

**TRIBOCHEMICAL REACTIONS AT THE WATER-LUBRICATED SILICON NITRIDE INTERFACE:  
GEL FORMATION MECHANISM**

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**ABSTRACT**

Silicon-based ceramics such as silicon nitride can be very effectively lubricated by water under certain conditions (1-3). After a wear-in period a condition of very low friction coefficient (<0.01) can be achieved for average contact pressures of 40 MPa and lower.

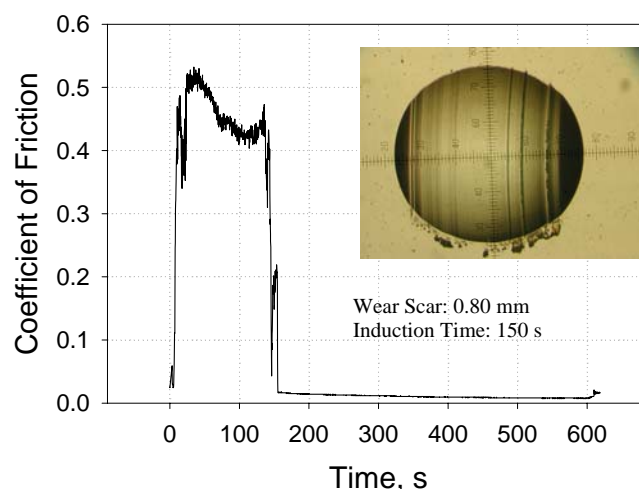
Tomizawa & Fischer (1) proposed a chemomechanical polishing mechanism to reduce surface roughness enabling the onset of hydrodynamic lubrication by water. We suggest that there is an additional soft hydrated silica gel layer adhering to the rubbing surfaces that provides a deformable protective film to enable effective hydrodynamic lubrication of water and protect the surfaces from occasional asperity contacts. The existence of such films was indicated by the nanomechanical data performed on worn surfaces.

**EXPERIMENTAL PROCEDURES**

Ball-on-three-flat (BTF) wear tests were conducted using a gold-coated ball pot to prevent interference from steel contacting the fluid and initiate unwanted tribochemical reactions. Tests were conducted at 600 rpm (0.23 m/s) and 5 kg applied load using silicon nitride specimens and water lubricant. These conditions are sufficient to produce mean Hertzian contact pressures of greater than 0.9 GPa at the beginning of the test, prior to any wear. Water with different pH was used as lubricant and time to achieve tribochemical lubrication (induction time) was measured as well as the wear scar diameter after fixed time periods. The presence of films within the contacting surfaces was observed optically and with AFM. The nanomechanical properties of the films were measured using a Hysitron Triboscope.

**RESULTS**

Ball-on-three-flat wear tests (600 rpm, 5 kg) indicated effective lubrication could be achieved in 150 seconds using de-ionized water with neutral pH (Figure 1). The wear scar was smooth but finely grooved in the direction of sliding and matched complementary grooves in the upper specimen.

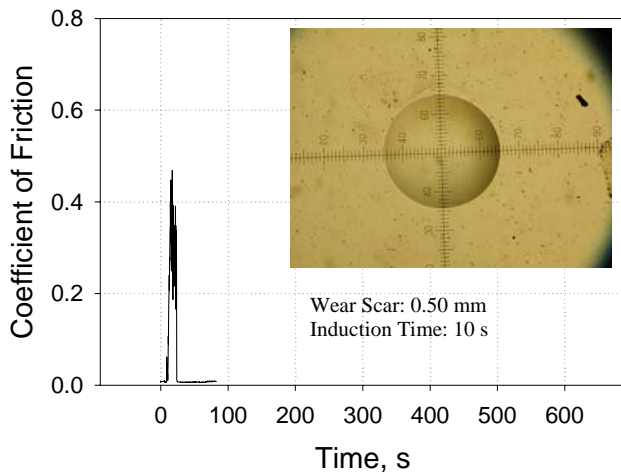


**Figure 1 Water-lubricated silicon nitride BTF test at pH 7**

At the beginning of the test, the friction coefficient is quite high: 0.4 to 0.5. It stays high until about 150 seconds into the test when it suddenly drops down to below 0.01 indicating a sudden change in lubrication mechanism has occurred. Mean pressure at the end of the test is approximately 40 MPa. Water taken from the test leaves a silicon-containing residue after evaporation (from dissolved silica) indicating that tribochemical reactions are taking place in the rubbing contact to create very smooth surfaces:

