ULTRA-LOW FRICTION COEFFICIENT IN THE SLIDING OF Si_3N_4-Al_2O_3 IN WATER: *AB INITIO* STUDY OF RUNNING-IN*

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Abstract

Tribological behavior of Si_3N_4 balls sliding against Al_2O_3 discs in water was investigated by studying the influence of parameters such as initial surface roughness and circular axial run-out of the discs. The objective was to relate these parameters with the occurrence of the phenomenon known as ultra-low friction coefficient (ULFC), which is characterized by $\mu < 0.01$, including the correlation with running-in duration. As a general trend, greater initial surface roughness and circular axial run-out resulted in greater running-in duration. In addition, it was verified that a mixed lubrication regime (hydrodynamic and boundary) is required to guarantee the occurrence of ULFC by comparing the calculated minimum film thickness with the composite roughness of the worn surfaces. Also, ICQ-OES analysis of the water after the tests indicated that a silicon concentration greater than 1.3 mg/l should be fundamental for the occurrence of $\mu < 0.01$.

Keywords: Ultra-low friction coefficient; Silicon nitride; Alumina; Water lubrication.

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* *Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.*

ISSN 2179-3956

1 INTRODUCTION

Since 1987, when Tomizawa and Fischer [1] estimated friction coefficients (μ) as low as 0.002 during sliding of silicon nitride (Si_3N_4) against itself in water, a lot of scientific and technological interest arose about water lubrication of advanced ceramics. Friction coefficients of that magnitude, obtained during those lubricating conditions, represent low energy loss together with zero environmental impact [2]. In this context, Ferreira [3] defined that $\mu < 0.01$, obtained in steady state, could be called ultra-low friction coefficient (ULFC). Besides self-mated Si_3N_4, ULFC was also observed for self-mated SiC [4, 5] and for unmated Al_2O_3-Si_3N_4 pair [2,3,6-8], during water lubrication.

It is well widespread that tribochemical reactions have a crucial role for the establishment of ULFC regime in water-lubricated ceramics [1,9,10]. However, the identification of the lubrication regime in steady state continues to be controversial amongst the main researchers of the area. In general, some authors [1,11] defend the hypothesis of a purely hydrodynamic lubrication regime, while others [5,9,12] believe that a mixed lubrication regime (hydrodynamic and boundary) occurs.

Furthermore, although more than three decades of research in this area, the running-in period (the transient period preceding the ULFC) remains misunderstood and practically unexplored. This fact is sustained by the complexity of the phenomenon occurring during the initial instants of sliding. Meanwhile, the comprehension of this transient period could, possibly, remedy doubts referring to friction and wear behavior along an entire tribological test [13].

The objective of this work was to perform an initial investigation about the running-in period preceding the ULFC of the Al_2O_3-Si_3N_4 ceramic pair lubricated with water. Running-in characteristics was correlated with Al_2O_3 discs surface roughness and circular axial run-out. In addition, tribochemical reactions were investigated through measurements of silicon concentration (formed during the sliding process) and electrical conductivity of the lubricating water. Finally, wear rates were also measured and reported.

2 MATERIAL AND METHODS

2.1 Material

Ball-on-disc tribological tests were performed. Deionized water was provided by Analytical Chemistry Laboratory (LQA) of the Federal University of Espírito Santo (UFES) and used as lubricant. Characteristics and properties of the samples are presented in Table 1.

Table 1. Characteristics and Properties of the Samples

Material	Geometry	Diameter (mm)	Density (g/cm³)	HV (GPa)	Surface Finish
Si_3N_4	Ball	11.11	3.248 ± 0.001	14.61 ± 0.23	Polished
Al_2O_3	Disc	54.0	3.919 ± 0.024	15.85 ± 0.83	Polished

2.2 Methods

All experiments were performed in the Laboratory of Tribology, Corrosion and Materials (TRICORRMAT) at UFES, using a PLINT TE67 tribometer. Friction force was measured with a load cell with 0.10 N of resolution at a frequency of 1 Hz.

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The lubricating water was pumped to the contact interface through a peristaltic pump in a closed circuit lubricating system.

The samples were cleaned in an ultrasonic bath with acetone during 30 minutes before and after the tribological tests. Worn surfaces were analyzed by optical microscopy and, in the case of the discs, by scanning electron microscopy (SEM, Zeiss EVO 40) and energy dispersive x-ray spectroscopy (EDS). These analyses were made in the Laboratory of Characterization of Materials Surfaces (LCSM) at UFES.

