Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B3-2

Deposition Technologies and Applications for Diamond-like Coatings

Moderators: Frank Papa, Gencoa Ltd., USA, Klaus Böbel, Bosch GmbH

8:00am **B3-2-1 Tribological Behavior of Unlubricated Sliding between Steel Ball and Si-DLC Deposited by Ultra-high-speed Coating Employing MVP Method**, *T Nakano, K Yamaguchi,* ***Ippei Tanaka****, H Kousaka,* Gifu University, Japan*; H Hashitomi,* Cnk Co., Ltd., Japan

Recently, with increasing demands for energy saving by friction reduction and lifetime extension by wear reduction, the application of DLC (Diamond-Like Carbon) is spreading gradually and steadily. In this field, higher-speed coating method with applicability to 3-dimensional shapes is strongly desired. Plasma CVD is a promising candidate for such demands due to its excellent capability for coating 3-dimensional shapes; however, typical coating speed of DLC with conventional plasma CVDs is not so high, ~1 µm/h; in addition, further drastic increase of the coating speed is not expected due to the use of low-density (n_e~10^8–10^{10} cm^{-3}) DC or RF plasma in such conventional methods. The use of higher-density plasma is considered to be essential for increasing the coating speed. Thus, we have proposed a high-speed coating method of DLC with a novel plasma CVD employing much higher-density plasma (n_e~10^{11}–10^{13} cm^{-3}), which is sustained by microwave propagation along plasma-sheath interface on metal surface. In our previous work, a considerably high deposition rate of 156 µm/h and hardness of 20.8 GPa was obtained. In this work, we investigated the effect of film composition on friction property of Si-containing a-C:H films in such ultra-high-speed DLC coating.

Si-containing a-C:H films (one type of DLC) were deposited on steel substrates by different 2 methods: DC plasma and microwave-excited high-density near plasma, or our newly proposed method, where the gas composition of Ar, CH_4, C_2H_2, and TMS in source gas flow was changed. Friction tests were conducted in a ball-on-disk apparatus under dry condition, where a SUJ2 ball 8 mm in diameter contacted to a DLC-coated disk at a normal load of 1 N. Sliding test was conducted for 60 minutes at a rotation speed of 250 rpm. The atomic composition of the films was evaluated by XPS for C, O, and Si, and RBS-ERDA for H/C.

The hydrogen and silicon contents were from 25 to 35 at% and from 7.76 to 28.43 at%, respectively. Friction coefficient of Si-containing a-C:H films was decreased from 0.12 to 0.025 with decreasing oxygen content from 0.75% to 4.15%. This result indicates the possibility of decreasing friction coefficient by oxygen content in Si-containing a-C:H films .

8:20am **B3-2-2 Tribological Behavior of DLC Coatings on AISI 4340 Steel Deposited in PECVD DC-Pulsed Technique with Additional Cathode for Automotive Applications**, ***MarcoA. Ramirez R.****, D Lugo,* National Institute for Spacial Research INPE, Brazil*; N Fukumasu, I Machado,* Surface Phenomena Laboratory - Polytechnic School - University of Sao Paulo - Brazil, Brazil*; E Mitma P., V Trava-Airoldi,* National Institute for Spacial Research INPE, Brazil

Diamond-Like Carbon (DLC) coatings have attracted significant attention due to its low friction, high hardness, high wear resistance, among others. These films meet conditions that can be used in some mechanical applications in aerospace and automotive industries. The major disadvantage of these coatings is the low adhesion on metallic substrates, caused by elevated compressive residual stresses after deposition. Some plasma conventional methods require a high consumption of energy that are used to grow DLC films, resulting in a high level of temperature and pressure during the deposition, which affects the adhesion of the film to the substrate. The use of PECVD-DC Pulsed with additional cathode, allows to grow DLC films in extremely low pressure and temperature. In this work, DLC coatings were deposited employing an asymmetrical bipolar pulsed-DC PECVD with additional cathode at temperature as low as 90 C and pressure as low as 0.1 Pa, which allowed a collisionless regime and a higher plasma density. Acetylene gas was used as a precursor. In order to overcome low adhesion of DLC films on steel substrate, a thin amorphous silicon interlayer was deposited as an interface. Resulting coatings were analised with SEM-FEG and Raman scattering spectroscopy in terms of morphology and atomic arrangement,respectively. The total residual stress was evaluated by the curvature method. The tribological behavior (friction and wear) was analyzed by reciprocating wear tests at room temperature. Adhesion was evaluated in accordance with the VDI3198 norm, based on a Rockwell C indentation test. XPS analyses, will also be used in order to get a relationship among the adhesion and the silicon interface on set nucleation parameters. The elevated coating hardness (higher than 25 GPa) promoted good wear resistance. These results suggest that the PECVD-DC Pulsed with additional cathode and acetylene as a precursor gas to grow DLC films on engineering steels may represent a new alternative to improve the mechanical behavior in automotive applications.

