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Silicon-incorporated diamond-like coatings for Si_3N_4 mechanical seals

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Abstract

Amorphous silicon carbide (a-SiC) and silicon-incorporated diamond-like carbon films (DLC-Si) were evaluated as protective and friction reduction coatings onto Si_3N_4 rings. Unlubricated tribological tests were performed with a pin-on-disk apparatus against stainless steel pins with loads ranging from 3 to 55 N and sliding velocities from 0.2 to 1.0 m/s under ambient air and 50–60% relative humidity. At the lowest loads, a-SiC coatings present a considerable improvement with respect to the behavior of uncoated disks since the friction coefficient is reduced to about 0.2 and the system is able to run stably for thousands of meters. At higher loads, however, a-SiC coatings fail. DLC-Si-coated rings, on the other hand, presented for loads up to 10 N a steady-state friction coefficient below 0.1 and very low wear rates. The lowest steady-state mean friction coefficient value of only 0.055 was obtained with a sliding velocity of 0.5 m/s. For higher loads in the range of 20 N, the friction coefficient drops to values around 0.1 but no steady state is reached. For the highest loads of over 50 N, a catastrophic behavior is observed. Typically, wear rates below 5×10^{-6} and 2×10^{-7} mm^3/N m were obtained for the ceramic rings and pins, respectively, with a load of 10 N and a sliding velocity of 0.5 m/s. Analysis of the steel pin contact surface by scanning electron microscopy (SEM)–energy dispersive X-ray spectrometry (EDS) and Auger spectroscopy revealed the formation of an adherent tribo-layer mainly composed by Si, C and O. The unique structure of DLC-Si films is thought to be responsible for the formation of the tribo-layer.

Keywords: Amorphous silicon carbide; Diamond-like carbon films; Si_3N_4 rings

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1. Introduction

Diamond-like amorphous carbon (DLC) has been extensively studied over the last years due to its outstanding combination of properties and great potential for technological applications, including optical, electrical, mechanical and tribological applications [1]. Silicon-incorporated diamond-like carbon films (DLC-Si) and amorphous silicon carbide films (a-SiC) also have attracted considerable attention and present a great potential for applications as hard coatings since these films present very high hardness and reduced residual internal stress, high deposition rates and good adhesion to most substrates, including various metal alloys, steels and glasses [2–9]. One of the main advantages of DLC-Si coatings over pure DLC films is the fact that the friction coefficient of the former is independent on ambient humidity [10].

Mechanical seals protect the environment from product leakage in equipment with rotating shafts or alternative movement parts (i.e. pumps, agitators, automotive engines, compressors, turbines, etc.). Outflow control is crucial when the working fluids are toxic, corrosive, flammable or explosive. Ceramics are attractive candidates for this application due to their combination of high-temperature hardness, high contact fatigue resistance, corrosion resistance and low inertial mass. Among this class of materials, silicon carbide (SiC) and alumina (Al_2O_3) have been applied as mechanical rings [11]. However, low fracture toughness is their main disadvantage. Furthermore, a demanding technology is needed to fully densify SiC, as very high sintering temperatures are required, which makes this

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ceramic an expensive and laborious product. Therefore, more recently a new system of ceramic mechanical seals based on silicon nitride (Si_3N_4) has been proposed [12].

Oguri et al. have performed ball-on-plate tests with DLC-Si-coated steel balls against high-speed tool steel plates and concluded that a graphite-like a-C layer is responsible for low friction in case of dry sliding while a silica layer was observed to be the cause of low friction when the tests were carried out in humid atmospheres [13,14]. Consistently, Kim et al. [15] and Yang et al. [16] studied the tribological behavior of DLC-Si films against a steel ball in a ball-on-disk test assembly under controlled atmosphere and concluded that the tribological behavior is strongly governed by the test environment and that low and stable friction behavior is related to the formation of a silicon rich tribo-layer and to the smoothening of wear tracks.

