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主 論 文 の 要 旨

Clarification of wear properties and wear mechanisms of DLC coatings in water at high temperature and high pressure

(高温高圧水中における DLC 膜の摩耗特性と摩耗メカニズムの解明)

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論 文 内 容 の 要 旨

In modern industry, high temperature environments are big challenge to the machines component. The sliding conventional parts (metal) which involve friction and wear could not sustain such environment due to deterioration and oxidation of the sliding parts at high temperature. However, this limitation can be solved by applying lubrication oil to reduce the friction and wear of the metal sliding parts. Solid lubricating coatings are among the best option to control friction and wear for some applications in industries, where friction dealing with environment of high pressurized water such as turbine power plant, steam power plant, nuclear, turbine generator, heat pump, and so on. Tribofilm which produces during friction could be a protective layer in boundary regime in the environment of high pressurized water which later reduce the friction. Solid lubricating coatings include nitride coatings, carbide coatings, oxide coatings, carbon coatings, soft metals, polymers coating and lamellar solids. Among of this solid lubricating coatings, carbon coatings which is the DLC coating attracts much attentions from researchers due to

their excellent mechanical properties and tribological properties such as low friction, high hardness, high wear resistance and chemical inertness. During friction, surface modification occurred and graphite-like layer produced on top of DLC coating surfaces that could prevent high friction on the sliding parts. It is important to ensure that this layer is not worn out due to friction. To date, no report discusses on wear properties and wear mechanisms of DLC coating in high temperature (100 °C to 300 °C) and high pressurized water (0.1 MPa to 30 MPa). Thus, it is important to clarify the wear mechanism of DLC coating such as hydrogenated amorphous carbon (a-C:H), tetrahedral amorphous carbon (ta-C) and amorphous silicon containing diamond like carbon (Si-DLC) during friction in high temperature and high pressurized water.

First, a new high temperature and high pressure autoclave tribotester was proposed and developed. The proposed tribotester was designed to investigate the wear properties of DLC coating pin sliding on stainless steel plate (SUS316) at high temperature (23 °C to 300 °C), high pressure (0.1 MPa to 30 MPa) in water environment with different dissolved oxygen concentration (DO) water (0.5 mg / L to 47.5 mg / L). The DLC coating pin slid in reciprocating motion on SUS316 stainless steel plate in autoclave chamber which swing like pendulum. The swing angle of the autoclave chamber was -21 ° to 21 °. During friction, the sliding speed was kept at 20 rpm for all the friction tests. 3 pins of DLC coating was used per sliding which arranged in triangular. Temperature of the water was automatically controlled by the heater. Pressure inside the autoclave chamber was bombarded by nitrogen, oxygen and mixing of nitrogen and oxygen gaseous. It is important to control the pressure in order to keep the water inside the autoclave chamber in liquid phase during friction test. The DO water in the autoclave chamber was determined by bubbling the nitrogen and oxygen gaseous. The wear volume of the DLC coating pins was determined by wear diameter of wear area. It is assumed that the wear area was flat. It was confirmed that the developed autoclave tribotester can sustain the wear test from 23 °C to 300 °C and 0.1 MPa to 30 MPa in water environment. The coefficient of friction (COF) result of developed autoclave tribotester was in agreement with commercial pin-on-disc tribotester. Thus it was verified that the developed high temperature and high pressure autoclave tribotester could be used for wear test of DLC coating in high temperature and high pressure water environment.

