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研究課題名（和文）Study of the Tribological Properties of Graphene and Related Materials Under Extreme Environments

研究課題名（英文）Study of the Tribological Properties of Graphene and Related Materials Under Extreme Environments

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研究成果の概要（和文）：グラフェン酸化物をベースとした非金属多層膜、これは水素貯蔵および流通システムに用いる圧力レギュレーター、フローレギュレーターおよびストップバルブの皮膜を目的としているが、これを金属基板に成膜した。初めてグラフェン酸化物ベースのコーティングで超潤滑（COF<0.002）を観察した。乾燥窒素と水素中でのグラフェン酸化物の滑りがオニオンライクカーボン（OLC）ナノ粒子を生成し、湿った雰囲気はOLC粒子を破壊することが分かった。DFTシミュレーションを用いて、滑り中のナノ粒子の動きを引き起こす機構または科学を調査した．このプロジェクトから2つの論文（ACS）と6つの学会プロシーディングを作成した

研究成果の概要（英文）：1. Graphene oxide based non-metallic multilayered coatings developed on steel substrates for the coating applications in pressure regulator, flow regulator and stop valves in the hydrogen storage and distribution systems. First time ever, superlubricity (COF < 0.002) is observed for graphene oxide based coatings. Onion-Like Carbon (OLC) nanoparticles were found to be generated during sliding of graphene oxide in dry nitrogen and hydrogen, while humid atmosphere destroys the OLC particles.
2. The mechanism or science behind the evolution of nanoparticles during sliding was investigated using DFT simulations. Two journal papers (ACS Applied material and interfaces) and six conference proceedings were produced from this project.

研究分野：Tribology

キーワード：graphene oxide　superlubricity　hydrogen and nitrogen　GO transfer film　layer-by-layer　solid lubricant　onion-like carbon　nanoparticles

１．研究開始当初の背景

The tribological behavior (i.e. friction and wear) of ultra-low friction materials and coatings in extreme environments (hydrogen) requires detailed investigation for reducing the energy loss from friction and to enhance the lifetime of components. The frictional properties of graphene and related materials and other layered materials such as graphene oxide (GO) and Molybdenum disulfide (MoS_2) have not yet been extensively explored under extreme environments such as hydrogen and nitrogen. Very basic friction tests performed on graphene in air have produced promising results, and graphene could feasibly replace DLC coatings. If we find out the conditions in which graphene shows good tribological performance, it could be suitable for many applications such as hydrogen fueling stations, FCVs, and MEMS/NEMS. In this project the macroscopic tribological properties of graphene and Molybdenum disulfide (MoS_2) will be studied in controlled environments such as hydrogen, nitrogen, argon, humidity, and oxygen. These macroscopic test results will be compared with nanotribological properties and the gap between nano and macro scales can be bridged. Solid conclusion will be drawn about the underlying tribological mechanisms of graphene's frictional properties.

２．研究の目的

The purpose of this research is to investigate the tribological behavior of layered solids such as graphene oxide and MoS_2 based non-metallic coatings on steel substrates in hydrogen and non-hydrogen environments for the coating applications in pressure regulator, flow regulator and stop valves in the hydrogen storage and distribution systems. The physical and chemical interpretations of the observed friction results will be used to construct an empirical model to predict the tribological behavior over wide range environmental and operating conditions. Hence, In the beginning, the role of every variable such as load, speed, environment on friction results is obtained through an experiments. I am also investigating the failure mechanics (i.e. contact mechanics and wear modes) of these coatings with respect to environments to design durable coatings (less wear).

３．研究の方法

To design a durable coating (low friction and wear) and to predict the tribological behavior over wide range of environmental and operating conditions, empirical models are necessary. In order to develop an empirical model, preliminary results and data are necessary. Hence, I developed a coating and performed tribological experiments. First time ever, super-low friction coefficients (COF, $\mu < 0.04$) were observed in hydrogen and nitrogen for GO based coatings. The energy conservation was up to 20 times in H_2 and N_2 than in humid ambient air. Physical and chemical interactions promoted by dry environments (H_2 and N_2) have led to super low friction. The physical interactions are studied by morphology study, film design, wear assessment, failure mechanics, contact mechanics and environmental control. Chemical interactions are studied by analytical chemical characterizations and DFT simulations. Understanding the influence of physical and chemical interactions is essential to identify the role of each variable on friction. Then, empirical model will be developed using this knowledge for estimation of friction for a wide range of environmental and other conditions such as load, speed, pressure and so on.