In this work, we report on the evaluation of the use of DLC-Si and a-SiC coatings as protective and friction reduction coatings on Si_3N_4 mechanical seals, deposited by plasma enhanced chemical vapor deposition (PECVD—glow discharge) and physical vapor deposition (PVD—magnetron sputtering), respectively. Results of unlubricated pin-on-disk tests show that DLC-Si coatings present superior performance since very low friction coefficients values and wear rates can be obtained. This behavior is attributed to the formation of an adherent tribo-layer mainly composed of Si, C and O.

2. Experimental

Silicon nitride rings or disks were fabricated in monolithic composition of 89.3 wt.% Si_3N_4 (HC Starck M11)/3.7 wt.% Al_2O_3 (Alcoa 116SG)/7.0 wt.% Y_2O_3 (HC Starck C fine). Powders mixtures were ball mixed for 4 h in 2-propanol media using alumina jar and balls. Samples isostatically pressed at 200 MPa were fully densified (>99% of the theoretical density) by pressureless sintering at 1750 °C for 2 h in nitrogen atmosphere and then followed by planar grinding and polishing. The final dimensions of the rings were: external diameter 44 mm, internal diameter 32 mm and thickness of 6 mm. Disks were produced with similar dimensions except, of course, for the internal diameter. Before film deposition, rings were submitted to additional polishing with 3 and 1 μm diamond pastes until a mirror-like surface was achieved. Typical rms surface roughness values were around 0.05 μm.

Ceramic rings/disks were coated by two different types techniques: (i) PVD (magnetron sputtering) and (ii) PECVD (glow discharge). PVD coatings were produced in a radio frequency (rf) magnetron sputtering system (US Gun II) from a 3-in. commercially pure polycrystalline SiC target using pure argon as sputtering gas. Substrates were placed on a sample holder at about 7 cm away from the target. Deposition conditions were: room temperature, argon pressure P=0.1 Pa, argon flow 10 sccm, rf power P_{RF}=400 W. No bias was applied to the substrates. In this way, stoichiometric amorphous SiC (a-SiC) coatings with hardness values higher than 30 GPa can be produced [2,4]. Additional information on the deposition and properties of these coatings can be found in previous publications [2–5]. PECVD coatings were deposited in a conventional rf (13.56 MHz) parallel plate glow discharge reactor from gaseous mixtures of methane and silane. Substrates were placed onto the cathode of the deposition system. Before deposition, the substrates were cleaned for 30 min by argon sputtering and a adhesive thin a-Si:H layer with thickness of about 20–30 nm was deposited. Deposition conditions were: room temperature, self-bias voltage −800 V, total gas flow 10 sccm, total gas pressure 2.0 Pa and silane content in the gas mixture 10 vol.%. Under these conditions, silicon-incorporated hydrogenated amorphous carbon films (DLC-Si) with hardness values around 20 GPa are obtained [7]. Additional details about the deposition and properties of these films can be found elsewhere [6–9]. Film thickness ranged from 2 to 3 μm in both cases. All films were amorphous.

The tribological experiments were performed in a microprocessed controlled tribometer (Plint and Partners, model TE-67) in a pin-on-ring planar contact configuration. The tests were conducted without lubricant, at room temperature, under ambient air and 50–60% relative humidity. Stainless steel (316 L) cylindrical pins with a flat end of 3 mm diameter were loaded against coated and uncoated Si_3N_4 rings with normal applied loads (F_n) ranging from 3 to 55 N and sliding speeds varying from 0.2 to 1.0 m/s. A data acquisition system was used to record at regular periods of time the frictional force (F_f), which was accessed by a bend-type loading cell, and the friction coefficient (f) was calculated as $f=F_f/F_n$. The wear coefficient, K, was determined as $K=V/(F_n \cdot x)$, where x was the sliding distance and V the wear volume, evaluated by weight loss in the samples using a microbalance with an accuracy of 10 μg.

Scratch tests were performed on a machined developed at UFRJ with a Rockwell “C” diamond (120° cone with a 200-μm radius hemispherical tip) tip as indenter. The tests were performed increasing the load at a rate of 10 N/mm. The tangential force was measured by a load cell and, in order to determine the critical load for coating delamination, the samples were also microscopically examined.