Contact type stylus profilometry (Taylor-Hobson Talysurf CLI1000) of the Al_2O_3 discs wear tracks were performed and, with the projected area of the profiles obtained, the wear volume of the samples was estimated. Diameters of the wear scars of the Si_3N_4 balls were measured with a stereomicroscope (Zeiss SteREO Discovery V12). Then, wear volume of the balls (V) was calculated using Equations 1 and 2.

$$\boldsymbol{h = R - \sqrt{R^2 - r^2}} \quad (1)$$

$$\boldsymbol{V = \frac{\pi h}{6}(3r^2 + h^2)} \quad (2)$$

Where $\boldsymbol{R}$ is the radius of the ball, $\boldsymbol{r}$ and $\boldsymbol{h}$ are the radius and height of the wear scar, respectively.

Surface roughness of the samples was evaluated, before and after the tribological tests, through the Taylor-Hobson profilometer, and the circular axial run-out was measured with a Mitutoyo Absolute ID-S112 model 543-691 digital indicator, with a resolution of 1 µm. The measurement of the circular axial run-out (h_2 - h_1), see Figure 1, was made before each test with the tip of the digital indicator positioned approximately in the region of contact of the ball on disc. The maximum value of h_2 – h_1 of an entire rotation of the disc is the circular axial run-out.

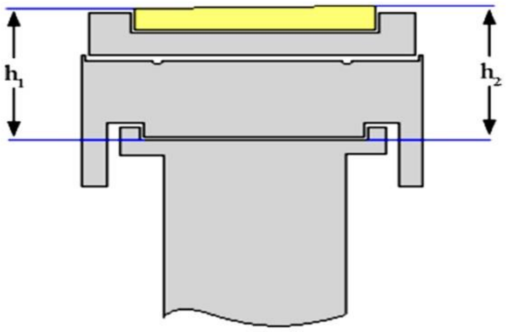

Figure 1. Representation of the circular axial run-out (h_2 – h_1) of the disc after mounted in the tribometer. Grey color corresponds to the components of the tribometer (holders and axis), while yellow color corresponds to the alumina disc [14].

Every test was performed at ambient temperature (25 °C) with a normal load of 34.4 N, sliding speed of 1 m/s, total sliding time of 6000 s and with a total volume of 800 ml of water used for lubrication. Initial surface roughness (R_q) of Si_3N_4 balls was almost constant and equal to 0.025 ± 0.002 µm. The variables of the test were the initial surface roughness of the discs and the circular axial run-out.

Finally, with the objective of quantify the evolution of silicon concentration in water during the tests, the water was collected in predetermined time steps for posterior analysis through inductively coupled plasma optical emission spectrometry (ICP-

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OES) at the Laboratory of Atomic Spectrometry of the Nucleus of Petroleum Chemistry (LABPETRO/UFES). Moreover, for selected tests, the electrical conductivity of the lubricating water was monitored by a BEL Engineering W12D digital bench conductivity analyzer, with a resolution of 0.1 µS/cm.

3 RESULTS AND DISCUSSION

Table 1 resumes the parameter values for each tribological test, remembering that the other parameters remained constant (normal load, sliding speed, temperature, sliding time, volume of lubricant and initial surface roughness of Si_3N_4 balls).

Table 1. Parameter values for each tribological test

Test Number	Initial R_q of the Discs (µm)	Circular Axial Run-out (µm)
1	0.328 ± 0.061	13
2	0.425 ± 0.049	38
3	0.504 ± 0.052	62
4	0.485 ± 0.056	46
5	0.378 ± 0.055	8
6	0.503 ± 0.054	48

Friction coefficient behavior as a function of time, for three distinct tests, is shown in Figure 2. At the beginning of the tests it is possible to note a region of high mean friction coefficient values with oscillations of high amplitude and frequency, which is known as the running-in period or transition regime. This behavior is attributed to high contact pressures generated at the peaks of the asperities due to the mechanical interaction between them [9]. After the running-in period, extremely low friction coefficient values, $\mu < 0.003$, were measured. Friction coefficient of this magnitude for the Si_3N_4-Al_2O_3 tribological pair was already reported in the literature and is called ultra-low friction coefficient (ULFC) [2, 3, 6-8, 14].