After the high temperature and high pressure autoclave tribotester was developed, the governing parameters on wear properties of a-C:H pin coating sliding on stainless steel plate (SUS316) were investigated. Hydrogenated amorphous diamond-like carbon a-C:H was used in this study. There are three governing parameters on wear of a-C:H coating were investigated; temperature (23, 100, and 300 °C), pressure (0.1, 10, and 30

MPa) and DO in water (0.73, 16.3 and 47.5 mg / L). The results revealed that the wear rate of a-C:H coating was strongly dependent on water temperature and DO concentration in water. Small increment of specific wear rate was observed when the water temperature is less than 100 °C. However, the specific wear rate steeply increased with an increase in water temperature especially above 100 °C. Around 10 times of wear rate was increased after friction at 23 °C to 300 °C. By increasing the DO in water at 300 °C, the wear rate was increased around 3 times from low DO to high DO in water. No significant increment of wear rate due to pressure although the pressure was increased from 10 MPa to 30 MPa at 300 °C. The high wear rate above 100 °C may due to structure change and oxidation of a-C:H coating. Preliminary result on Raman spectroscopy showed increase of I_D/I_G at 300 °C. Thus, two main governing parameter on wear of a-C:H coating in water which are temperature and DO in water was identified.

Then the wear mechanism of a-C:H coating in high temperature and high pressurized water is focused. The wear test was conducted at temperature of 100, 200, 250 and 300 °C. The pressure inside the autoclave chamber was kept to 10 MPa to ensure all the wear test in liquid phase. The DO water was set to 0.5 mg / L for oxygen poor water and 40 mg / L for oxygen rich water. Based on the Auger electron spectra (AES) results, the oxygen atom was penetrating into the a-C:H coating after friction test in high temperature and high pressurized water for oxygen rich water. This is a sign of oxidation occurrence due to high oxygen concentration in water. This was not found in a-C:H coating after friction in low DO concentration. After investigating the mechanical properties of a-C:H film top surface by using Atomic Force Microscopy (AFM) nano scratch method, it was found that the top surface of a-C:H coating was softened at 300 °C. The inside wear area top surface of a-C:H coating was more soften as oxygen inside the film was higher. Results from X-Ray Photoelectron Spectroscopy (XPS) analysis revealed that, the inside wear area top surface of a-C:H coating was modified and transform from sp^3 to sp^2 . This is an agreement with Raman spectroscopy results, where the I_D/I_G of a-C:H coating was increased corresponds to structure change of the film. Based on the Arrhenius plot, the wear loss of a-C:H coating was also due to vaporization of carbon inside the coating. The Arrhenius plot showed that, the reached activation energy for tribochemical wear was above 200 °C for a-C:H coating with high DO in water. Based on all the systematically analysis, it is deduced that the wear mechanism of a-C:H coating was due to the softening of the top most surface of a-C:H coating and vaporization of the carbon from a-C:H coating was due to tribochemical wear.

Better thermal stability, high oxidation resistance and high wear resistance of a-C:H coating could be realized by incorporating silicon (Si) into a-C:H coating or using

high sp^3 ta-C coating. Based on the previous wear mechanism, the wear rate was increase due to softening of a-C:H coating top surface and oxidation. Similar wear test procedures were conducted for ta-C and Si-DLC coating and the results were compared with a-C:H coating. The results revealed that the wear rate of Si-DLC coating was significantly reduced above 100 °C as compared to ta-C and a-C:H coatings. Around 10 times reduction of a-C:H coating wear rate at 300 °C was achieved. Oxidation studies by AES showed that, incorporating Si in DLC coating was suppressing the oxygen amount in DLC coating especially above 100 °C. No significant structure change was observed on Si-DLC coating when compared the result of Raman Spectroscopy with a-C:H coating without Si. This was proved by AFM nano scratch test where only a-C:H coating top layer was softened at high temperature friction. Si-DLC coating maintained it properties where no significant hardness change on top surface of wear area after friction in high temperature and high pressurized water. Thus, it is confirmed that Si could enhance the wear resistance of DLC coating by suppressing structure change and oxidation of DLC coating. It is suggested that Si-DLC coating is the best surface coating material for the application in the machinery which involve in high temperature, high pressure and high oxidation water (23 °C to 300 °C, 0.1 MPa to 10 MPa, and DO: 0.5 mg / L to 50 mg / L).