Disks and pins surfaces were also examined by scanning electron microscopy (SEM) and analysed by both energy dispersive X-ray spectrometry (EDS) and Auger electron spectroscopy (AES). AES was performed in a PHI-SAM 590 Auger microprobe in the survey mode, using a primary electron beam of energy 2 keV and current 8 mA.

3. Results and discussion

Fig. 1 shows the results of the pin-on-disk tests performed on the Si_3N_4 disks coated with a-SiC PVD coatings in comparison to an uncoated disk. A sliding speed

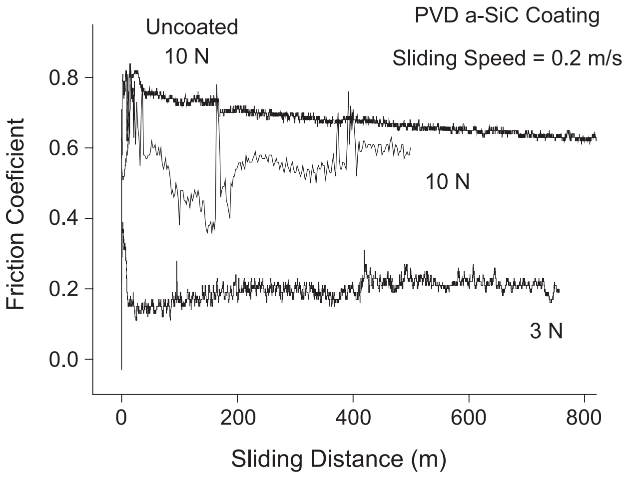

Fig. 1. Friction coefficient of Si_3N_4 ceramic disks coated with a-SiC film deposited by rf magnetron sputtering against a 316-L stainless steel pin. The test was performed with a sliding speed of 0.2 m/s and two different loads 3 and 10 N. For comparison, the result obtained for an uncoated disk with a load of 10 N is also shown.

of 0.2 m/s and loads of 3 and 10 N were employed in these tests. In case of the uncoated disk, the friction coefficient initially rises up to about 0.8 and then slowly decreases towards 0.6 due to the smoothening of the contact surfaces. In case of the a-SiC-coated disk, when using a 3-N load, an abrupt initial increase of the friction coefficient to about 0.4 occurs in the first 10 or 20 m of the test. After that, the friction coefficient rapid decreases to about 0.15 and then slowly stabilizes around 0.2. The observed decrease of the friction evidences the formation of a lubricating tribo-layer, which protects the surface of the steel pin against wear while keeping friction at relatively low values. The obtained wear rate for the ceramic disk (considering a mean density of 3.2 g/cm^3 for the disk+coating) is around 2×10^{-5} mm^3/N m, while the pin showed a slight increase on its mass due the formation of the tribo-layer.

When using a 10-N load, after a large initial increase of the friction coefficient, there is a slow tendency of reducing friction but a stable condition is never achieved and the friction coefficient varies around 0.6, which would be the expected value for the uncoated disk. Eventual rapid variations of the friction coefficient indicate the possibility of a catastrophic failure of the coating. In this case, the disk wear rate is about twice as large as in the previous one, that is about 4×10^{-5} mm^3/N m, while the pin does not show variations on its mass.

PECVD coatings showed an improved behavior regarding friction reduction and wear protection of the ceramic disks. Fig. 2 shows the results of the pin-on-disk tests performed with the DLC-Si-coated disks using a sliding sped of 0.2 m/s for loads of 10, 20 and 55 N. When using a load of 3 N (not shown in the figure), the friction coefficient presents an initial peak followed by a slow decrease to values around 0.1. With a 10-N load, the friction coefficient initially reaches a value of about 0.6, rapidly decreases to 0.3 and then slowly decreases and stabilizes at around a mean value of 0.08, evidencing the formation of a lubricating tribo-layer. With 20 N, the friction coefficient tends to stabilize at values around 0.1 although this condition is attained much more slowly than in previous case. Finally, using a load of 55 N, the friction coefficient seems to decrease in the beginning of the test but then the coating does not support the strong forces involved and the system fails. The disks presented wear rates in the range of 2–5×10^{-6} mm^3/N m in all cases except when a load of 55 N was used. This is one order of magnitude lower than in case of sputtered a-SiC coatings. After running the test for about 3000 m, the pin wear rate is equal to or below 5×10^{-7} mm^3/N m.