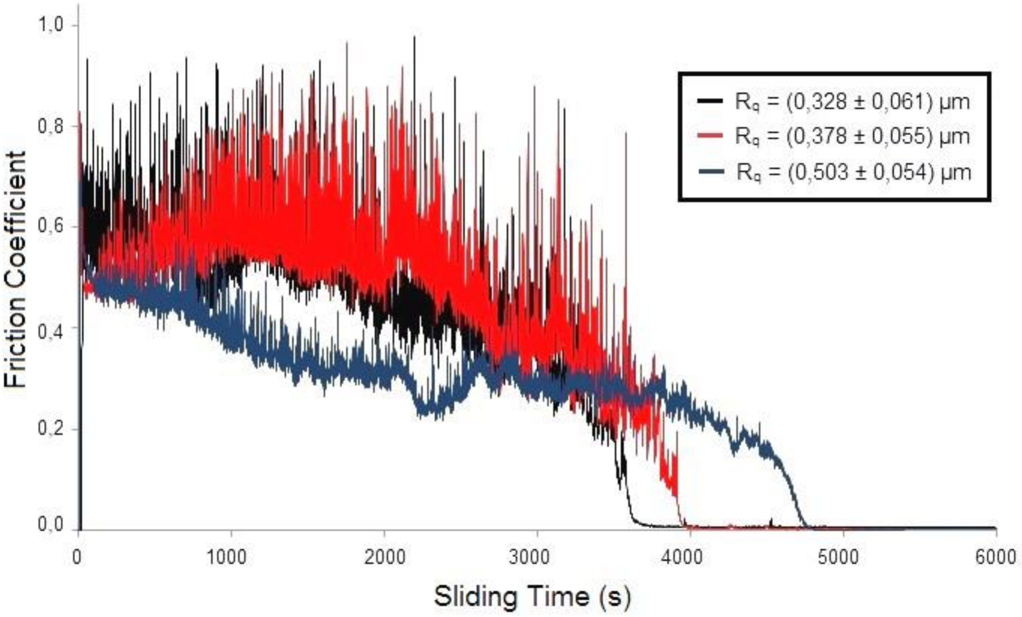

Figure 2. Friction coefficient behavior as a function of time for three different tests.

Also for Figure 2, it is possible to observe that the greater initial surface roughness (R_q) of the discs, the more is the duration of running-in. R_q values versus time of

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transition to steady state regime (or ULFC regime) are showed in Figure 3. There is a tendency of increasing transition time with increasing initial surface roughness of the discs. This result agrees with the literature [3, 17]. One accepted explanation is that smoother surfaces need less time to adjust themselves for an adequate lubrication condition to occur the regime of ULFC. The accommodation of the surfaces intimately related to the tribochemical reactions (wear process) occurring at the contacting asperities. The greater the surface roughness, greater is the Hertzian pressure at the peak of asperities, leading to more wear and reducing the mean contact pressure at the interface that slows down the rate of tribochemical reactions [17].

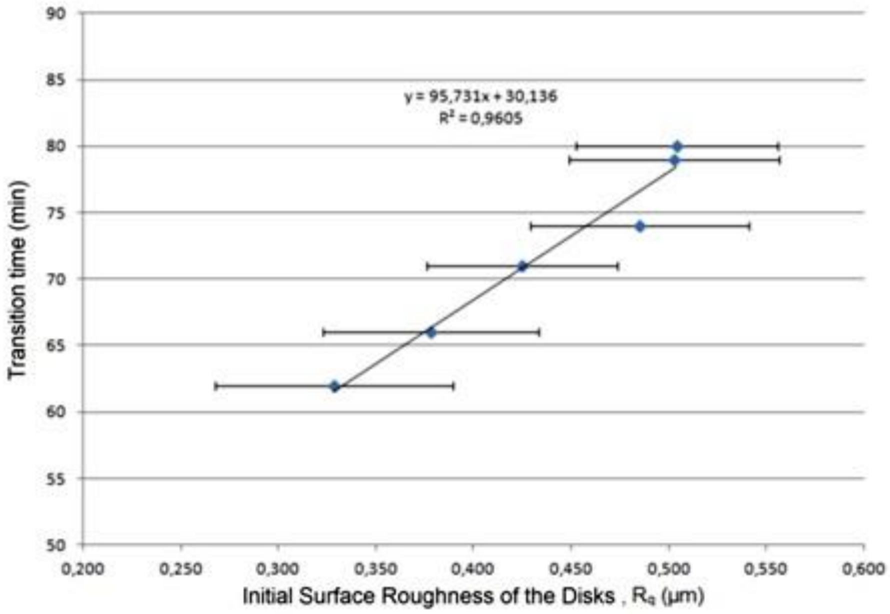

Figure 3. Relation between initial surface roughness of the alumina discs and transition time.