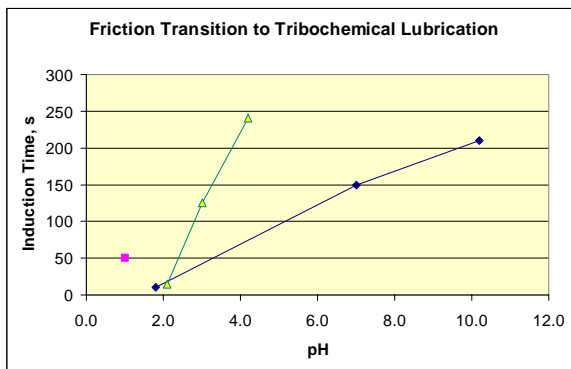
- $\text{Si}_3\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{SiO}_2 + 4\text{NH}_3$
- $\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Si}(\text{OH})_4$

Tests conducted using water at pH 1.8 achieved very rapid effective lubrication as shown in Figure 2. The wear scar was circular in shape, very small and smooth, and did not have the grooving associated with previous tests at pH 7. Mean pressure at the end of the test was estimated at approximately 100 MPa.



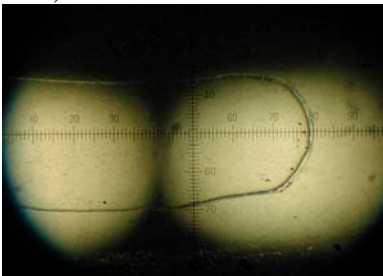
**Figure 2 Water-lubricated silicon nitride BTF test at pH 2**

A series of tests conducted at different pH indicated that optimal performance was consistently achieved near pH 2 (Figure 3) even though three different batches of silicon nitride were used (two hot isostatically pressed and a hot pressed material). This induction time minima corresponds with the isoelectric point for silica and suggests that gel formation may play an important role in the lubrication mechanism.



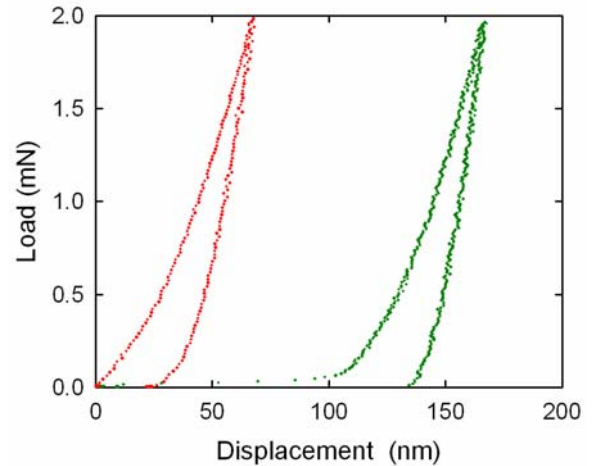
**Figure 3 Tribochemical lubrication induction time for different pH water using three silicon nitride ceramics**

Films could be observed in and around the wear scars for many of the successfully lubricated tests. In one case, for a set of specimens in which the load was reduced under full speed, a film was clearly observed on the upper halo wear scar surface (Figure 4).



**Figure 4 Optical photomicrograph of gel film on upper specimen wear track**

Manual probing of the film indicated it was relatively soft in nature. Nanomechanical property measurements of the films (Figure 5) conducted using a Hysitron Triboscope confirmed the soft, pliant nature of these films. The leftmost, red data set represents a typical indentation curve for silicon nitride. The rightmost, green trace represents an indentation curve for a region at the edge of the wear scar and shows a soft film encountered in the first 100 nm of the indentation. Once through the soft film, the subsurface nanomechanical response is very similar to the silicon nitride.



**Figure 5 Nanoindentation curves for silicon nitride and film on silicon nitride**

Attempts to use suspensions of silica gel in water solutions as “seed” precursors for gel film formation did not significantly improve either the wear-in time or load carrying capacity (as measured by mean contact pressure) of the system. This suggests that the gel film formation must come as an outgrowth from the surface itself in order to be effective.

## CONCLUSIONS

The time required for effective lubrication of silicon nitride ceramics varies with pH. The shortest times were achieved with a pH near 2. At this low pH, effective lubrication could be achieved in 10 seconds or less. We hypothesize that the key tribochemical reactions taking place between water and silicon-based ceramics not only polish the surface asperities, but produce a soft hydrated silica gel layer in-situ. This soft gel layer provides a soft, protective, water-loving surface between the sliding surfaces and allows a functional gradient transition between the hard ceramic surfaces and the liquid water.

## REFERENCES

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