\) [70] respectively. Barus law can predict the viscosity (\(\eta\)) at a pressure (\(P\), in Pa) and mathematically expressed by Eq. (4) [70].

\[
\eta = \eta_0 e^{aP}
\]  
(4)

where \(\eta_0\) is viscosity at atmospheric pressure.

Plugging in \(\eta_0\) as 288 mPa s, 32 mPa s and 1 mPa s for Fomblin\(^\text{®}\), paraffin and water respectively and employing Eq. (4), the corresponding viscosities at 6 MPa are 376 mPa s, 35 mPa s and 1 mPa s. Increased viscosity for Fomblin\(^\text{®}\) oil at higher normal pressures can therefore contribute to the lowering in FC values due to decreased solid–solid contacts. Also, the presence of the nanopores can contribute to the lowering in FC values with increase in load. This is because surface cavities or pores exert higher hydrodynamic pressure on the sliding surfaces [71,72,39]. Consequently, higher film thicknesses are achieved and result in decreased FCS. Furthermore, it can be hypothesized that high normal pressures could also increase the capillary suction of the oil into the unfused counter bodies. Thus, film thicknesses could be increased and reduce the solid–solid contacts.

Briefly, these nanoporous networks are efficient oil reservoirs and therefore 90% density yielded the lowest FC as compared to other densifications. The combination of average pore diameters, pore size distributions, pore fraction and surface roughness in 90% densification seems to be optimum as compared to that of 70% and 80% densifications. Indeed, we have earlier proposed that the microstructural ratio \(\frac{\text{Alumina Volume}}{\text{Gas Void Volume}}\) seems to qualitatively predict the FC trend in these Al\(_2\)O\(_3\) specimens [43].

3.4. Wear rates

Archard’s wear equation can estimate the total wear rate (Q, in mm\(^3\) m\(^{-1}\)) i.e. volume removed per sliding distance and mathematically expressed by Eq. (5) [73]. The pre-factor (K) is a dimensionless constant called wear-coefficient which is always less than one [73]. The ratio (K/H) is called the dimensional wear-coefficient or specific wear rate. \(F_N\) is the applied normal load (in N) and H is the hardness of the softer contacting surface.

\[
Q = \frac{KF_N}{H}
\]  
(5)

The weight differences of the specimens prior and post sliding tests were measured using a high precision weighing balance having a readability of 10\(^{-4}\) g. The density of fully sintered Al\(_2\)O\(_3\) was used while estimating the volume of the wear debris. Dividing this volume with sliding distance gives Q. Using this Q and Eq. (5), the dimensional wear-coefficient (K/H) and dimensionless wear-coefficient (K) are estimated for all the tribo-pairs by using the Vickers hardness (HV\(_{0.1}\)) values and are graphically summarized in Fig. 7(a-b).

It is evidently seen that dimensional wear-coefficient (K/H) show a decreasing trend for an increase in the Al\(_2\)O\(_3\) density (Fig. 7a). The Vickers hardness data is superimposed to show an increasing trend for the increase in alumina density primarily due to a decrease in the pore fraction despite a grain growth beyond 90% densification (see Fig. 2). The specific wear rates in 70%, 80% and 90% dense specimens lie between 10\(^{-5}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) and 10\(^{-6}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) revealing mild wear and show a decrease with increase in the alumina density. However, for 95% and 99.5% dense specimens, the wear is very low (<10\(^{-7}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) i.e. could not be detected by weighing balance employed (precision of 10\(^{-7}\) g). There are two major influencing factors for this wear rate trend, which are the microstructure (OP fraction, pore diameters, tortuosity of the network, CP fraction, grain sizes) and the Vickers hardness. The amount of OP decreased with increase in alumina density up to 95% after which it is totally closed porosity. However, the amount of CP has been steady until 90% densification and increased strongly following that (see Fig. 2b). The average pore diameters and distributions for 70% and 80% densifications
are similar. However, for 90% densification, the average pore diameters are smaller and distribution shifted to the left (see Fig. 2c). These open porous networks and ruptured closed pores at the surface act as lubricant reservoirs during the sliding. On the other hand, the Vickers hardness is continuously increasing as the alumina density increased from 70% to 99.5% (see Fig. 7a, right y-axis).

