Supporting Information

Perfluoropolyether-Impregnated Mesoporous Alumina Composites Overcome the Dewetting–Tribological Properties Trade-Off

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Section S1

Open Porosity (OP) and Closed Porosity (CP) in Mesoporous Alumina Samples

Table S1. Open porosity (OP) and closed porosity (CP) of 70-99.5 % dense mesoporous Al_2O_3 samples

Relative density of Al_2O_3 (%)	**OP (%)**	**CP (%)**	**TP (%)**
70	28.66±2.24	1.4±1.7	30±3
80	19.05±2.14	1.2±2.1	20±3
90	8.62±1.58	1.7±0.9	10±3
95	0.05±0.01	3.2±2.1	5±1
99.5	0	0.5±0.1	0.5±0.1

Section S2

Grain Sizes and Morphology of Sintered 70-99.5 % dense Mesoporous Alumina Samples

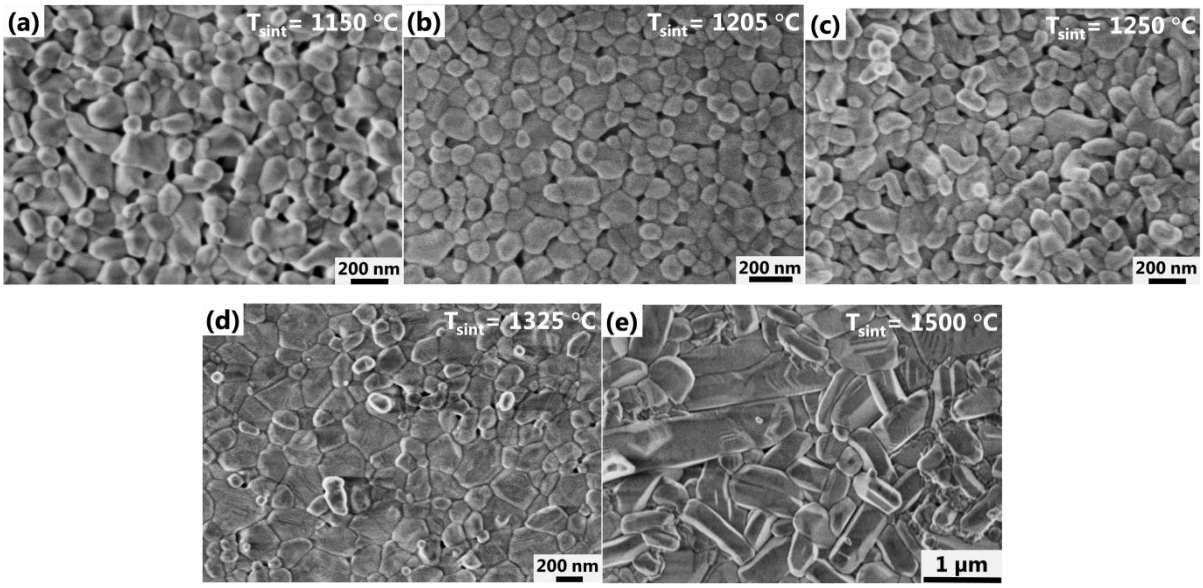

Figure S1. (a-e) SEM pictures of as-sintered Mesoporous Al_2O_3 samples at temperatures of 1150 °C, 1205 °C, 1250 °C, 1325 °C and 1500 °C to yield 70 %, 80 %, 90 %, 95 % and 99.5 % densities respectively.

Table S2. Average grain diameters of as-sintered MPA samples as a function of alumina density

Alumina relative density (%)	Average grain diameter (nm)
70	150±25
80	150±25
90	150±25
95	330±40
99.5	1580±500

Section S3

Roughness (R_a) Measurements of Unworn and Worn Samples

A total of 30 roughness (R_a) measurements were carried out on 3 samples from each densification and the average values are plotted before wear and post wear as a function of Al_2O_3 density in Figure S2.

It can be observed from Figure S2 that for 70 5, 80 % and 90 % dense samples, the R_a values before and after wear are not much different.

