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Tribochemistry of hydrogenated amorphous carbon through analysis of Mechanically Stimulated Gas Emission

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ABSTRACT

Analysis of Mechanically Stimulated Gas Emission Spectrometry data combined with characterization of chemical composition, structure and mechanical properties of various hydrogenated amorphous carbon coatings has allowed shedding light on the possible reactions of tribochemical degradation. These reactions are conceivably driven by the mechanical deformation and stress rather than by frictional heating. A close correlation between the increase in proportion of *sp*^{3} CH$_x$ groups in the coating and the rate of CH_4 emission was observed. Emission of methane is suggested to involve abstraction of methyl radical followed by recombination with hydrogen atom. Generation of ethane has to be due to recombination of two abstracted methyl radicals rather than an ethyl radical with hydrogen atom. The rate of H_2 emission steeply and non-linearly increased with the hydrogen content in the coating. Hydrogen generation can involve both liberation of occluded H_2 and re-combinative reaction.

1. Introduction

Superlubricity of hydrogenated amorphous carbon (a-C:H) under ultrahigh vacuum and inert atmosphere is very attractive for practical applications in aerospace and nanoelectronics sectors; however, the durability of a-C:H solid lubricants must be significantly enhanced. Break-up of super-low friction (SLF) associated with seizure and severe coating damage has been basically attributed to hydrogen depletion in a-C:H or H-terminated a-C [1–7]. Recently it was shown that, under moderate sliding conditions, hydrogen emission must be related to tribochemistry rather to thermal desorption [7–9]. In these latter references, computer simulation is performed with a thermostat, so frictional heating is weak. The chemical reactions involved in hydrogen liberation from a-C:H remain poorly understood. For this purpose a new method based on the analysis of mass-spectra of Mechanically Stimulated Gas Emission (MSGE) was developed [10,11] and used [9] for real time probing of tribochemical degradation in ultrahigh vacuum (UHV) of four a-C:H coatings with hydrogen content between 15 and 46 at.%. Fig. 1 shows the total gas emission rate for H_2 and CH_4 as a function of hydrogen content in the coatings. The emission rate significantly increased with the increase in hydrogen content. Furthermore, higher alkanes (C_2H_6 and C_3H_8), CO and CO_2 were found for the most hydrogenated coatings (46 at.% of H), whereas for the coatings obtained by Ar^+ beam assisted deposition, Ar was the dominant emitted gas.

Since MSGE is a probe of tribochemical degradation of a-C:H, both of them depend on the chemical composition and physical properties of the coating, which vary with the deposition parameters. Therefore the present work is aimed at characterizing the elemental composition, structure, surface chemical composition, density, elastic modulus and nanohardness of the same four a-C:H coatings used in the previous work [9]. On the basis of these results the possible chemical reactions laying behind tribochemical degradation of various a-C:H are proposed.

2. Experimental techniques and procedure

2.1. Coatings

The first two coatings (D-1 and D-2) were deposited using the Ion Beam Deposition method, whereas the other two (D-3 and D-4) using the Plasma Assisted Chemical Vapour Deposition with various gas precursors and deposition conditions. The details of the coatings deposition were described in the previous work [9]. The main deposition parameters are summarized in Table S2 in Supplementary materials.

2.2. RBS and ERDA

Elemental chemical composition of the coatings was determined using Rutherford Backscattering Spectroscopy (RBS) with He^{2+} ions at

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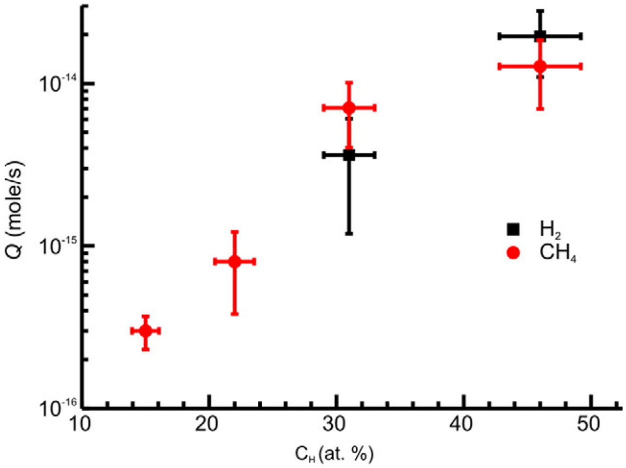

Fig. 1. Emission rate of H_2 and CH_4 under friction of four amorphous carbon coatings as a function of hydrogen content in the coating.
From the data reported in [9].

3.045 MeV and ion current in the range between 11.5 and 13.8 nA. The total ion dose received by a coating was 5 μC. Hydrogen content in these coatings was determined previously [9] and used in the present work to correct the absolute concentrations of other elements.