In order to de-convolute the effect of hardness and porosity, the dimensionless wear-coefficients trend can be used (see Fig. 7b) which show a maximum for 90% dense tribo-pair interestingly. This is because the hardness also depends on the microstructure but not the same way as the wear-rate. For example, wear-rate in unlubricated alumina can be seen to have linear dependence on grain diameters when the data was analyzed from literature [13,60] while hardness has inverse square root dependence as per Hall-Petch equation. Similarly, the effect of pore fractions, pore diameters, tortuosity on the wear-rates and hardness can also be different. 70%, 80% and 90% dense specimens have ultrafine grains and may have enhanced wear-resistance as compared to 95% and 99.5% dense specimens having micron grain diameters [74].

This is in accordance with that reported in literature where increase in the average grain size can reduce the wear-resistance in abrasive wear unlubricated sliding contacts [13,17,18]. Nevertheless, we can see that 90% dense specimens have smaller pore diameters (see Fig. 2c) as compared to 70% and 80% specimens thus decreasing the amount of oil that can be squeezed out by the capillary forces during the sliding. This implies that pore fraction of 10% (OP = 8.6%, CP = 1.4%) and avg. pore diameters (25 nm) in 90% dense specimens are not the optimum in providing high wear-resistance. The optimum pore fractions could be in the range of 20–30 % and avg. pore diameters ~ 35–50 nm which are from 70% and 80% dense specimens. Thus, keeping this in mind, we can consider different initial particle diameters or bimodal or trimodal size distributions and also optimize the sintering process using double step or multiple steps to control the grain growth kinetics. This can lead to different pore diameters, grain diameters, tortuosity for the same 90% density and thus can decrease the wear-resistance. More studies are needed in this regard for better optimization. The standard deviations in both the wear-rate and wear-coefficient graphs in majority of the specimens are too small and are not visible.

3.5. Wear mechanisms

The worn specimens were heated to 600 °C to evaporate all the oil from the specimens prior to microscopy studies. The wear tracks of 70% dense Al₂O₃ can be seen with naked eyes while that
of 80%, 90%, 95% and 99.5% specimens are not visible. Even the optical microscopy could only reveal a fewer number of scratches but not a distinct wear track in the latter specimens. Fig. 8a presents the collection of representative SEM images of worn regions of 70% dense Al₂O₃. One can see several microscaled scratches. There are also tribo-sintered regions where the grains from the debris and also from the surfaces are sintered due to the local high heat and pressure during sliding. This results in flat and polished regions locally surrounded by porous regions that are intrinsic of the specimen’s microstructure. In unlubricated Al₂O₃, it was reported that these tribosintered films can be as thick as 6 μm [75]. Additionally, there are micro debris generated and chunks of them are visible which can be as big as 50 μm. There are no evidences of nano debris in this specimen which could have been generated from chipping of the grains. The debris are often bigger than the grain diameters of the specimen. This could be because in 70%, 80% and 90% dense specimens, the grain boundaries are weaker as compared to the grains as only partial sintering has occurred and therefore the predominant mode of crack propagation would be at the grain boundaries. This hints that the wear has occurred by two and three body (debris being third body) intergranular fracture. The microstructures of worn 80% and 90% dense Al₂O₃ are majorly similar to that of 70% and hence not presented. In 90% dense specimens, there were a few regions (not shown) wherein minute debris particles were observed which are much smaller than the grains indicating the possibility of the transgranular fracture also.

In 95% and 99.5% dense alumina specimens, scratches, cracks and nano debris were observed in SEM as displayed in Fig. 8b and c respectively. The nano debris present hints us that the wear has occurred mainly by transgranular fracture and third body abrasion caused by the formed debris. This means at 90% densification, there occurs a transition from intergranular to transgranular fracture of the grains due to increase in strength of the grain necks with the adjacent ones as the sintering gets completed.

