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Kusano, Yukihiro; Taormina, Stefania; Michelsen, Poul; Nakayama, K.

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Triboplasma – its generation and application for surface modification

Y. Kusano*[1], S. Taormina[1], P.K. Michelsen[1], K. Nakayama[2]
[1]*Risø National Laboratory for Sustainable Energy, Technical University of Denmark, P.O. Box 49, DK-4000 Roskilde, Denmark*
[2]*Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8564, Japan*
*e-mail: yukihiro.kusano@risoe.dk

Abstract

A triboplasma is a gas discharge induced by tribological stimulation. A triboplasma induced by tribo-electrification has been experimentally detected around a sliding contact. The detailed mechanism in tribo-electrification is unknown, but empirical “tribo-electric series” and Coehn´s law can be helpful for predicting the ordering of the tendency for charge acquisition in rubbing.

Like other discharge plasmas, a triboplasma can be useful for surface modification such as adhesion improvement of certain surfaces. The method is attractive, since the generation of a triboplasma is simple, its treatment effect is expected to be similar to that of normal process plasmas, and simultaneous mechanical rubbing can enhance the treatment effect.

1 Introduction

A plasma is an ionized gas. Active species of ions, electrons, high-energy neutrals, radicals as well as ultra violet (UV) photons are generated in plasmas and can be used for modification of material surfaces. Plasma surface treatments for adhesion improvement are attractive because they can be operated at room temperature, they do not require any use of solvents and toxic chemicals, the bulk properties are retained, a surface can be cleaned and weak-layers can be eliminated simultaneously with the surface modification, oxygen and/or nitrogen containing functional groups are easily introduced onto the surfaces, enhancing interactions with adhesives, and physical and chemical micro-etching is expected, improving the mechanical interlocking with adhesives.

Plasma surface treatments at low pressures are well known, while plasma surface treatment at atmospheric pressure has been developed more recently [1]. Atmospheric pressure plasma treatments have been applied to several polymeric materials for adhesion improvement [2,3]. However, expensive power supplies for generation of such plasmas often prevent them from practical industrial applications.

Tribological activation at material surfaces induces several physical processes including emission of photons, electrons and lattice components, tribo-electrification, generation of a triboplasma, change of the electrical conductivity, excitation of lattice vibrations, formation and migration of lattice and electron defects, local heating-up of the solids, formation of fresh surfaces, enlargement of the surfaces, fracture processes, material abrasion, material transitions between solids, amorphization, inserting of impurities, and plastic deformation [4]. Among them a triboplasma is defined as a gas discharge generated by tribological activation. Examples include lightning, sparks from flint striking steel, frictional van der Graaff generators, and the ignition of an explosion in an unloaded petroleum tanker during cleaning of the hold with a high pressure water spray. Based on the magma-plasma model, a severe tribological activation leads to a quasi-adiabatic energy accumulation, formation of an “energy bubble” at the deformation zone, high excitation states, strong lattice loosening, structural disruptions, detachment of lattice components, photons and electrons, and subsequent generation of a triboplasma [5]. This kind of triboplasma is already used for a dental application, where aluminium oxide can be coated tightly with the aid of a triboplasma [6]. However, the severe tribological activation can damage the surface and bulk properties of materials significantly.

On the other hand, a triboplasma can also be generated by tribo-electrification without severe activation, which can be useful for the application of plasma surface modification, since the treatment effect is expected to be similar to that by normal process plasmas.

In the present work mechanisms of tribo-electrification, generation of a triboplasma and its application for surface modification is discussed.

2 Tribo-electrification

Tribo-electrification is a production of electrostatic by rubbing together of dissimilar material surfaces. An empirical classification scheme for the ordering of the tendency for charge acquisition in rubbing is available, called “tribo-electric series” [7]. Molecular level interaction at the contact can primarily affect the order of the tribo-electric series. For polymeric materials Coehn´s law predicts that the order of materials in the list corresponds with that of dielectric constants [8]. However, the order in of the tribo-electric series is different in different databases, and tribo-electrification can occur even when same materials with differing roughness are rubbed together. This asymmetric rubbing can induce asymmetric heating; a smaller contact area can become hotter. The concentration of mobile charged carriers increases at the hotter smaller area, and subsequently the charges tend to transfer from the smaller area to the larger. On the other hand, the asymmetric rubbing can induce a greater charge supply from a contaminant at the larger area, resulting in the charge transfer from the larger area to the smaller. In addition, other properties at the contact surfaces can affect the order of the tribo-electric series, including surface layers of water, oxides, and hydrocarbons, and yield strengths of materials [8]. The detailed physical mechanism in tribo-electrification is a long unsolved problem.