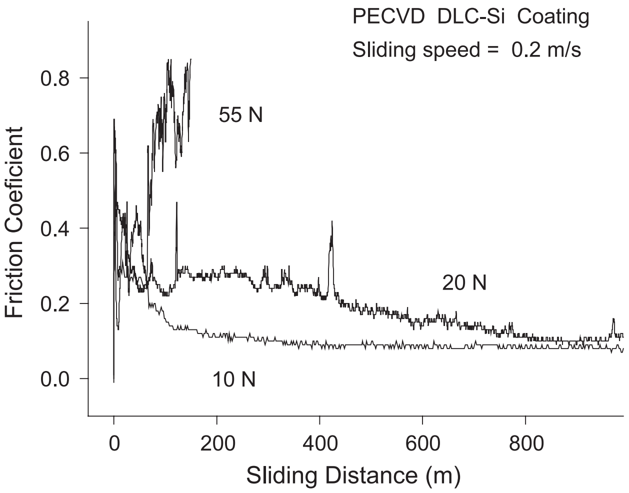

Fig. 2. Friction coefficient of Si_3N_4 ceramic disks coated with DLC-Si film deposited by rf glow discharge against a 316-L stainless steel pin. The test was performed with a sliding speed of 0.2 m/s and three different loads 10, 20 and 55 N.

Fig. 3 shows the results of pin-on-disk tests run with higher sliding speeds of 0.5 and 1.0 m/s and a load of 10 N. In all cases (including the one with 0.2 m/s—Fig. 2), after an initial peak, the system achieves a stationary condition with a friction coefficient below 0.1, which again evidences

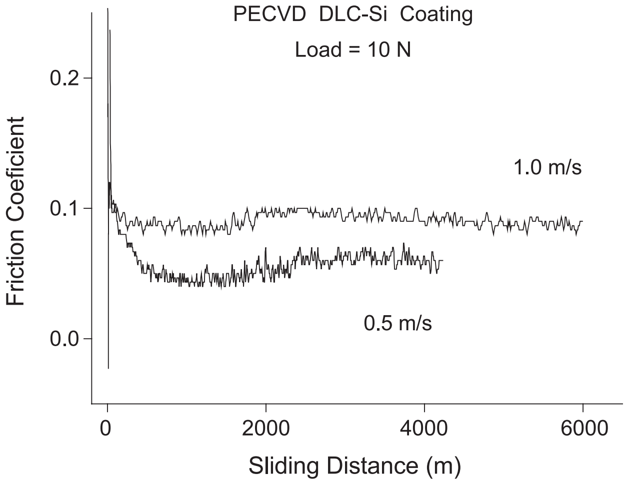

Fig. 3. Friction coefficient of Si_3N_4 ceramic disks coated with DLC-Si film deposited by rf glow discharge against a 316-L stainless steel pin. The test was performed with a load of 10 N and sliding speeds of 0.5 and 1.0 m/s.

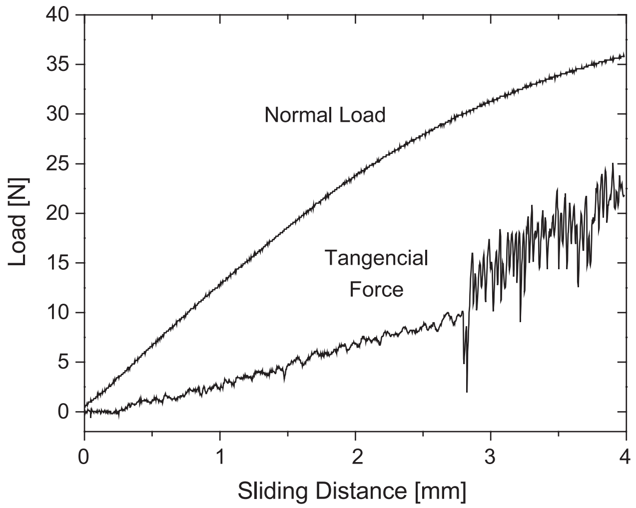

Fig. 4. Scratch test of a Si_3N_4 ceramic disks coated with DLC-Si film, showing the normal load and tangential force versus sliding distance.