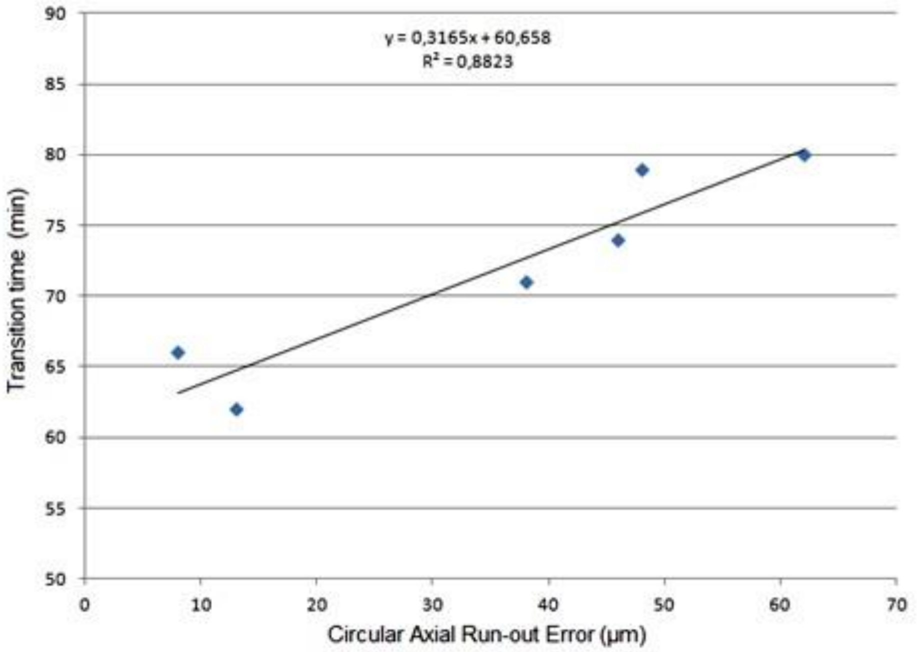

Figure 4. Relation between transition time and circular axial run-out of the alumina discs.

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Another factor that affected the duration of running-in was the circular axial run-out of the disc (Figure 4). It is possible to observe that greater circular axial run-out results in greater running-in duration. This result agrees with Santos [14].

One possible explanation for this behavior is that, for a given rotational speed, the higher the circular axial run-out, greater is the amplitude of vibrations induced in the tribosystem. There is a possibility that these induced vibrations cause oscillations in the contact pressure at the peak of the asperities, which in turn affect tribochemical reaction kinetics, and, as a consequence, disturbs the establishment of the lubricating film (including break-in of the lubricating film). The influence of tribosystem stiffness and vibration was discussed by Antonov *et al.* [15].

The next step of the study was to investigate kinetics tribochemical reactions through the measurement of the evolution of silicon (Si) concentration in the lubricating water. Hydrated silica is expected to form as a result of tribochemical reactions between Si_3N_4 and water, according to the Equations 3 and 4.

$$Si_3N_4 + 6H_2O \rightarrow 3SiO_2 + 4NH_3 \quad (3)$$

$$SiO_2 + 2H_2O \rightarrow Si(OH)_4 \quad (4)$$

Friction coefficient behavior and Si concentration as a function of time for one of the tribological tests are presented in Figure 5. Furthermore, evolutions of Si concentration for two different tests that resulted in $\mu < 0.003$, are shown in Figure 6. In particular for Figure 6, it is possible to note that Si concentration at the end of running-in indicated through letters *a* and *b* is close to 1.3 mg/l. Supposedly, this value is the limit concentration that enables ULFC to occur for the tested operating conditions. For tests where Si concentration remained below this threshold, friction coefficients were one order of magnitude higher than ULFC.