４．研究成果

1. We successfully developed a 300nm thin (PEI/GO)n films on steel using layer-by-layer (LBL) technique.
2. We successfully demonstrated for the first time that the Graphene oxide can provide the superlubricity (COF ~ 0.005) in macroscale engineering applications. We also postulated that the moisture in the air or nitrogen can significantly affect the tribology of Graphene oxide or GO based lamellar coatings.
3. We also proposed nano-roller low friction mechanism for the observed superlubricity in dry environments (N_2 and H_2) for the first time.
4. We also provided an insight into how water or dry gases such as N_2, intercalates between the graphene oxide layers to influence the Nano scrolls formation, using DFT simulations.
5. We made a profound investigation on carbon transfer film formation with six different polymer counterface balls, in air and dry nitrogen environments. The relationship between tribopairs (ball and surface), environments and friction behavior is investigated.
6. We concluded that the hardness and surface energy of counterface ball are more important parameters out of 20 plus parameters that seem to influence the formation of tribo-films, and consequently very low COFs in this system
7. We plan to make an empirical model using these findings to predict the tribological behavior of system that are running in hydrogen and other environments.

５．主な発表論文等

（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計　3　件）(All journals are peer-reviewed)

1. Prabakaran Saravanan, Sundaramurthy J, Duong H M and S. K. Sinha. A comprehensive study on the self-lubrication mechanisms of SU-8 composites. *Tribology International*, 95 (**2016**) 391–405. (DOI: 10.1016/j.triboint.2015.11.044;) URL : http://dx.doi.org/10.1016/j.triboint.2015.11.044)
2. Prabakaran Saravanan, R. Selyanchyn, H. Tanaka, D. Darekar, A. Staykov, S. Fujikawa, S. M.Lyth and J. Sugimura. Macroscale superlubricity of multilayer polyethylenimine / graphene oxide coatings in different gas environments. *ACS Appl. Mater. Interfaces*, 8 (40) (**2016**) 27179 - 27187. (DOI: 10.1021/acsami.6b06779; URL: http://dx.doi.org/10.1021/acsami.6b06779)
3. Prabakaran Saravanan, R. Selyanchyn, H. Tanaka, S. Fujikawa, S. M. Lyth and J. Sugimura. Superlubricity of graphene oxide mediated by stable tribo-film formation in nitrogen atmosphere. Submitted to *Carbon*.

〔学会発表〕（計　5　件）

1. Prabakaran Saravanan, Roman Selyanchyn, Shigenori Fujikawa, Jochi Sugimura, "Frictional Behavior of (PEI/GO)X Solid Lubricant Coatings on Steel Substrates in Extreme Environments",**71st STLE Annual Meeting, 2016, May 15- 19, LAS VEGAS, USA**.
2. Prabakaran Saravanan, Roman Selyanchyn, Hiroyoshi Tanaka, Jochi Sugimura, "Ultra-low Friction of Polyethylenimine / Graphene Oxide Lamellar Coatings in

Various Atmospheres.", **STLE Tribology Frontiers Conference, 2016, November 13-15, Chicago, USA.**

3. Prabakaran Saravanan, Hiroyoshi Tanaka, Jochi Sugimura, "Macroscale Superlubricity of polyethylenimine / graphene oxide coatings Films in Dry Environments.", **JAST Autumn Tribology Conference, 2016, October 12-14, Niigata, JAPAN.**
4. Prabakaran Saravanan, Hiroyoshi Tanaka, Jochi Sugimura, "Superlubricity of (PEI/GO)n multilayer coatings in Various Environments." **JSPS-DST Asian Academic Seminar, 2016, December 14-20, Tokyo, JAPAN.**
5. Prabakaran Saravanan, Roman Selyanchyn, Stephen Lyth, Hiroyoshi Tanaka, Aleksander Staykov, Shigenori Fujikawa, Joichi Sugimura, "Tribology of (PEI/GO)n multilayer coatings in Various Environments", **HYDROGENIUS & I2CNER Tribology Symposium, 2016, February 13-14, Fukuoka, JAPAN**.

〔図書〕（計　1　件）

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〔その他〕
ホームページ等

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Collaboration on energy related research