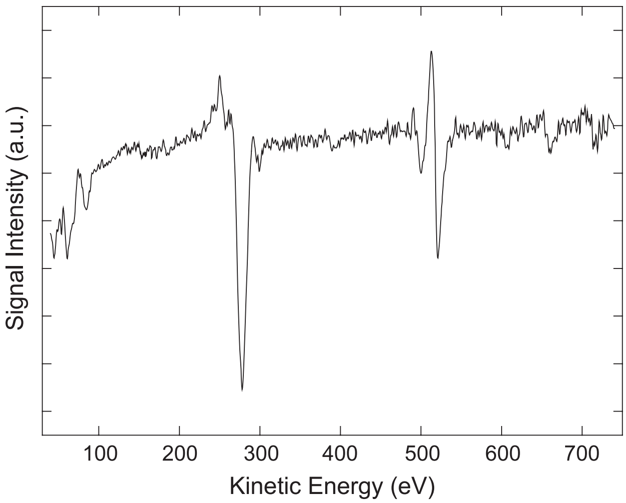

Fig. 6. AES spectrum of the adherent transfer layer on the contact surface of a steel pin after performing a pin-on-disk test against a Si_3N_4 ceramic disk coated with DLC-Si film.

the formation of a stable tribo-layer. The formation of this lubricating layer apparently occurs in the initial 10 m of the test. The wear rate of the disks were around or below 5×10^{-6} mm^3/N m and for the pins equal to or below 2×10^{-7} mm^3/N m after running 6000 m.

In order to determine the mechanical resistance of the coatings scratch tests were performed on the ceramic samples coated with DLC-Si films. Fig. 4 shows the results of such a test. Comparison of the tangential force measurement with the microscopic examination of the sample allowed the determination of a critical load for coating delamination of about 30.5 N. Friction coefficient (not shown in the figure) is around the same values determined on the pin-on-disk tests (~0.05–0.10).

The surface of the pins and disks were analyzed by SEM and AES in order to obtain more information about the formation of the tribo-layer. Fig. 5a and b show SEM micrographs obtained of the pin surface at two different magnifications. It is evident from the pictures that a transfer