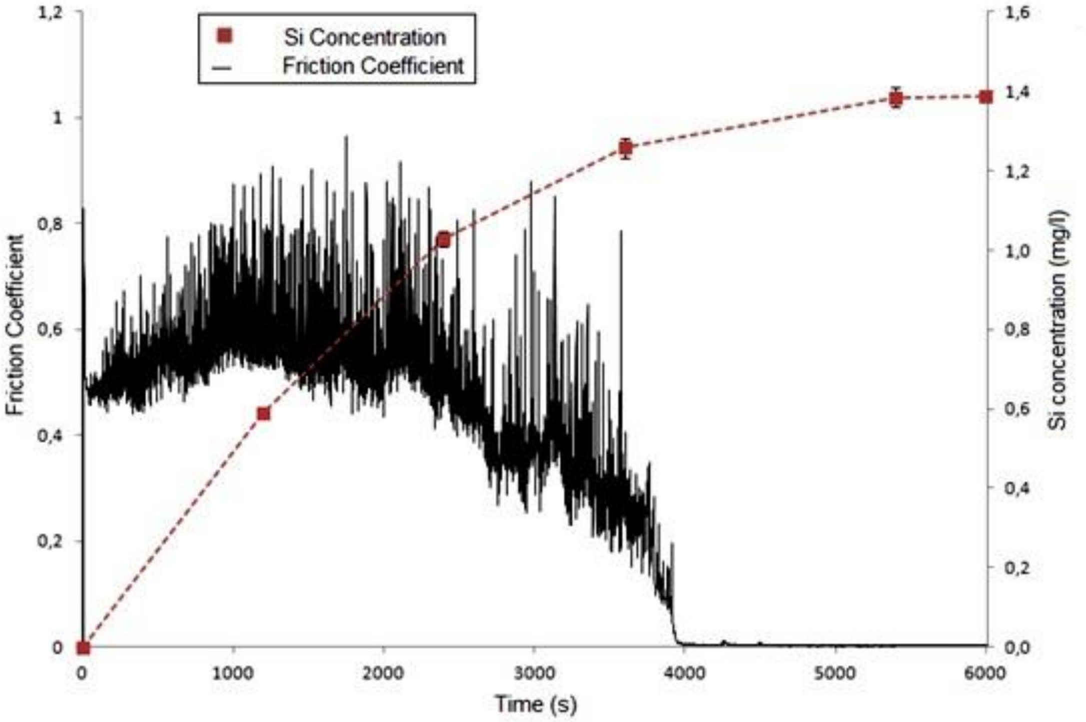

Figure 5. Friction coefficient and Si concentration evolution during one of the tribological tests.

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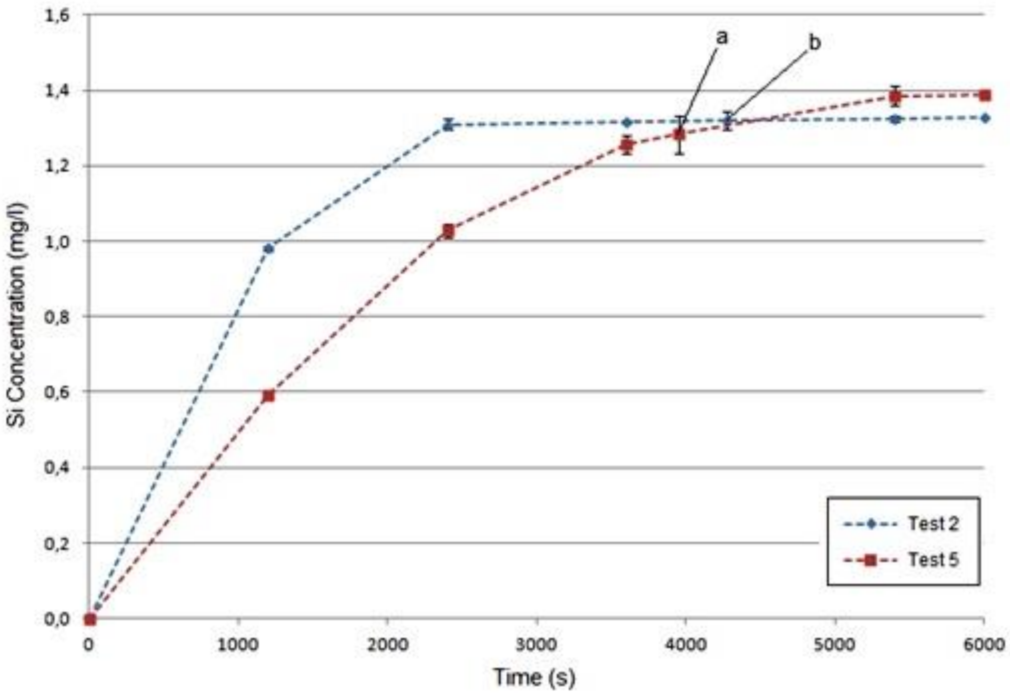

Figure 6. Si concentration evolution as a function of time for two different tests. The points *a* and *b* (obtained by linear interpolation) indicate the Si concentration at the instant of transition to ULFC.