2.3. XPS

X-ray Photoelectron Spectrometry (XPS) measurements were carried out in an UHV chamber with a base pressure of 1×10^{-10} mbar. The angle between the hemispherical analyser (Specs-PHOIBOS100) and the plane of the surface was 60°. An X-ray radiation source with the MgK_α line (1253.6 eV) was used. C 1s and O 1s core levels were measured with a step in kinetic energy of 0.1 eV and pass energy of 15 eV. Before the analysis, the contribution of the MgK_α satellite line was subtracted. The spectra were normalized by maximum and subjected to a Shirley background subtraction formalism [12]. Distribution of chemical elements in depth was studied employing Ar^+ sputtering with the rate of 0.23 nm/min. To account for sample surface charging, the binding energy scale in the XPS spectra was aligned taking as reference the C 1s core line at 285 eV. For peak fitting, 80% Gaussian and 20% Lorentzian products were used. Information about the relative abundance of carbon hybridised *sp*, sp^2 and sp^3 fractions was obtained by decomposition of C 1s core electron binding energy spectra employing the constrains fitting procedure, already published [13–15].

2.4. ATR FTIR

Owing to the localised nature of C–H vibrations and the sensitivity of their frequency to the nature of C–C back bonds the analysis of the C–H vibrational modes with infrared spectroscopy has a considerable potential for structural investigations of a-C:H [16]. A single bounce Attenuated Total Reflection Fourier-Transformed Infrared Spectroscopy (ATR FTIR) was used to study the structure of the coatings. Four scans with a resolution of 2 cm^{-1} were averaged for each sample. The measurements were repeated several times at different positions and angular orientation on each sample yielding good reproducibility.

The spectra were decomposed by Gaussian-shape contributions which were carefully identified using available literature data [16–26]. In this work we focused on the qualitative analysis aimed at the identification of alkyl, alkenyl and aryl groups and coordination of carbon atoms.

2.5. Nanoindentation

Hardness and elastic modulus were determined by nanoindentation using Berkovich diamond indenter. Nanoindentation tests were performed on Nanoindenter XP (Nanoinstruments Innovation Center, MTS systems, TN, USA) using the continuous stiffness measurement methodology (CSM) [27]. Previous to the indentation tests on the samples, the contact area function of the tip vs. penetration depth (up to 100 nm) was calibrated using a standard fused silica block up to maximum penetration depth of 100 nm. In order to avoid the influence of the substrate in the measurement, the contact stiffness evolution was used in order to select suitable values of both properties [27].

3. Experimental results and discussion

3.1. ERDA and RBS

Elemental compositions of the coatings determined from the RBS and ERDA data are shown in Fig. 2. For all studied coatings absolute H concentration increased from the deeper layers of the coating to a free surface. In the same manner the H/C ratio is also increased that is consistent with previous publications and was related by various authors to

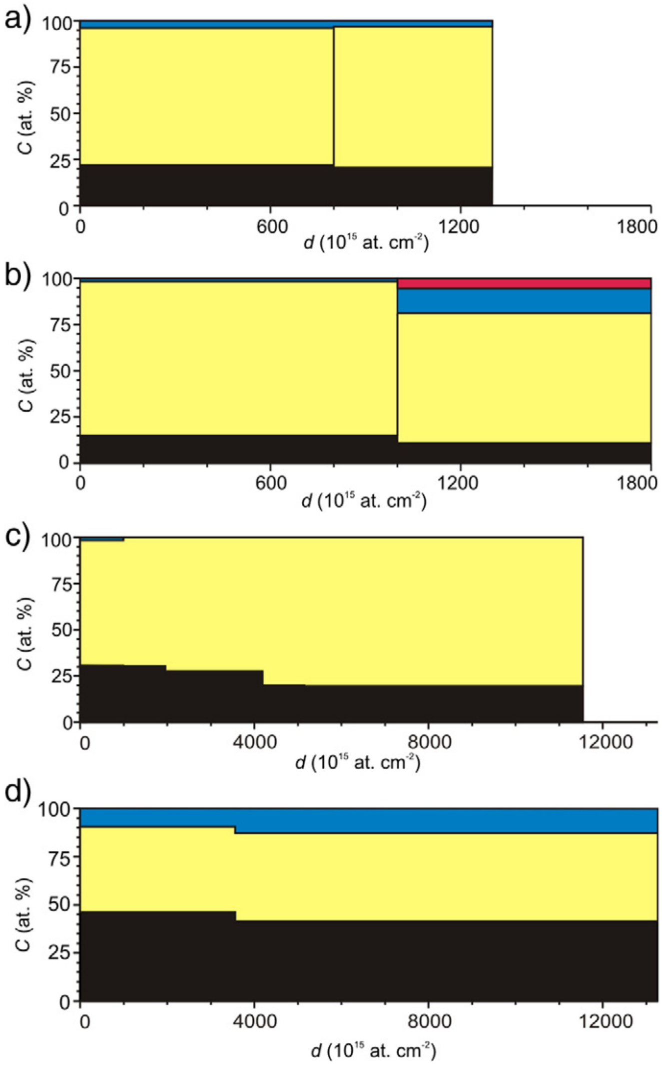

Fig. 2. Relative chemical composition of the coatings measured by RBS and ERDA: a) D-1; b) D-2; c) D-3; and d) D-4. *d* is the depth (black — H, yellow — C, blue — O, pink — Ar).