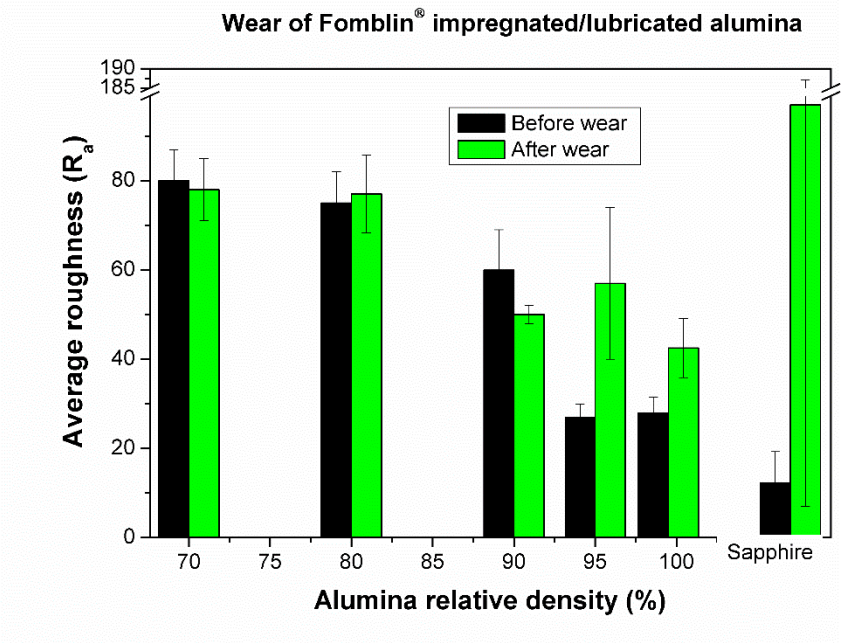

Figure S2. The measured average roughness (R_a) values of 70–99.5 % dense alumina and sapphire samples before and after step-load tribological experiments as presented in Figure 2 of main manuscript.

Section S4

Wetting Evaluations of Worn Samples Immediately After Wear

Hexadecane as the test liquid

In this section, the representative wetting properties of Hexadecane drop atop worn surface of Fomblin® oil impregnated 70 % dense MPA samples are presented, immediately after wear i.e. 5 mins post tribological test. A typical optical image is shown in Figure S3a to indicate a 28° static contact angle (SCA). Similar ranges of SCAs were observed when the alumina matrix density is 80 % and 90 %. For a comparison, an optical image showcasing a 54° equilibrium SCA of Hexadecane drop atop unworn region of the *unflooded* sample prior to wear is indicated in Figure S3b.

Smaller SCA in the worn region immediately after wear indicates an increased area fraction of omniphilic regions of Al_2O_3 that are insufficiently covered by Fomblin® oil. This is why; the Hexadecane drops in the worn regions immediately after wear do not slide even when the sample is turned upside down and resulted in a highly sticky interface.