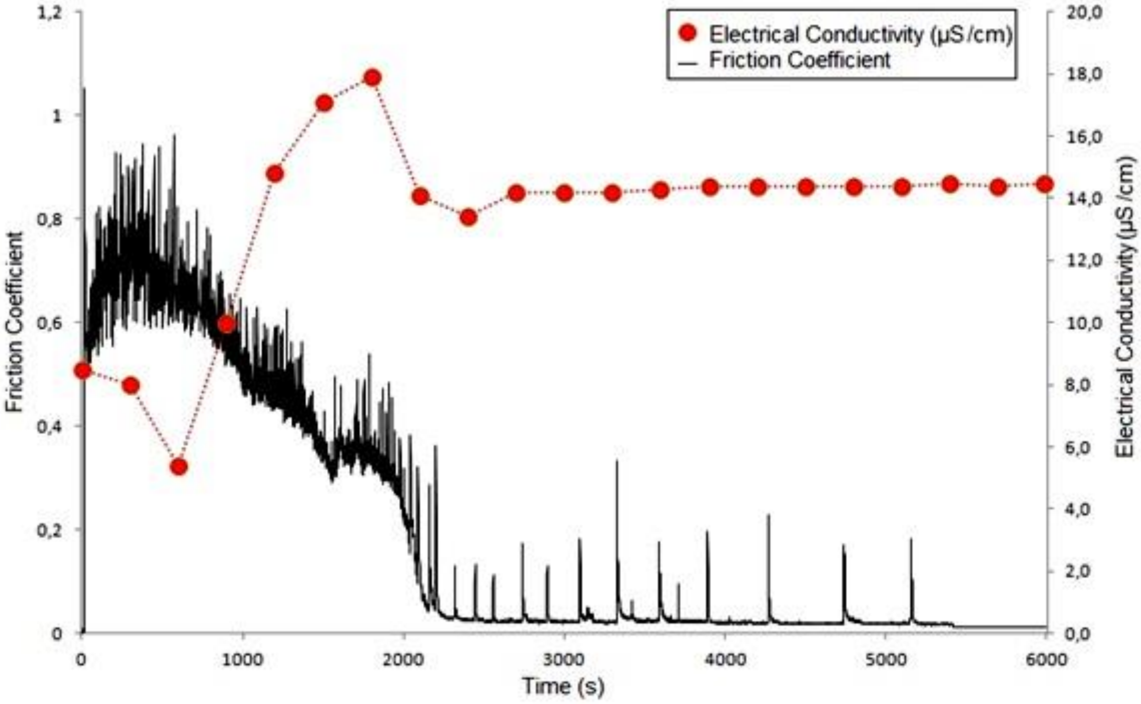

Figure 7. Friction coefficient and electrical conductivity behavior in one of the tribological tests.

When studying SiC sliding against itself, Matsuda *et al.* [5] also measured Si concentration after 3000 m of sliding distance (in the present work it was 6000 m). They found a Si concentration of 0.290 mg/l and confirmed the occurrence of tribochemical reactions. Matsuda *et al.* [5] argued that this Si concentration was responsible for the formation of a tribofilm fundamental in the reduction of friction as well as expected for Si_3N_4-Al_2O_3 unmated pair [2]. The lowest Si concentration found by Matsuda *et al.* [5] in relation to the measured in the present work may be

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associated to the difference in sliding distances as well as the superior reaction rate of the Si_3N_4 in relation to SiC when sliding in water [10,17].

Tribochemical reactions behavior was also investigated through monitoring the electrical conductivity of the lubricating water. According to Xu and Kato [9], the electrical conductivity can be used to estimate variations in the concentration of ions formed during sliding, and, as a consequence, kinetics of tribochemical reactions. Evolution of electrical conductivity during a tribological test is shown in Figure 7. The resulted pattern is similar to that of Xu and Kato [9] for Si_3N_4 sliding against itself.

Despite the consensus of the importance of tribochemical reactions for obtaining ULFC, explanations about the prevailing lubrication regime diverge. Some authors [1,11] attribute this phenomenon to an establishment of a purely hydrodynamic lubrication regime associated with the formation of extremely smooth surfaces, while others [5,9,12] defend the hypothesis of a mixed lubrication regime resulted from the formation of smooth surfaces (responsible for the hydrodynamic parcel) and a soft tribofilm of highly hydrated silica that confers boundary lubrication characteristics.

As a method to verify the regime of lubrication, equations proposed by Jordi *et al.* [11], using classical Reynolds equation for 1D bearing, were utilized to estimate the minimum film thickness of lubricant for the particular geometry of contact observed in this work (circular planar surface sliding against planar surface). In the present work, calculated minimum film thickness ranged from 0.270 to 0.290 µm. By comparing these values with values of composite surface roughness after tests, calculated according to Equation 5 and presented in Table 2, it is possible to conclude that the hydrodynamic film does not separate completely the surfaces because each calculated composite surface roughness is higher than the estimated minimum film thickness of lubricant. Therefore, a mixed lubrication regime is necessary for reaching ULFC for the Si_3N_4-Al_2O_3 tribological pair sliding in water for the tested operating conditions.

$$\boldsymbol{R_{q,composite}} = \sqrt{\boldsymbol{R^2_{q,disc}} + \boldsymbol{R^2_{q,ball}}} \qquad (5)$$

Table 2. Roughness values (R_q) measured (or calculated) after each tribological test