3.6. Roughness measurements

The measured average roughness (Rₐ) of tribo-pairs prior and post sliding tests are graphically summarized in Fig. 9 as a function of Al₂O₃ density. For 70%, 80% and 90% dense specimens, the roughness showed a slight decrease after wearing them. This means that the tribosintered flat regions are influencing the roughness strongly as compared to the scratches and debris generated (refer to Fig. 8a). Nevertheless for 95%, 99.5% dense Al₂O₃, sapphire, a significant increase in roughness is observed. Although they have higher hardness and stronger grain necks as compared to 70–90% densifications, continuous oil replenishment is limited as the open porous network is not present. In 70–90% dense specimens, it was previously demonstrated that oil replenishment at the contacting surfaces is strongly supported by capillarity action [51,52], thus keeping a certain minimum film thickness throughout the test thus reducing the asperity contacts. However for 95–99.5% dense specimens, lubricant can be pushed away laterally during reciprocating sliding. Surface diffusion phenomenon is the rate limiting replenishment mechanism involved in the above case. This process has been shown to be extremely slow [43,51] in these material systems. Similar trends of Rₐ were observed for their respective counter bodies (see Fig. 9b). Large standard deviation in Rₐ values are associated with strong heterogeneity in worn regions as confirmed with electron microscopy investigations.

4. Conclusions

This study demonstrates the design and fabrication of exceptionally durable nanoporous Al₂O₃ lubricant reservoirs with widely varying microstructures comprising of grain sizes from 150 ± 50 nm to 1005 ± 805 nm, total porosity fractions from 0.5% to 30% (i.e. 99.5% to 70% relative densities) and surface roughnesses of 9–88 nm. Overall, FCs exhibited a decreasing trend as a function of Al₂O₃ density as: 70% > 80% > 95% > 99.5% > sapphire ≈ 90%. Thus, it can be deduced that Fomblin® Y 25/6 oil infused nanoporous Al₂O₃ outperform the surface lubricated fully dense alumina.

Furthermore, an increase in the sliding frequency from 1 Hz to 24 Hz led to only a small decrease in the FC (by 0.06). Similarly, a decrease in the lubricant’s viscosity from 289 mPa-s to 19 mPa-s has increased the FC by 0.05. The estimated wear rates (K/H) continuously decreased with an increase in the Al₂O₃ density from 70% to 99.5% and range from 10⁻⁶ to < 10⁻⁸ mm³ N⁻¹ m⁻¹. Nevertheless, the dimensionless wear-coefficients (K) show a maximum for 90% dense specimens and can be attributed to the optimal microstructural features. The wear occurred by intergranular and transgranular fracture modes and a transition from the former to the latter occurred at ~ 90% Al₂O₃ density. Thus, 90% densification shows an optimum for achieving the lowest FCs, optimal self-replenishment and small wear-coefficients thus unleashing the potential of nanoporous oil reservoir network.

FC mainly decreased with an increase in the normal load (10–220 N) and could be due to high-pressure viscosity coefficient of Fomblin® oil. An ultra-low FC of 0.025 was attained for self-mating 95% dense Al₂O₃ at 60 N. Interestingly, as-sintered rough specimens have also demonstrated low FCs, and only differed by a maximum of 0.07 only as compared to that of polished ones. Both the polished and as-sintered liquid infused Al₂O₃ surfaces could be potentially utilized in bearings as well as in anti-icing, anti-fouling and anti-sticking applications.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author contributions

Sriharitha Rowthu conceived and performed all the experiments, analyzed them as well as proposed and developed the scientific discussion. Sriharitha Rowthu has also drafted the manuscript. Pushkar Deshpande performed some of the reproducibility friction and roughness experiments, plotted and analyzed the results as well as participated in the scientific discussion. Adityyan Annamalai has contributed to the literature survey and aided with the referencing and editing a couple of images. Patrik Hoffmann had scientific discussions and corrected the manuscript. All the authors have reviewed and finalized the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The raw data required to reproduce these findings are available to download from [http://dx.doi.org/10.17632/4twskvkg7x.1].

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matdes.2021.109821.

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