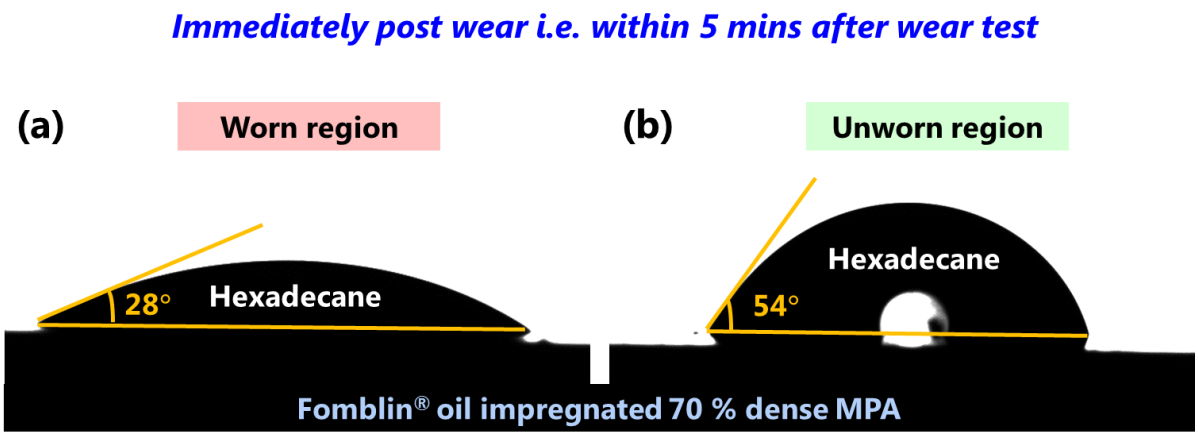

Figure S3. Representative optical images of Hexadecane drops lying atop Fomblin® oil impregnated 70 % dense MPA sample in the (a) worn region immediately after wear i.e. 5 mins post tribological measurement and (b) unworn regions of *unflooded* sample prior to wear

Section S5

Hexadecane SCAs Predictions Using Wenzel's Theory

In this section, the SCAs of Hexadecane drop atop *unflooded* Fomblin® oil impregnated MPA composites are estimated as per Wenzel's theory[1]. In the synthesized *unflooded* Fomblin® oil impregnated/lubricated Al_2O_3 surfaces, the surface chemical heterogeneity was not controlled and therefore unknown. As per Wenzel's theory, the Al_2O_3 roughness and solid fraction in contact with the Hexadecane drop affects the resulting SCAs. Assuming that the Al_2O_3 roughness elements are completely covered by a few monolayers of Fomblin® oil conformally, then Wenzel equation (S1)[1] can be used to estimate the SCAs (θ_w).

$$cos\theta_w = r_w cos\theta_{flat} \quad \text{(S1)}$$

where $\theta_{flat} \approx 45°$ as measured and r_w is the Wenzel wetting roughness which is mathematically expressed by Equation (S2)[2]. The optical profilometer was used to measure the parameter (S_{dr}) which is a ratio of the increment of the interfacial surface area relative to the 2D projected area. Eventually, r_w is mathematically co-related to S_{dr} parameter using Equation (S3).

$$r_w = \frac{True\ area}{Apparent\ area} \quad \text{(S2)}$$

$$r_w = \frac{S_{dr}}{100} + 1 \quad \text{(S3)}$$

For a completely flat surface, the true surface area and the apparent area are the same resulting in S_{dr} = 0 %, which further yields a value of r_w = 1. The practical lateral resolution achievable from optical profilometer is much bigger than the pore sizes (50 nm pore diameters) of MPA samples, and therefore, the pores cannot be revealed by this technique. Basically, the principle of optical profilometry is essentially the formation of interference fringes due to variation in the path lengths travelled by the light in the sample as compared to a reference material. In the case of mesoporous alumina (MPA) samples, which are composite materials comprising air and Al_2O_3 which have refractive indices of 1 and 1.7 respectively. Therefore, the optical path lengths in air and Al_2O_3 vary significantly and may influence the roughness values. Hence, a complimentary technique is necessary to ensure the accuracy of the roughness values. Eventually, Atomic Force Microscopy (AFM) was employed for verification.

The roughness measurements were obtained using ScanAsyst–Air–HR probe (silicon nitride tip with 2 nm radius) in tapping mode using Bruker AFM, USA with 2 Hz scan rate. The typical AFM 2D profiles of the polished 70 % and 95 % dense, polished MPA sample surfaces are presented in Figure S4. The typical scan areas are 35×35 μm^2 and the measurements were repeated on three places of each densification.

