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Tribological effect of iron oxide residual on the DLC film surface under seawater and saline solutions

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ABSTRACT

This paper discusses the seawater and saline solutions effects on the tribological behavior of diamond-like carbon (DLC) films. The adsorption of Fe on DLC surface is one of the mechanisms that is believed to be the cause of the decrease in dispersive component of the surface energy and increase of the I_D/I_G ratio leading to low friction coefficient and wear rate under corrosive environments. Tribological behaviors DLC films were experimentally evaluated under corrosive environments by using steel ball and DLC coated steel flat under rotational sliding conditions. The DLC films were prepared on 440 stainless steel disks by DC-pulsed PECVD using methane as a precursor gas. Two different set of tribological system was assembled, one when the liquids and the pairs were put inside of a stainless steel vessel and others inside of a PTFE. Every tribological test was performed under 10 N normal load120 mms^{-1} of sliding speed. The friction coefficients were evaluated during 1000 cycles.

1. Introduction

The recent interest of the petroleum companies on improving the efficiency and viability of oil ducts flow have been increased in the several last years [1,2]. However the commercial extraction viability has some obstacles, such as drilling of the salt layer that can block and hold the drill pipes. Drill and flow pipes are made with seamless steel coated with resin to decrease the wear and corrosion. However, this resin wears very quickly due to contact sliding between steel cables and inner wall of the drill pipes. In addition, corrosion of the steel components due to great pressure and the sulfur dioxide presence decreases the efficiency and viability. The water from the oil extraction generally contains high salinity, oil particles in suspension and chemicals added as demulsifying and defoaming [3]. The corrosive environment can result deposition/precipitation of corrosion products in the metal surface and increase wear inside of the drill and flow pipes. DLC coatings are well known for their low friction, high wear resistance, and the combination of inert character of DLC films to most chemicals and their amorphous structure which makes them almost defect free makes these coatings good candidates for oil ducts.

Technologies based on the flow of oil through ducts coated with DLC films represent an alternative way [1]. DLC coatings can potentially increase the efficiency by reducing the friction, wear and corrosion on the drill pipes. Such an improvement will reduce the operating costs by reducing the equipment downtime for maintenance and extend the life of the existing machinery. The most common way to control corrosion in oil ducts is by chemical inhibition, but it is not fully understood. The mechanism can be dominated by inhibitor adsorption on the surface of film and/or metal; the inhibitor provokes a small extent of corrosion on the film surface and/or metal and is also adsorbed forming a compact protective thin layer. The inhibitor forms a precipitate on the surface metal in such a way to protect it. The protective combination of corrosion product/inhibitor layer is dynamic [4]. Inhibitors have also been shown to be effective in reducing erosion [5]. The tribocorrosion area involves rheological properties and interaction among mechanical friction, wear processes and several chemical corrosion processes [6]. Tribocorrosion includes the solid particle erosion, sliding wear and oxidation as surface degradation process. The presence of suspended solids, the erosion–corrosion rate can increase by 25–100 times greater than the uniform corrosion rate [7]. In severe operating conditions, such as erosion–corrosion conditions, corrosion resistant alloys such as 13Cr martensitic stainless steel (CRAs) are widely used in oil industry [8]. The martensitic grades are mainly used where hardness, strength, wear and corrosion resistance are required, and chromium improves oxidation resistance of the steel in sulfuric atmospheres.

The objective of the present work is to study the behavior of friction coefficient and wear rate when iron oxide residual is deposited on DLC film surface under seawater and saline solutions of 3 and 5 mass% NaCl in distilled water. This experimental study presents the correlation of iron oxide residual with decreasing of dispersive component of surface energy and increase of DLC film ID/IG ratio, in order to understand the chemical mechanisms evolved under aggressive environments.

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2. Experimental procedures

In this study, DLC films with 20% hydrogen concentration were deposited on 440 stainless steel disks by using pulsed-DC discharge under controlled conditions, using carbonitride diffusion process as interlayer [9–11]. The substrates were cleaned with acetone and additionally cleaned by argon discharge with 1 sccm gas flow at 11.3 Pa working pressure and a discharge voltage of −700 V for 30 min prior to deposition. The 440 stainless steel surface was modified by diffusion process during one hour at 430 °C using N_2, H_2 e CH_4 gases forming a carbonitride layer [12]. This carbonitride interlayer has around 8 GPa of hardness and 10 μm of thickness [12]. The DLC film 20% hydrogenated was deposited using methane to a thickness of ~2.0 μm. The deposition was performed using 1 sccm of gas flow, during 2 h at 11.3 Pa and a discharge voltage of −700 V.

2.1. Tribological tests

Tribological tests were done in affected environment and all characterizations were performed before and after all tests, as described before. The tribological tests were performed on 4 mm diameter 440 steel ball and 80 mm diameter 440 steel flat pairs with and without DLC film. The tribological tests are done in seawater, with 0.3 mass% NaCl and 7.9 pH, and saline solutions of 3 and 5 mass% NaCl in distilled water, with 5.5 and 5.6 pH respectively at room temperature. The saline solutions were prepared according to DIN 50905 norms. The substrate was embedded in saline solutions using two different vessel, stainless steel and Teflon in order to understand how some corrosion products may contribute in the behavior of DLC film under corrosive solution. The schematic diagram of tribotest system is shown in Fig. 1.

