Evolution of tribologically induced chemical and structural degradation in hydrogenated a-C coatings

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ABSTRACT

The coatings with gradually varying chemical composition and structure were obtained by PECVD method from methane precursor and various admixtures of Ar. The composition of emitted gases and triboemission behaviour were studied for these coatings and correlated with the coating properties and deposition conditions. A new analytical approach was developed that allowed identification of the emitted gas species with much higher accuracy than conventional techniques. For the first time, triboemission of alkanes higher than propane was observed. By the application of kinetic model to the analysis of triboemission time series, chemical and structural degradation in carbon coatings could be traced in course of tribological tests.

1. Introduction

Amorphous carbon (a-C) coatings serve in widespread tribological applications to improve wear resistance and to reduce friction. Mechanical and tribological properties of a-C can be flexibly tailored by varying sp^2 to sp^3 ratio, hydrogen concentration and doping elements [1]. Aijaz et al. [2] demonstrated that the electron density and/or temperature in plasma are the key factor to tune physical properties, composition and chemistry of a-C. The control of these parameters can be achieved by adjusting the concentration and composition of the precursor gases. The addition of argon, neon or other heavy gases to the process gas results in modification of the chemical bonding of carbon, changing hydrogen and nanovoids distribution in the coating, and trapping inert gases in the coating [2,3].

Among various a-C classes hydrogenated amorphous carbon (a-C:H) has attracted much attention since the discovery of its near-frictionless and near-wearless properties under vacuum or inert atmosphere [4]. A large amount of research has been conducted to gain molecular-level understanding of advanced tribological properties of a-C:H and the

mechanisms of their degradation [5–12]. It was found that ultra-low friction regime usually sets in after a run-in period, during which a thin modified surface layer on the coating and a transfer film on a counterbody evolve. The transfer film results from formation and breaking of covalent bonds [13]. The transfer film, the debris, and the modified surface layer tend to have higher sp^2 bonding [14,15] that is associated with hydrogen loss and graphitization of metastable sp^3 bonds [16,17]. High hydrogen content has a significant effect on reduction of friction and wear rates due to passivation of dangling bonds and suppression of C—C bonds formation across the interface [6,8,13,15,18–20]. Furthermore, repulsive electrostatic forces [21] at hydrogen-terminated surfaces reduce adhesion, while tribochemical generation of dihydrogen molecules at the sliding interface enlarges the distance between the surfaces because of the steric effect [18]. It was also demonstrated that the coating failure relies on the hydrogen depletion in it, and that this process is reversible [22].

Despite the efforts made to elucidate the a-C:H degradation, understanding of its tribochemical bases is still a challenging task. The main difficulty in studying tribological and associated tribophysical and

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tribochemical phenomena is the technical limitation for *in situ* characterization of increasingly complex physical and chemical processes on micro- and macroscales interfaces. Although the combination of certain surface characterization techniques with the tribological ones has been an important advancement that afforded the opportunity to trace plastic flow, fracture, formation and cleavage of chemical bonds, excitation of vibrational and electronic states, etc. at the contact zone [23–27], the combined techniques have a number of geometry, materials and environment constrains. A new technique based on the analysis of Mechanically Stimulated Gas Emission (MSGE) has been developed recently [28–30]. The main advantage of this technique, MSGE-Mass Spectrometry (MSGE-MS), is that it allows analyzing the evolution of tribochemical and structural processes occurring in a buried interface. MSGE-MS has been a further improvement of *in situ* mass-spectrometry coupled with a tribological experimental set-up [31–38], which was successively applied to the exploratory research of tribochemical degradation and gas triboemission from various types of a-C and a-C:H [39–41]. These studies showed that the main emitted gas species from a-C:H were methane and hydrogen. Traces of CO, H_2O, ethane, propane and CO_2 with undetermined proportions were also observed [39,42]. Triboemission of various gas species showed a complex behaviour, which could be linked to either friction or wear [43]. For example, Ar emission seemed to correlate with plastic deformation and fracture. In turn, H_2 and CH_4 triboemission showed more complex behaviours with the emission rate being nearly parabolic function of H content [40]. It was suggested that both H_2 and CH_4 triboemission rely on tribochemical processes [41]. All researches discarded frictional heating as the driving force for gas triboemission under mild sliding conditions [17,42].

The main objective of this work is to study evolution of structural and chemical degradation for a series of a-C:H coatings through the analysis of gas triboemission time series using MSGE-MS. The coatings were obtained using PECVD method with varying Ar/methane ratios in the precursor gases. Tribological and triboemission characteristics of a-C:H coatings were correlated with their physico-chemical properties and deposition conditions. Better time resolution of mass-spectra in comparison with the previous works and a new data analysis method based on behavioural analysis, linear regression fitting and statistical hypothesis testing allowed us to identify the emitted gas species more accurately. The possible tribochemical processes leading to the H_2 and hydrocarbons triboemission were discussed. The evolution of structural degradation was traced through the analysis of Ar emission using a kinetic triboemission model.

