

論文の内容の要旨

論文題目 Structural Characterization of Hydrogenated Amorphous Carbon (a-C:H)
Coating by Solid State ^{13}C NMR and Its Wear Mechanism under Shear
(固体 ^{13}C NMR法を用いた水素化非晶質炭素薄膜構造特性評価とせん断応力下の摩耗
メカニズムの解析)

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In this thesis, structural characterization of hydrogenated amorphous carbon (a-C:H) coating has been studied by applying solid state ^{13}C NMR. The $\text{sp}^3/(\text{sp}^3+\text{sp}^2)$ ratio of ion-vapor deposited a-C:H coating was obtained by ^{13}C MAS. As the bias voltage increased from 0.5 kV to 2 kV, both the hardness and residual stress of studied a-C:H coating reached at its maximum value and then gradually reduced with further increase of bias voltage up to 3.5 kV, whereas the $\text{sp}^3/(\text{sp}^3+\text{sp}^2)$ ratio continuously reduced with the increase of bias voltage within 0.5~3.5 kV. Thus, it can be argued that the mechanical property of a-C:H coating is proportional to the fraction of non-hydrogenated sp^3 C, rather than the total population of sp^3 phase carbons. Also, the higher $\text{sp}^3/(\text{sp}^3+\text{sp}^2)$ ratio obtained by ^{13}C CPMAS with various contact time within 0.2~20 ms than that of ^{13}C MAS implied that there was a type of sp^2 clusters that was distant from hydrogenated carbons.

Meanwhile, unique structural heterogeneity was observed in ion-vapor deposited a-C:H coatings by performing ^{13}C MAS and ^1H - ^{13}C CPMAS experiments. Two distinct types of sp^2 C clusters were discovered: one of them denoted as $\text{sp}^2 \text{C}'$ in content of 3~12 at.% was non-protonated specifically localized in hydrogen-absent regions, while the other dominant one denoted as $\text{sp}^2 \text{C}''$ was hydrogenated or at least proximate to proton spins. On basis of the notably analogous variation of $\text{sp}^2 \text{C}'$ content and Raman parameters as function of substrate bias voltage in the whole range of 0.5 kV~3.5 kV, a model of nanoclustering configuration was proposed that the $\text{sp}^2 \text{C}'$ clusters were embedded between $\text{sp}^2 \text{C}''$ clusters and amorphous sp^3 C

matrix as trapped interfaces or boundaries where the sp^2 carbon bonds were highly distorted. Continuous increase of bias voltage would promote the nano-clustering and re-ordering of dominant $sp^2 C''$ clusters, thus results in a marked decrease of interspace and a change of the content of $sp^2 C'$ clusters.

Further exponential fitting analysis on the magnetization relaxation behavior of $sp^2 C''$, $sp^2 C'$ and $sp^3 C$ revealed that the magnetization recovery of $sp^2 C''$ exhibited a typical stretched-exponential approximation with stretched power α equal 0.8 and T_1 equal 2.8 s, while $sp^2 C'$ showed single-exponential approximation with T_1 equal 5 s due to its hydrogen-free property, and $sp^3 C$ showed weak single-exponential approximation with T_1 equal 3.7 s. The difference of T_1 value among $sp^2 C''$, $sp^2 C'$ and $sp^3 C$ proved the existence of distinct sp^2 clusters in studied a-C:H coatings, and the stretched-exponential approximation of $sp^2 C''$ was caused by prominent presence of paramagnetic centers. In case of 1H spins, the magnetization recovery showed better bi-exponential approximation with long and short $T_1(H)$ fluctuated within 25~55 ms and 0.1~0.3 ms approximately in content of 70%~80% and 30%~20%, respectively, varying with various bias voltages. The interrupted ^{13}C saturation recovery with an interval of short $T_1(H)$ component showed that most of quick-relaxing protons were localized nearby $sp^2 C''$ clusters. Such a short $T_1(H)$ was only possibly resulted from a relaxation mechanism associated with electron-nuclear dipolar interaction or spinning diffusion, and its partial distribution in $sp^2 C''$ clusters may imply more complex configurations of unpaired electrons in studied a-C:H coatings. Additionally, the correlations between clustering structure of sp^2 sites and the optical property of a-C:H coating has also been studied. Results shows a monotonic dependence of E_g and E_{04} on deposition bias voltage which indicates the primary influence sp^2 fraction on optical gap, rather than the configuration of $sp^2 C'$ sites in boundary areas of dominant $sp^2 C''$ clusters as expected. This gradual transition of optical property with increasing deposition bias voltage is attribute to the medium range order of sp^2 sites in amorphous carbon framework.

Furthermore, the wear mechanism of ion-vapor deposited a-C:H coating has been

investigated by using a ball-on-plate device in N₂ atmosphere (with few presence of humid air) and ambient air. An Obvious correlation between the nanoclustering structure of a-C:H coating and its friction performance was observed, especially as tribotests conducted in N₂ atmosphere. We found comparatively higher friction coefficient in diamond-like coating, namely as bias voltage was 1.0~2.0 kV, and lower friction coefficient of polymer-like coating and graphite-like coatings (still with hydrogen content about 18 at.%). Qualitative analysis of wear marks revealed that compared with as-deposited coating, the ball scar derived from B2.0 coating showed largest growth of I(D)/I(G) and reduce of G peak width, as well as moderate up-shift of G peak, which implied a great transformation of sp³ C to sp² C in aromatic rings in amorphous manner, whereas the ball scar derived from B0.5 coating showed a reduce of I(D)/I(G), as well as slight decrease of G peak width and moderated increase of G peak position, which implied a transformation of sp² C from rings to chains with coordination with hydrogens showing good lubricity. One possible explanation on such correlation is that the boundary sites trapping around sp² clusters may inhibit the formation of lubricant transfer layers enriched of sp² C-H bonds in chains under dry sliding conditions. Meanwhile, by performing one set of overlapping tribotests of a-C:H coating/steel ball tribopairs in ambient air, both the morphology and chemical characteristics of transfer layers were tracked by *ex situ* optical microscopy, XPS and SEM/EDX. Experimental results show that Carbon-based transfer layer was built up in the first sliding cycle in all the tribotests, and covered by an oxygen-rich chemisorption layer on the top surface. At the beginning of running-in period, the steel ball was consumed more rapidly than a-C:H coating, so that transfer layer was mainly composed of loosely compacted debris with relatively higher content of iron oxides, and consequently brought out severe third-body abrasion of counterface. As sliding went by, the size of wear debris decreased a lot while the compactness of transfer layer and its adherence to spherical surface improved markedly, thus resulted in a gradual reduce of wear and friction coefficient. A three-stage model was presented to describe the wearing process of studied a-C:H coating/steel ball

tribopairs sliding in ambient air. Meanwhile, a close correlation between the average contact pressure and the wear rate of steel ball is discussed. The XPS detection of Ar⁺-cleaned transfer layer showed that except for the typical graphitization of transferred carbon materials, a noticeable tribochemical oxidation of carbon also occurred on the top surface of transfer layer and impacted the friction force strongly. The average CoFs increased correspondingly with the total content of C/O bonds in this tribochemical oxidation layer. Obvious correlations between the nanoclustering structure of a-C:H coating and its friction performance was observed in tribotests conducted in N₂ atmosphere. The steady state friction coefficients of a-C:H coatings deposited under various bias voltage within 0.5~3.5 kV developed synchronously to the fraction of sp² C' cluster, which is an effective indicator of cluster disordering of carbon framework.