8:40am **B3-2-3 Structural Evolution and Temperature-sensitivity of W-containing Diamond-like Carbon Films Deposited by a Hybrid Linear Ion Beam Systems**, ***Peng Guo****, L Sun, P Ke, A Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

In present study, W-containing diamond-like carbon (W-DLC) films (0.3~70.4 at.%) were fabricated by a hybrid beams system consisting of a DC magnetron sputtering and a linear ion source. The influence of composition and microstructure on the room temperature (300 K) resistivity and temperature coefficient of resistance (TCR, 300~400 K) of the W-DLC films were also investigated. As evidenced by XPS, XRD, TEM and Raman measurements, the microstructure of W-DLC films evolved from amorphous carbon matrix with dissolved W atoms into composite materials made of WC_{1-x}/W_2C nanocrystallites embedded in amorphous carbon matrix with increasing W concentration. The electrical resistivity of the temperature of all the films exhibited a negative TCR. The mechanism of the temperature sensitivity in the W-DLC films was also discussed.

9:00am **B3-2-4 Effects of Carbon Content and Argon Flow Rate on the Triboperformance of Self-lubricating WS_2/a-C Sputtered Coating**, ***Huatang Cao****, J Th.M De Hosson, Y Pei,* University of Groningen, Netherlands

Layered transition metal dichalcogenides (TMD) such as WS_2 are materials well-known for their solid lubrication properties [1]. However, the lubricating property degrades through oxidation or moisture and it is also limited by its low hardness and low load-bearing capacity. In contrast amorphous diamond-like carbon (DLC) films are reported to have many features that contribute to excellent tribological characteristics, such as high hardness, anti-wear property with both low friction coefficient and low wear rate[2]. The present research aims at depositing WS_2/a-C nanocomposite coatings by magnetron co-sputtering method. The effects of carbon content and argon flow rate on the microstructure and mechanical performance were investigated. The WS_2/a-C nanocomposite tribocoating was scrutinized by electron microscopy and mechanical testing. Transmission electron microscopy reveals feathery WS_2 platelets, randomly distributed in the amorphous carbon matrix. The nanocomposite coating turns out to be more amorphous-like with increasing carbon content. Nanoindentations tests show that the hardness and elastic modulus of the coating increase with increasing carbon addition while decreasing with a higher argon flow from 10 sccm to 25 sccm.

Ball-on-disk tribotests (100Cr6 steel ball as a counterpart) show that the coefficient of friction can be as low as 0.017 in a dry environment (<5% relative humidity). It reaches 0.15 in a high humidity surrounding and remains stable within 20000 sliding cycles.

References:

1. S. Prasad, J. Zabinski. Super slippery solids, Nature 387, 761-763(1997).

2. A. Nossa, A. Cavaleiro, N.J.M. Carvalho, B.J. Kooi, and J.Th.M. De Hosson, On the microstructure of tungsten disulfide films alloyed with carbon and nitrogen, Thin Solid Films 484 (1-2), 389-395(2005).

9:20am **B3-2-5 Industrial Development of Carbon-based Coatings**, ***Ruud Jacobs****, G Fransen, R Tietema, D Doerwald, J Landsbergen,* IHI Hauzer Techno Coating B.V., Netherlands **INVITED**

In this presentation an overview will be presented on the developments of carbon-based coatings for applications in automotive technology.

Initially the introduction of high pressure diesel injection technology required the introduction of wear resistant coatings to protect the steel parts against wear to prevent leakage of pressure and damage to components. In the earliest phase of development, metal doped DLC's produced by sputtering were applied, soon however because of a demand for higher wear protection followed by the introduction of hydrogenated DLC's produced in hybrid sputter/PECVD processes. Due to the improved fuel efficiency, power densities increased causing strain on other components in the engine, as well as in the valve and power train, consequentially leading to a demand for wear protection coatings on those parts as well.

In the last decade the requirement for reduced emissions of CO_2 gave a strong boost to the market for components. Reduced friction, reduced weight and increased efficiency in fuel combustion were necessary to meet the new demands.

Developments in lubricants tend to go in the direction of lower viscosity. Hybrid technology and start-stop engines increase the operating time of the engine in mixed-mode lubrication. Both trends in automotive development direct to increasing wear resistance requirements. This has been leading to large scale introduction of ta-C (tetrahedral carbon) coatings produced by arc technology after 2010. These ta-C coatings are offering for many cases an optimum of highest hardness in combination with lowest friction, but a post-treatment is required to optimize the surface quality of the coated components. Newest developments in tribological contacts tend to go in the direction of higher operating temperatures combined with high wear resistance and minimum friction, whereas also the cost of the system plays an important role.