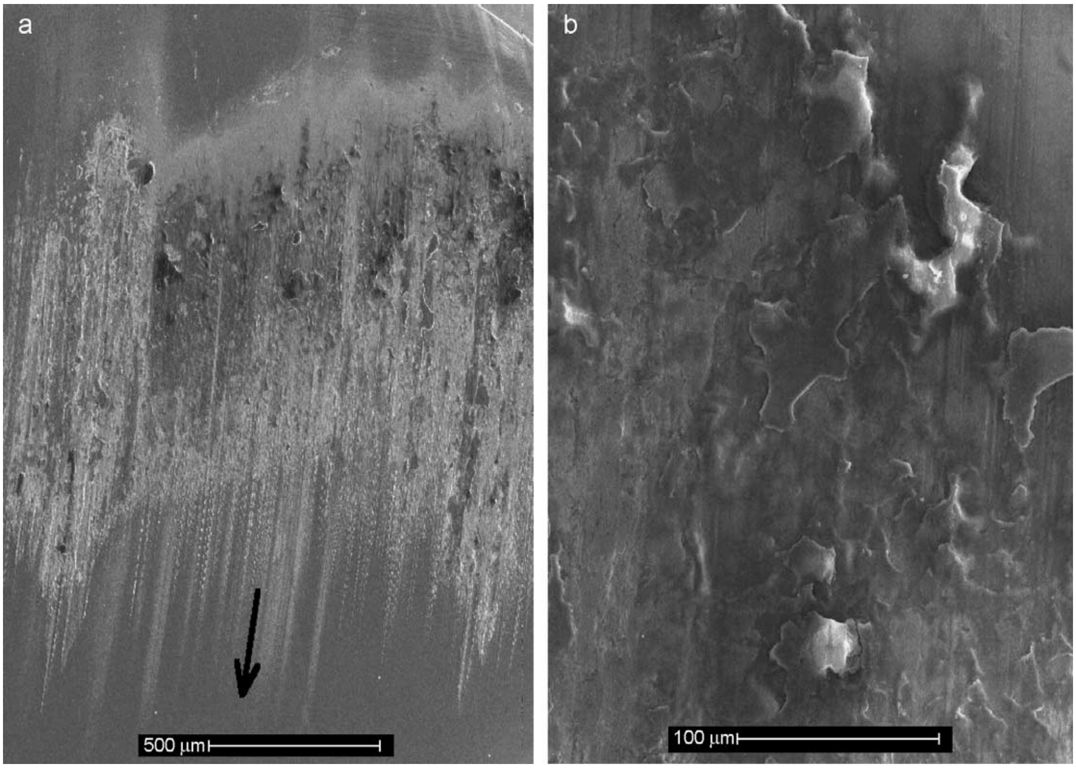

Fig. 5. SEM micrographs of the contact surface of a stainless steel pin after performing a pin-on-disk test against a Si_3N_4 ceramic disks coated with DLC-Si film. The black arrow shows the direction of sliding.

layer is formed on the surface of the steel pin. EDS analysis showed the presence of Si and O in the tribo-layer as well as a small peak related to carbon. Auger analysis (Fig. 6) of the transfer layer has shown that its composition is basically composed of Si, C and O. Indeed, apart from the peaks related to the steel pin, in Fig. 6, one can also clearly identify the peaks related to Si (92 eV), C (272 eV) and O (510 eV). An additional small peak at 215 eV is a result of ion implantation during sputtering with Ar ions.

In agreement with other authors [13–16], it is therefore reasonable to relate the effect of friction and wear reduction to the presence of a tribo-layer mainly composed by Si, C and O. However, the comparison between the present results obtained with PVD a-SiC and PECVD DLC-Si coatings indicate that the simple presence of Si and C in the coating is not sufficient to assure low friction coefficients and wear rates. Although the detailed mechanism of low friction between DLC-Si and steel pin is yet to be formulated, one must consider that a stable low friction behavior will only occur in case an adherent tribo-layer can be formed. For this purpose, the structure of the coating material is of great importance. PVD a-SiC, which is thought to be the amorphous counterpart of crystalline SiC, may present some amounts of homonuclear Si–Si and C–C bonds, but is essentially formed by sp^3 heteronuclear Si–C bonds [2,17]. On the other hand, although DLC-Si presents increased density of sp^3 carbon atoms, its structure is quite similar to pure DLC, containing a considerable density of sp^2 carbon atoms and hydrogen [6]. This unique structure of DLC-Si is thought to be responsible for the formation of the observed stable tribo-layer.

4. Conclusions

In this work, a-SiC and DLC-Si were successfully produced as protective and friction reduction coatings onto Si_3N_4 ceramic rings. Unlubricated tribological tests were performed with a pin-on-disk apparatus against stainless steel pins with loads ranging from 3 to 55 N and sliding velocities from 0.2 to 1.0 m/s under ambient air and 50–60% relative humidity. Results show that a-SiC coatings improve the performance of the ceramic disks since at the lowest loads the friction coefficient is reduced to about 0.2 and the system is able to run stably for thousands of meters. At higher loads, however, a-SiC coatings fail. On the other hand, DLC-Si-coated rings presented for loads of up to 10 N steady-state friction coefficients below 0.1. The lowest steady-state mean friction coefficient value of only 0.055 was obtained with a load of 10 N and a sliding velocity of 0.5 m/s. For higher loads in the range of 20 N, the friction coefficient drops to values around 0.1 but no steady state is reached. For the highest loads of 55 N, a catastrophic behavior is observed. Wear rates around 2×10^{-6} mm^3/N m were obtained for the ceramic rings with a load of 10 N and a sliding velocity of 0.5 m/s. Under the same conditions, the wear rates for the steel pins were below 5×10^{-7} mm^3/N m. The improved behavior of DLC-Si coatings is attributed to the formation of an adherent tribo-layer composed by Si, C and O, which is formed as a consequence of the unique structure of DLC-Si films.

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