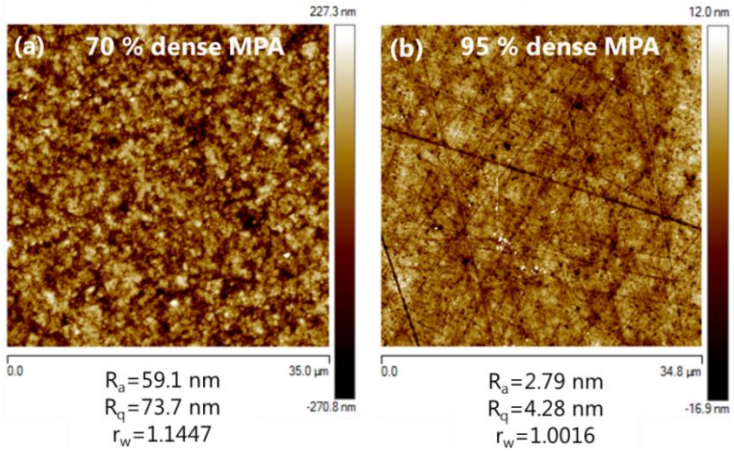

Figure S4. (a–b) Representative AFM images of 70 % and 95 % dense, polished MPA samples are presented along with their roughness (R_a, R_q and r_w) values.

The R_a values of 70 % and 95 % densifications obtained from AFM measurements are 60±5 nm and 3±0.5 nm while that obtained from optical profilometer are 88±14 nm and 38±14 nm respectively. A comparison of the values suggests that the orders of magnitude of the roughness values are similar while using both the techniques. Due to the feasibility to scan large areas (up to several mm^2) and easy access, the roughness measurements for other densifications were carried out using an optical profilometer. We see that predicted SCAs (using r_w values from AFM) of Hexadecane drop atop 70 % dense Al_2O_3 based composite is higher than that of 90 % dense based Al_2O_3 composite as seen from Table S3.

Table S3. Estimated SCAs of Hexadecane drop atop Fomblin® oil unflooded impregnated/lubricated MPA for varying Al_2O_3 matrix density

Relative density (%)	**Roughness (r_w) from optical profilometer**	**Estimated θ_w using r_w from profilometer**	**Roughness (r_w) from AFM**	**Estimated θ_w using r_w from AFM**
70	1.008±0.006	44.5°	1.1447	36°
80	1.014±0.003	44.7°	-NA-	-
90	1.008±0.007	45°	1.0016	45°
95	1.003±0.002	44.8°	-NA-	-
99.5	1.002±0.001	44.9°		

Section S6

Measured ACA, RCS and CAH prior to and post abrasion

Table S4. Measured ACAs, RCAs and CAH of Hexadecane drops atop unworn and worn Fomblin® oil impregnated/lubricated Al_2O_3 samples

Relative Density (%)	Unworn, prior to wear, unflooded configuration			After wear, 15 h self-healed		
	ACA (°)	RCA (°)	CAH (°)	ACA (°)	RCA (°)	CAH (°)
70±3	19±1	8±2	11±2	75±5	40±3	35±4
80±3	20±2	6±2	14±2	63±4	14±4	49±5
90±3	18±2	2±1	16±1	60±3	32±4	28±3
95±1	14±2	4±1	9±2	–NA–		
99.5±0.5	16±1	6±1	11±1			
Sapphire	26±2	7±1	18±2			

Section S7

List of microstructural parameters of Al_2O_3 samples

Table S5. The measured OP, TP, grain diameters (d_{grain}), R_a values of mesoporous Al_2O_3 samples

Relative density (%)	OP (%)	TP (%)	d_{grain} (nm)	R_a (nm)
70	28.66±2.24	30±3	150±25	80±7
80	19.05±2.14	20±3	150±25	75±7
90	8.62±1.58	10±3	150±25	60±9
95	0.05±0.01	5±1	330±40	27±3
99.5	0	0.5±0.1	1580±500	28±3.5
Sapphire	0	0	-NA-	12.3±7

References

(1) Wenzel, R. N. Resistance of Solid Surfaces to Wetting by Water. *Industrial \& Engineering Chemistry* **1936**, *28*, 988–994.

(2) Barbieri, L. Wetting Properties of Flat-Top Periodically Structured Superhydrophobic Surfaces. *PhD thesis, EPFL* **2007**.