10:00am **B3-2-7 Glow Discharge and Deposition of Thick DLC Film in Cage-shaped Hollow Cathode System with Adjustable Bias***, **Xiubo Tian**, M Wu, C Gong,* Harbin Institute of Technology, China*; R Wei,* Southwest Research Institute, USA

Diamond-like-carbon (DLC) has been widely utilized in related industries to tribological, optical, electrical applications, etc. A cage-shaped hollow cathode discharge (C-HCD) has been utilized to produce high-density plasma for deposition of DLC films. To further optimize the microstructure and surface properties of the DLC films, a new approach is proposed, in which the energy of ions incident to the sample surface can be independently controlled by an additional bias between the samples and the metal cage (mesh). The samples are biased with a voltage from 0V to -500V with respect to the cage biased with 1000-4000V (pulse). The internal sample bias has a critical effect on the cage hollow cathode discharge. Generally the glow discharge of C-HCD system is enhanced by the sample bias. However with a higher C-HCD current, there exists a certain sample bias which weakens the glow discharge. It is attributed to the competing effect of both self-discharge and ion consumption induced by negatively-biased sample. Compared to conventional method, additional bias effectively removes thecarbon contamination and some macro-burring on the sample surface. And the bias also leads to the formation of the surface protuberances with nanoscale size. The clean surface and mechanical lock structure have effectively improved the adhesion between the film and substrate. Si-DLC films have been synthesized with a mixture of Ar, C_2H_2 and tetramethylsilane (TMS). The results demonstrate that the DLC films have been deposited with a higher rate (4~6um/h) due to higher plasma density produced by high-current pulse in the mesh cage. The intense ion bombardment significantly densified the microstructure and reduced the H contents, and consequently increased the nanohardness (*H*) of DLC films. As an example, a DLC film was deposited on HSS with thickness of 40um and critical load of ~100N. Our results have proven that this novel set up may be a very effective tool to fabricate DLC films with high deposition rate and excellent surface properties with denser microstrcture.

10:20am **B3-2-8 Enhanced Adhesion Of Hard Dlc Coatings On Metallic And Insulating Substrates***, **Ivan Fernandez**,* Nano4energy Sl, Spain

Diamond-Like Carbon (DLC) coatings have been recognized as one of the most valuable engineering materials for various industrial applications including manufacturing, transportation, biomedical and microelectronics. Among its properties, DLC has good frictional behaviour combined with high surface hardness, offering an elevated protection against abrasive wear.

As the industrial success of DLC films in tribological contacts is strongly dependent on their adhesion properties, two different approaches were used to enhance DLC coating adhesion onto both metallic and insulating substrates.

- HiPIMS metal ion etching and implantation with both Ti and Cr plasmas was used to pre-treat the M2-HSS metallic substrates, obtaining Rockwell HF1 values and critical loads in the macro-scratch tests above 100N .

- Positive ion-assisted pre-treatment [1] was used to etch glass substrates and promote strong adhesion of thin DLC layers. Taber abrasion tests were performed to evaluate the pre-treatment process effect on the coating adhesion. A significant DLC coating adhesion improvement was observed.

10:40am **B3-2-9 Low Friction of Graphene Nanocrystalline Embedded Carbon Nitride Coatings Prepared with MCECR Plasma Sputtering***, **Pengfei Wang**,* Institute of Nanosurface Science and Engineering, Shenzhen University, China*; W Zhang,* Xi'an Jiaotong University, China*; D Diao,* Shenzhen University, China

The excellent mechanical and tribological behaviors of amorphous carbon nitride coatings, especially the super-low friction performance (friction coefficient of less than 0.01 in dry nitrogen gas environment) made them good candidates as solid lubrication coatings in advanced engineering applications. However, the low friction mechanism of carbon nitride coatings in nitrogen gas environment is still not yet clearly understood. The objective of this research is to clarify the key factors of atomic composition and structure of the carbon nitride coating itself in achieving the low friction in nitrogen gas environment.

In this work, graphene nanocrystalline embedded carbon nitride (GNECN) coatings were fabricated with the mirror confinement electron cyclotron resonance (MCECR) plasma sputtering method under low energy electron irradiation. It is clearly observed that the deposition rate, internal stress, surface roughness and hardness of the prepared GNECN coatings change with the variation of the flow ratio of argon and nitrogen gas in the operating gas under a pressure of 0.04 Pa. Moreover, graphene nanocrystalline structure was identified in the amorphous carbon nitride matrix from the analyses of TEM, XPS and Raman spectroscopy. Furthermore, stable and low friction coefficient of less than 0.05 of GNECN coating was achieved after a short run-in period when slid against Si_3N_4 ball in nitrogen gas environment. A uniform transfer film was formed on the worn surface of counterpart ball material according to the optical image. It is believed that the introduction of graphene nanocrystalline structure plays a key role in achieving low and stable friction coefficient of GNECN coatings, which could help us better understanding the low friction mechanism of CNx coatings in nitrogen gas environment from the viewpoint of the composition and structure of the coating. Moreover, the clarification of the relationship between the low friction behavior and electric output property of the contact surfaces is beneficial for understanding the tribo-electrification principle as well as exploring the application of GNECN coatings in tribo-energy field.

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