The friction and wear tests were carried out by using a UMT-CETR ball-on-disk tribometer in the rotational mode with $0.12\ \mathrm{m\ s^{-1}}$ constant linear sliding speed under 10 N normal load for duration of 1000 cycles. The initial average Hertzian contact pressure ranged from 1.25 to 1.87 GPa, assuming that the ball is in direct contact with DLC film surface [13]. The tests were run five times for each pair combination. A new position on the ball/disk was used for each test, and the friction coefficients were collected from the steady-state region [14]. After tests, the saline solutions were collected and filtered using qualitative filter (Qualy, with 14 μm of porosity). The filtered material collected was analyzed using Energy Dispersive X-ray Spectroscopy (EDS) attachment of Scanning Electron Microscope (SEM). Also, the surface energy and Raman scattering spectroscopy analysis has been figure out in order to study DLC surface changes.

2.2. Quantification of the iron oxide residual mass

In order to quantify the iron oxide residual mass, the friction and wear tests were repeated letting the saline solutions in contact with the stainless steel vessel in different times. After that, the residual in the seawater and saline solutions were filtered (Framex, with 2.5 μm of porosity) and quantified using an analytical weight balance.

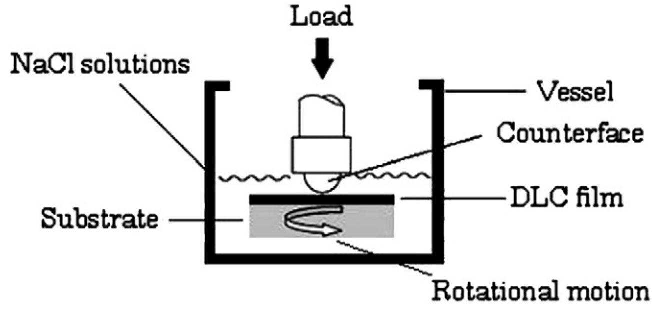

Fig. 1. Schematic diagram of a friction in saline solutions.

The redox titration (using permanganate) was used to estimate the amount of the analyte (Fe^{2+}) presented in filtered powder. In this experiment, $KMnO_4$ was used to determine the percentage of Fe^{2+} by mass in an unknown sample. The oxidation of Fe^{2+} to Fe^{3+} was carried out acidic solution to prevent the air oxidation of Fe^{2+}. Phosphoric acid, H_3PO_4, was added to form a colorless complex with Fe^{3+} ion. The $KMnO_4$ solution (about 0.02 M) was first standardized by titration using Mohr's salt, ferrous ammonium sulfate hexahydrate, $(Fe(NH_4)_2(SO_4)_2(H_2O)_6$ as the source of Fe^{2+}. The Fe^{2+} was oxidized to Fe^{3+} while the MnO_4^- is reduced to Mn^{2+}. The exact molarity of the $KMnO_4$ was then determined.

$$Fe(NH_4)_2(SO_4)_2(H_2O)_6 \rightarrow Fe^{2+}_{(aq)} + 2NH^{+}_{4(aq)} + 2SO^{2-}_{4(aq)} + 8H_2O_{(l)} \tag{1}$$

$$MnO_4^- + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}\ \text{(unbalanced)} \tag{2}$$

Next, the standardized $KMnO_4$ was reacted with a known mass of an unknown sample containing Fe^{2+}. The mass and percent by mass of Fe^{2+} in the unknown was then calculated.

2.3. Surface energy analysis

The surface energy composed of polar and dispersive components of the DLC film was evaluated by the measurement of contact angle using liquid drop goniometry. All the measurements were performed in atmospheric condition at room temperature and repeated at least five times for each sample before and after tests under saline solutions. Water and diodo-methane were used to calculate the surface energy (Table 1). All liquids were provided in an analytical-reagent quality and chosen to cover the wide range from very polar liquid (water) through to very dispersive liquid (diodomethane). A droplet with a volume of 2.5 μL was released onto the surface of the sample from a syringe needle. Each measurement was repeated five times.

The interfacial tension between two condensed phases can be determined by Young' equation [15], according to:

$$cos\theta\gamma_{LV} = \gamma_{SV} - \gamma_{SL} \tag{3}$$

where θ is the measured contact angle between liquid and solid, and γ_{LV}, γ_{SV} and γ_{SL} are the interfacial energies of the liquid/vapor, solid/vapor and solid/liquid interfaces, respectively. Determination of polar and dispersive components of the surface energy of the materials can be solved by approximating $\gamma^D{}_S$ and $\gamma^P{}_S$ from a single measurement of θ by Eq. (4).

$$\gamma_{LV}(1 + cos\theta) = 2\sqrt{\gamma_L^P\gamma_S^P} + 2\sqrt{\gamma_L^D\gamma_S^P} \tag{4}$$

where γ_L^P and γ_S^P are the polar components of the liquids phase surface energy and solid phase, respectively. While γ_L^D and γ_S^D are the dispersive component of the surface energy of liquid and solid phase, respectively. Including contact angles measurements of two different liquids with well known polar and dispersive components of surface energy (Table 1).

Table 1
Surface tension and surface components of liquids used in contact angle test (dyne/cm).

Surface tension data (mN/m)	γ_L^D	γ_L^P	γ_{LV}
Water	21.8	51.0	72.8
Diodomethane	48.5	2.3	50.8