2. Materials and methods

Amorphous carbon coatings were deposited on polished AISI 420 stainless steel substrates using pulsed Plasma Enhanced Chemical Vapour Deposition (PECVD). Argon/methane mixtures with flow proportions: 18.9/81.1, 6.8/93.2 and 0/100 were used as a process gas for the coatings D-050, D-051 and D-052, correspondingly. A pulsed bias of −1000 V, frequency 30 kHz and duty cycle 27% was applied to the substrates during deposition. Substrate temperature was 20 °C. Deposition time was kept at 60 min for all samples (Table 1).

In a complementary experiment Ar triboemission from a coating obtained by Ion Beam Deposition (IBD) technique was studied. The

Table 1
Deposition parameters and properties of a-C:H processed samples.

Sample	Gas pressure (Pa)	Ar/CH$_4$ ratio	Film thickness (μm)	Hardness (GPa)
D-050	8	18.9/81.1	0.70	19.5 ± 3.2
D-051	10	6.8/93.2	0.65	22.2 ± 2.7
D-052	10	0/100	1.50	20.8 ± 1.9

coating was identical to D-2 in Ref. [39]. The coating was deposited on a silicon substrate from two ion sources fed by cyclohexane and argon, respectively. The ratio argon/cyclohexane was 33/67.

Gas triboemission from the materials was characterized using MSGE-MS [29], which combines the following essential components: a specially designed ultrahigh vacuum reciprocating motion friction cell with near-zero intrinsic triboemission, a dynamic expansion system for quantification of minute (< 1 nmol/s) gas emission rates, and a mass-spectrometer. An alumina ball with the diameter 2 mm was used as a counterbody. Normal load ranged between 0.86 N and 2.13 N, while sliding speed was 0.18–0.4 m/s. Several mass-spectrometer channels corresponding to ions with different mass-to-charge ratio, m/z, were measured during rubbing and after its end in order to determine the variations related with mechanical activation of the sample. The background measured before the beginning of rubbing was subtracted from each signal. The resulting time series, i.e. differential mass-spectrometer (DMS) signals, were analyzed following previously described procedure [44]. If the ion current increase during rubbing was not statistically significant at significance level 0.05, the corresponding channel was excluded from further examination.

Friction force could not be measured simultaneously with the gas emission because of cross-talk interference between the force gauges and the analytical equipment (the pressure gauges and the mass-spectrometer). Therefore, a separate series of experiment was conducted to measure friction force under vacuum using ultrahigh vacuum tribometer Ca^{3}UHV [29] with reciprocating motion pin-on-flat configuration. A boron glass ball, 3 mm in diameter, was a counterbody. The maximum sliding velocity and acceleration were 60 mm/s and 15 mm/s^2, correspondingly. The sliding distance was 2 mm and the number of sweeps in each test was 400. Three repeated tests were done with the normal loads 1.96 N, 4.91 N and 9.81 N.

Chemical composition of the coatings was characterized using Elastic Recoil Detection Analysis (ERDA) and Rutherford Backscattering Spectrometry (RBS) with He$^+$ beam of 3 MeV energy. Mono- or bilayer coating models were developed and fitted to the experimental data by means of the Simplex algorithm using SIMNRA software [45]. Raman spectrometry and Attenuated Total Reflection Fourier-Transformed Infrared (ATR-FTIR) spectrometry were used to study chemical bonding in the coatings. The hardness of the coatings was measured by means of instrumented nanoindentation technique.

3. Results

3.1. Mechanically stimulated gas emission

3.1.1. Emission behaviours

An initial exploratory test was carried out on each sample. In this test the ion time series with m/z from 1 to 100 were measured. A previously developed statistical method [44] was used to sift through the measured data and to rule out the signals, whose response to rubbing was not statistically significant (in comparison with the background noise) at the critical level 0.05. The statistically significant channels are listed on Table 2.

Previous works showed that the assignment of the ion species to molecular or radical precursors can be facilitated if the channels are grouped according to their behaviour patterns [40,44,46]. For this purpose, the behavioural analysis of the measured dta was carried out. Fig. 1 shows the representative plots of the selected ions time series, in which three behavioural patterns are clearly noted. The first one, denoted λ, applies to m/z 20 and 40, which were ascribed to Ar^{++} and Ar$^+$, respectively. It is characterized by two stages. In the first stage (1a in Fig. 1 (a)) a burst with a sharp rise occurred just at the beginning of rubbing. Then, the emission rate decreased nearly linearly with time. The first stage lasted about 200 rubbing cycles (100 s). The second stage came out after a short transition and was characterized by a series of chaotic bursts (2a in Fig. 1 (a)). Mean emission rate in the second stage