Test Number	R_q of the Discs (µm)	R_q of the Balls (µm)	Composite R_q (µm)
1	0.317 ± 0.099	0.0241 ± 0.0018	0.318 ± 0.099
2	0.383 ± 0.099	0.0294 ± 0.0029	0.384 ± 0.099
3	0.404 ± 0,110	0.0244 ± 0.0032	0.405 ± 0.110
4	0.314 ± 0.073	0,0220 ± 0.0025	0.315 ± 0.073
5	0.328 ± 0.092	0.0251 ± 0.0031	0.329 ± 0.092
6	0.335 ± 0.061	0.0263 ± 0.0024	0.336 ± 0.061

By confronting Tables 1 and 2, a diminution in surface roughness of the discs is noted. This result agrees with some works in the literature, e.g. [1,3,9]. According with several authors [9,10,12,16,17], that as the sliding distance increases, the wear mode changes from mechanically dominated wear to tribochemically dominated wear and the surface smoothening is a result of the tribochemical wear which has a fundamental role to obtained the steady-state friction coefficient of mean value in the range of 0.001.

Finally, wear rates are shown in Figure 8. Wear rates for Si_3N_4 balls were about three times higher than for Al_2O_3 discs. Other authors [2,3,6,7,8,14] observed the same trend for this tribological pair. One possible explanation is the geometry of the test that favors wear of the Si_3N_4 balls. The ball contacts continually the rotating disc while for the disc, for a given point on its wear track, the contact is intermittent.

Figure 9 shows SEM images of a wear track from one of the Al_2O_3 discs. Smooth regions are observed, characteristic of tribochemical wear mechanism [9]. SEM images obtained by Xu and Kato [9] and Chen *et al.* [17] for self-mated Si_3N_4 sliding in water also show smooth worn surfaces attributed to dominant tribochemical wear in the regime of low friction.

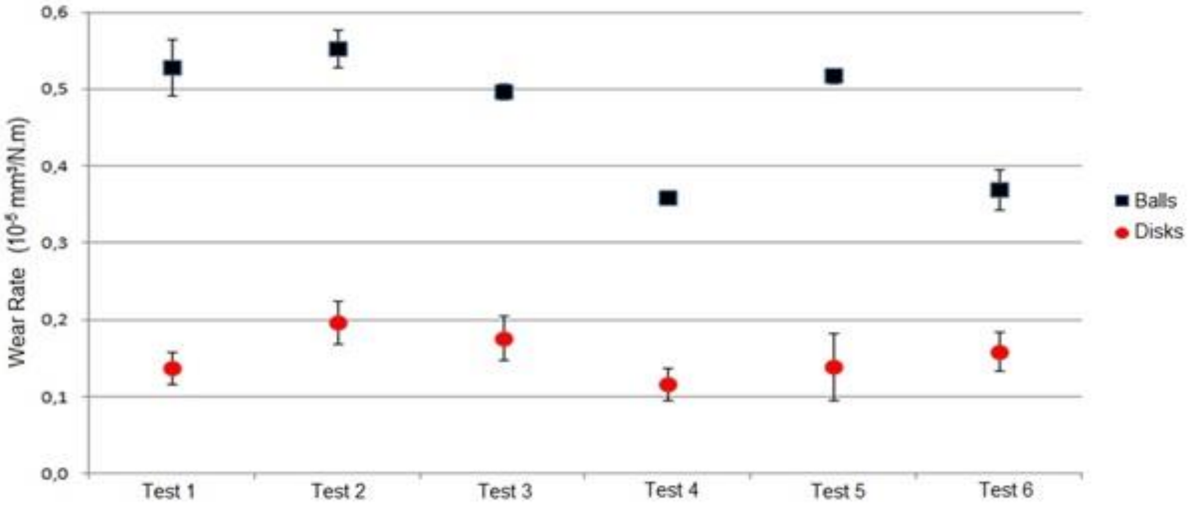

Figure 8. Wear rates for Si_3N_4 balls and Al_2O_3 discs for each tribological test.