3 Generation of a plasma induced by tribo-electrification

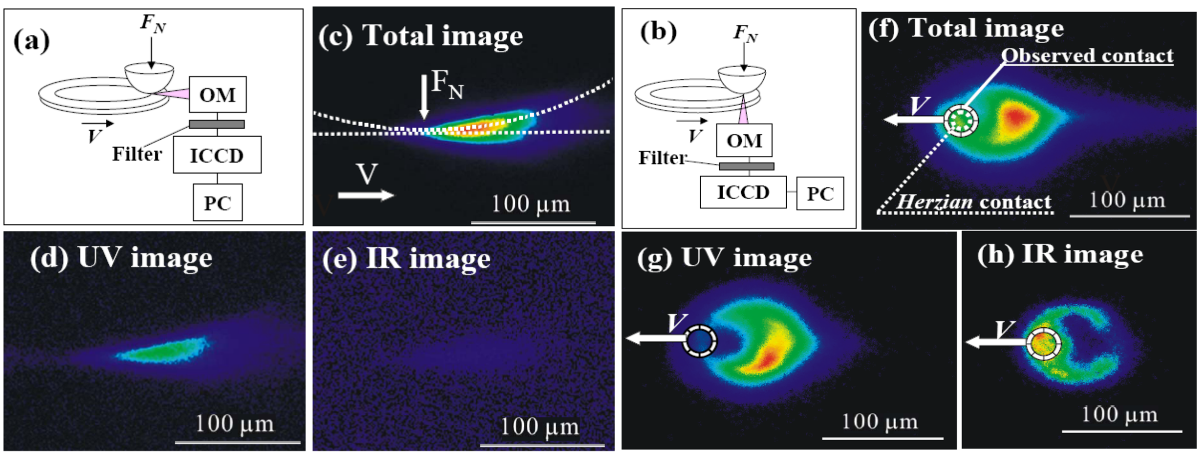

Figure 1. A pin-on-rotating sapphire disk apparatus for observation of a triboplasma (a,b). OM: optical microscope, ICCD: intensified charge coupled device, PC: personal computer. Total (c), UV (d), and IR (e) images of a triboplasma observed from the side of the apparatus. Total (f), UV (g), and IR (h) images of a triboplasma observed through the sapphire disk [9].

A triboplasma is experimentally detected around a sliding contact with a pin- or ball-on-rotating disk apparatus [9,10]. Figure 1 shows the images of a triboplasma generated by a sliding contact between a diamond hemisphere and a sapphire plate in atmospheric pressure air. Intense infrared (IR) emission is detected at the sliding contact, indicating that the surface is heated by the friction. On the other hand intense UV emission from the gas discharge is observed outside the sliding contact, whose location has a gap between the pin and the disk ranging from 1.3 μm [11] and 7.8 μm [12]. The observed plasma is different from a triboplasma based on the magma-plasma model, where photons emit at the sliding contact induced by frictional heating or high energy states at the deformed layer beneath the sliding contact. In addition intensity of charge emission around the sliding contact increases as an increase in resistivity of the materials [13]. It is therefore indicated that this triboplasma is generated by tribo-electrification as shown in Figure 2. It is further suggested that the results show a good agreement with Paschen´s law predicting a gas breakdown with a voltage 330 V at a gap 7.5 μm in atmospheric pressure air. However, further investigation is necessary for better understanding a triboplasma induced by tribo-electrification.

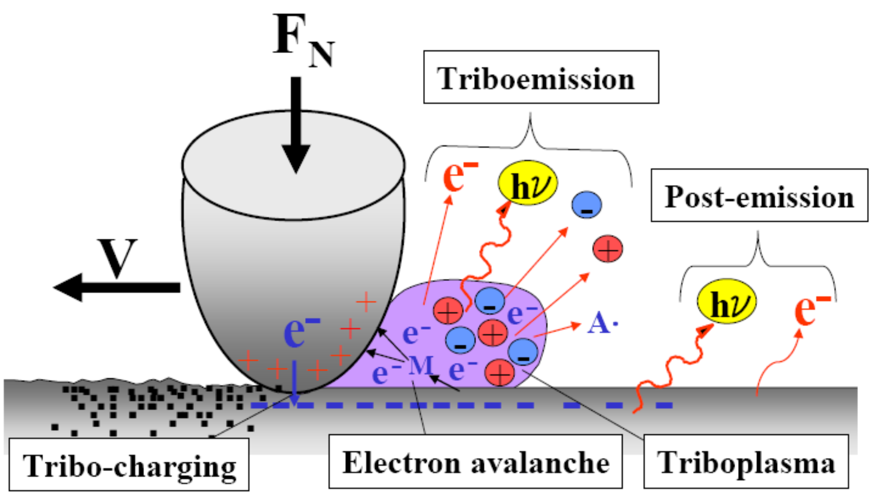

Figure 2. Tribo-electromagnetic phenomena induced by sliding [9].

4 Surface modification by a triboplasma

The study of triboplasmas is of significant interest for understanding tribological phenomena in terms of electrical charging, and chemical reactions at the sliding contacts, monitoring tribological phenomena, surface modification of materials, and understanding discharges in daily life. Since the study of the triboplasma was initiated by tribological research and applications, the related literature has mainly been devoted to understanding and monitoring tribological phenomena. On the other hand, application of triboplasma for surface modification is not extensively studied.

A tribological stimulation at a surface can induce tribo-physical and tribo-chemical phenomena, which can be classified into three reactions taking place “at”, “near” and “far from” the contact areas [14]. The reactions far from the sliding contact take place associated with electrification, emission of exo-electrons, tribo-luminescence, or lattice defects with relatively long relaxation times [4]. Typically the number of the exo-electrons is too small to cause substantial chemical reactions.

Surface modification by a triboplasma induced by tribo-electrification mostly takes place near

the sliding contact. Optical emission spectroscopy of a triboplasma in atmospheric pressure air indicates that it is a general air discharge mainly consisting of N_2 peaks [15]. As general discharge plasmas can efficiently modify material surfaces, similar effect can be expected for a triboplasma. The method is attractive, since the generation of a triboplasma is simple and simultaneous mechanical rubbing can enhance the treatment effect. Examples of surface modification by a triboplasma include decomposition of a fluoropolymer lubricant [16], and plasma-polymerization of n-butane using a ball-on-rotating disk apparatus [17].
Reactions at the sliding contact, mainly governed by external mechanical parameters, also play an important roll, involving crystal structure changes and acid base reactions [14]. It is generally difficult to determine the locations of specific reaction by surface characterization after the treatment. *In situ* observation at the sliding contact might give a new insight for the tribo-physical and tribo-chemical phenomena [14].

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