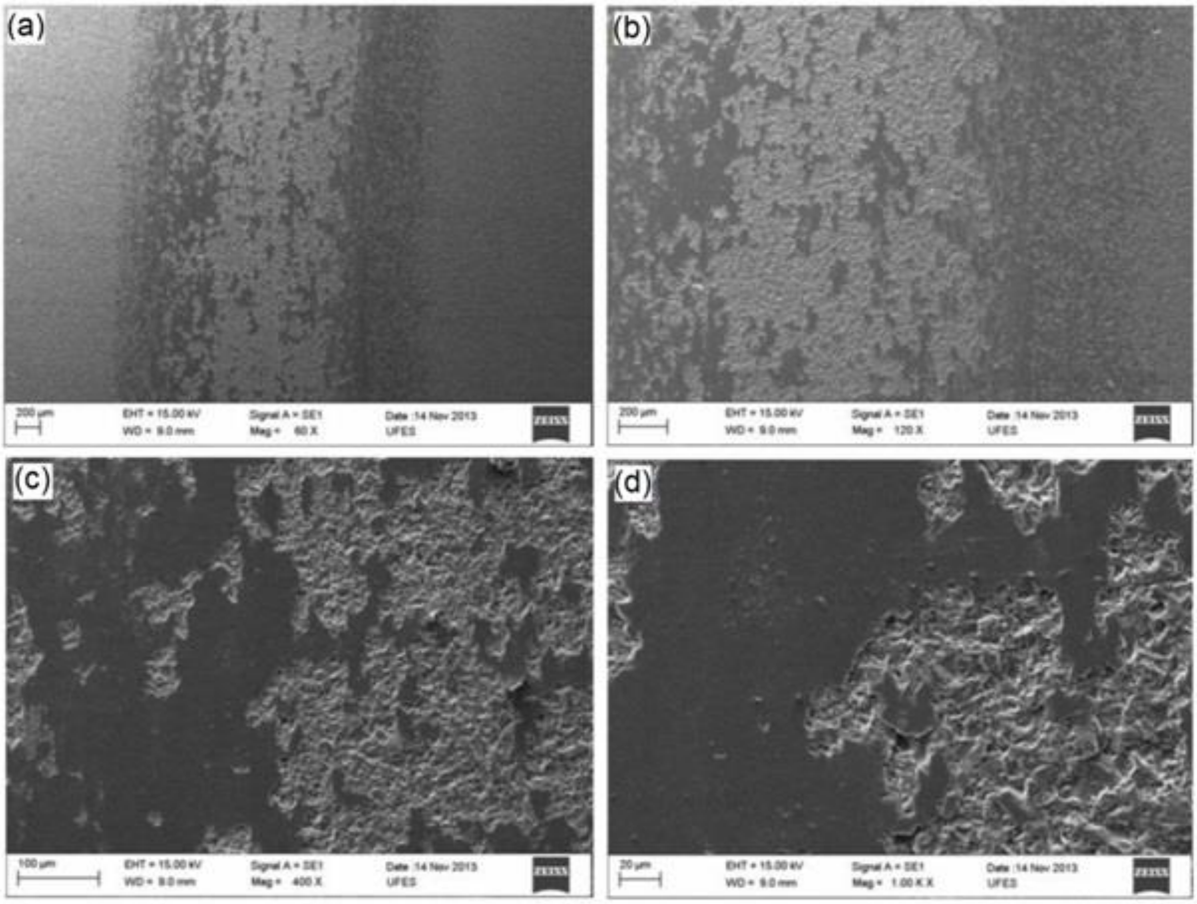

Figure 9. Wear track from an Al_2O_3 disc obtained by SEM. Magnifications of (a) 60 X, (b) 120 X, (c) 400 X and (d) 1000 X.

Furthermore, two distinct regions in the wear tracks of the discs were observed. A smoother region (darker in the images) and a rougher region (brighter). EDS microanalysis of both regions reveals that smoother areas have a silicon weight concentration between 10 and 12%, while for rougher areas silicon contents are negligible. These results indicates that material removed from the Si_3N_4 balls was transferred to the wear tracks of the discs. Ferreira *et al.* [2] suggested that tribochemical reaction products from the ceramic materials and water adhere to the valleys of the asperities and contribute for smoothing the surfaces.

4 CONCLUSIONS

- ULFC regime ($\mu < 0.003$) was observed when sliding Si_3N_4 against Al_2O_3 in water;
- By comparing estimated minimum film thickness with calculated composite roughness of the worn surfaces, it is proved that, under the tested conditions, a mixed lubrication regime occurs;
- Higher initial surface roughness of the discs results in greater running-in duration;
- There is a tendency of higher circular axial run-out to lead longer running-in duration;
- Surface roughness of the discs lowered during the tribological tests due to tribochemical reactions;
- Wear rates of Si_3N_4 balls were about three times higher than Al_2O_3 discs;
- ULFC regime was observed only when silicon concentration in lubricating water after the tests were greater than 1.3 mg/l;
- Electrical conductivity of the lubricating water stabilizes after the running-in period;
- SEM images shows two distinct regions formed in the worn surfaces of the discs. Smooth regions with 10 to 12% silicon weight concentration and rougher regions with negligible silicon content.

Acknowledgments

Authors thank to TRICORRMAT/UFES, LQA/UFES, LABPETRO/UFES and LCSM/UFES for the technical support and CAPES and PRH-29/ANP for the financial support.

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